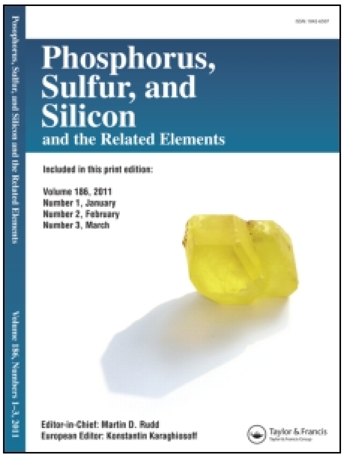

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INFLUENCE OF IODINE ON THE REACTIVITY OF TETRAPHOSPHORUS TRISULFIDE IN ORGANIC REACTIONS

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INFLUENCE OF IODINE ON THE REACTIVITY OF TETRAPHOSPHORUS TRISULFIDE IN ORGANIC REACTIONS

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The reactivity of β-tetraphosphorus trisulfide is increased through involvement of elemental iodine in the reactions with dialkyl disulfides, thioacetals and animals. The reactions of β- and α-diiodotetraphosphorus trisulfides with disulfides, thioacetals and aminals were studied. The proposed reaction mechanism is discussed.

Key words: β-Tetraphosphorus trisulfide, β- and α-diiodotetraphosphorus trisulfides, iodine, disulfides, thioacetals, aminals, organothiophosphorus compounds.

INTRODUCTION

In a series of phosphorus sulfides the lower ones possess decreased chemical reactivity in organic reactions. Thus, we have previously shown that β-tetraphosphorus trisulfide 1 reacts with thioacetals, aminals and sulfenamides under severe conditions (100–200°C, up to 12 h) in the absence of any additives to form some organothiophosphorus compounds.[1–3] Tetraphosphorus trisulfide is photochemically oxidized by disulfides under UV irradiation to give trithiophosphites and tetrathiophosphates.[4,5] We have previously found that the reactions of 1 with thioacetals, aminals, sulfenamides and dialkyl disulfidts are facilitated by organic amines and benzoyl peroxide.[1] In order to increase the reactivity of 1 and to decrease the reaction temperature we introduced elemental iodine into these reactions. We present the results of this study in this article.

RESULTS AND DISCUSSION

In spite of the fact that the reaction of phosphorus sulfide 1 with disulfides is facilitated by UV irradiation, amines and benzoyl peroxide[1–6] the reactivity of 1 in the reaction with disulfides in the absence of any additives remained unknown. The reaction of 1 with dialkyl disulfides 2a,b appeared to take place at 180–200°C for 4 h in a flask with stirring with the formation of trialkyltetrathiophosphates 3a,b and trialkyltrithiophosphites 4a,b (Equation (1), and Table I).

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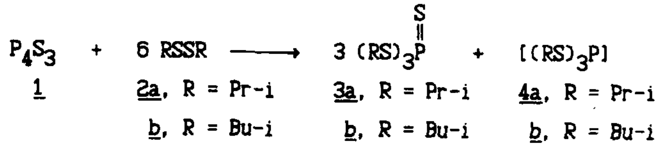


$$\underset{\mathbf{1}}{P_4S_3} + 6\,RSSR \longrightarrow 3\,(RS)_3P{=}S + [(RS)_3P] \qquad (1)$$

2a, R = Pr-i; **b**, R = Bu-i — **3a**, R = Pr-i; **b**, R = Bu-i — **4a**, R = Pr-i; **b**, R = Bu-i

TABLE I
Experimental data and yields of the products obtained

Initial compounds			Reaction conditions		Yield
			temp., °C/time, h, solvent		Prod. (%)
1	2a		180-200/4.5		3a ($77^{b}/64^{c}$)
1	2b		180-200/8		3b ($58^{b}/44^{c}$)
1	2c	I_2	20/7	B^{d}	3c (74^{c})
18a	2c		20/1	B^{d}	3c (81^{c})
1	2b	I_2	20/5	B^{d}	3b (98^{c}); 4b (33^{c})
18a	2d		20/3	B^{d}	3d (87)
1	6a		$200/12^{a}$		7a (44^{c}); 8a (31^{c})
1	6a	I_2	20/4	B^{d}	7a (59^{c}); 8a (41^{c})
18a	6a		20/5	B^{d}	7a (60^{c}); 8a (25^{c})
1	6b	I_2	20/4	B^{d}	7b (77^{c})
18a	6c		20/7	B^{d}	7c (64^{c}); 8c (16^{c})
1	12a		$130/4^{a}$		13a (61^{c})
1	12a	I_2	20/9	B^{d}	13a (60^{c})
18a	12a		20/4	B^{d}	13a (41^{c})
1	12b		$140/5^{a}$		13b (36^{c})
1	12b	I_2	20/10	B^{d}	13b (30^{c})
18a	12b		20/360	B^{d}	13b (41^{c})

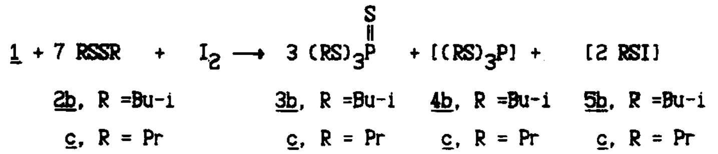
[a] See reference 1.
[b] Yield of crude product.
[c] Yield of isolated product.
[d] Benzene.

However, trialkyltrithiophosphites 4 were not isolated from the reaction mixture, perhaps, owing to their sulfurization under severe reaction conditions (180–200°C) with the additional formation of tetrathiophosphates 3.

The structures of the products 3 have been established by IR, ^{1}H and ^{31}P NMR, mass spectral data, by microanalyses and by comparison of their physical constants with literature data. Reaction conditions and the yields of products are tabulated in Table I.

We decided to introduce crystalline iodine into the previously studied reactions of 1 with dialkyl disulfides 2, thioacetals and aminals. This technique may result in reactivity enhancements of 1 and decrease in reaction temperature via the formation of more reactive intermediates.

Thus, the formation of tetrathiophosphates 3b,c and trithiophosphites 4b,c occurred already at 20°C for 5–7 h in the reaction of 1 with disulfides 2b,c in the presence of elemental iodine in anhydrous benzene (Equation (2), Table I).

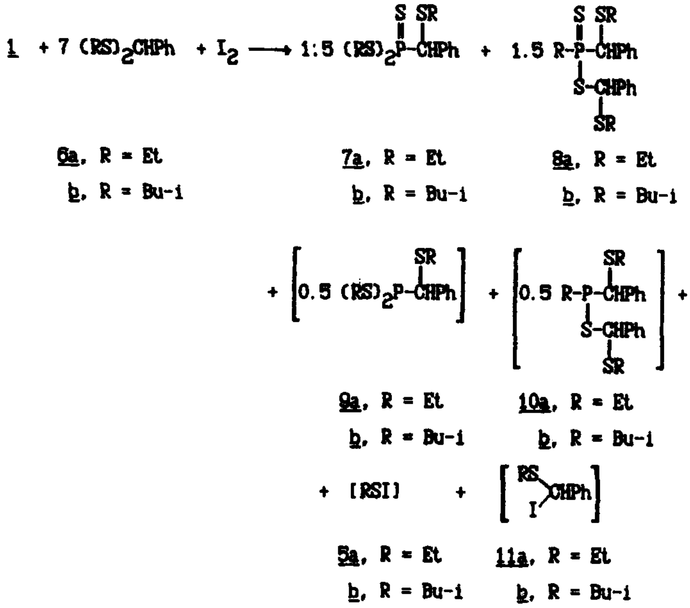


$$\underline{1} + 7\,RSSR + I_2 \longrightarrow 3\,(RS)_3\overset{S}{\overset{\|}{P}} + [(RS)_3P] + [2\,RSI] \qquad (2)$$

2b, R = Bu-i; c, R = Pr — 3b, R = Bu-i; c, R = Pr — 4b, R = Bu-i; c, R = Pr — 5b, R = Bu-i; c, R = Pr

Thus, the use of iodine results in the decrease of the reaction temperature (from 180–200 to 20°C). Alkylsulfenyliodides 5 which should be formed in accordance with the stoichiometry of Equation (2) were not isolated in their distilled form as they decompose under reaction conditions (20°C) to form the same disulfides 2 and iodine.[6]

We have tried to find the range of application of this effective technique of reactivity enhancement and extended it on other reagents, e.g. thioacetals and aminals. Thus, we have previously shown that phosphorus sulfide 1 reacts with thioacetals 6 in sealed tubes at 200°C for 2–12 h to form S,S′-dialkyl-1-(alkylthio)benzyl trithiophosphonates 7 and S-(1-alkylthiobenzyl)-1-(alkylthio)benzyl alkyldithiophosphinates 8.[1] This reaction was also facilitated when iodine was employed. Thus, produces 7a,b and 8a,b were obtained in the reaction of 1 with thioacetals 6a,b in the presence of iodine in benzene at 20°C for 4h (Equation (3), Table I).



$$\underline{1} + 7\,(RS)_2CHPh + I_2 \longrightarrow 1.5\,(RS)_2P(=S)\text{-}CH(SR)Ph + 1.5\,R\text{-}P(=S)(CH(SR)Ph)\text{-}S\text{-}CH(Ph)SR$$

6a, R = Et; b, R = Bu-i — 7a, R = Et; b, R = Bu-i — 8a, R = Et; b, R = Bu-i

$$+ \left[0.5\,(RS)_2P\text{-}CH(SR)Ph\right] + \left[0.5\,R\text{-}P(CH(SR)Ph)\text{-}S\text{-}CH(Ph)SR\right] + \qquad (3)$$

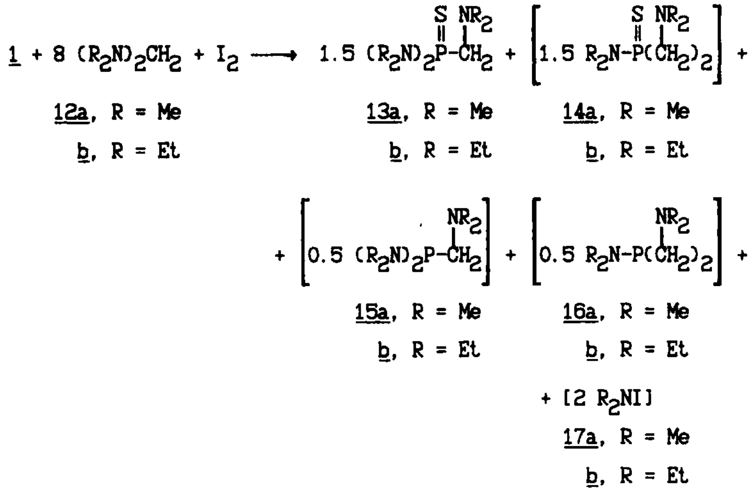
9a, R = Et; b, R = Bu-i — 10a, R = Et; b, R = Bu-i

$$+ [RSI] + [RS(I)CHPh]$$

5a, R = Et; b, R = Bu-i — 11a, R = Et; b, R = Bu-i

A comparison of the reaction conditions of the method with iodine with those without any additives is shown in Table I. Use of iodine in the reaction of 1 with thioacetals 6 did not result in any significant improvement in yields of products 7 and 8 as compared to the results of conventional methodology (Table I). The trivalent phosphorus products 9 and 10 were not isolated from the reaction mixture. Neither were sulfenyl iodides 5 and phenyl(alkylthio)methyl iodides 11 isolated owing to their instability under the reaction conditions.

The reaction temperature of the reaction of 1 with aminals 12a,b which produces N,N′-tetraalkyl-1-N″-(dialkylamino)methyl diamidothionophosphonates 13a,b[1] is reduced from 130–140°C (sealed tube) to 20°C (stirred benzene mixture) in the presence of iodine (Equation (4), Table I).



$$\underline{1} + 8\,(R_2N)_2CH_2 + I_2 \longrightarrow 1.5\,(R_2N)_2\overset{\overset{S}{\|}}{P}-\overset{\overset{NR_2}{|}}{C}H_2 + \left[1.5\,R_2N-\overset{\overset{S}{\|}}{P}(\overset{\overset{NR_2}{|}}{C}H_2)_2\right] + \left[0.5\,(R_2N)_2P-\overset{\overset{NR_2}{|}}{C}H_2\right] + \left[0.5\,R_2N-P(\overset{\overset{NR_2}{|}}{C}H_2)_2\right] + [2\,R_2NI] \qquad (4)$$

12a, R = Me; b, R = Et

13a, R = Me; b, R = Et

14a, R = Me; b, R = Et

15a, R = Me; b, R = Et

16a, R = Me; b, R = Et

17a, R = Me; b, R = Et

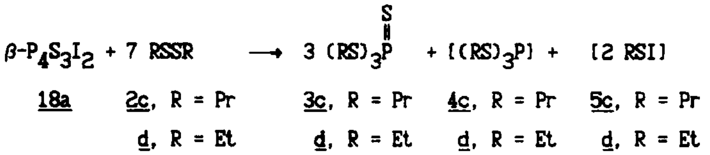
The products 14, 15 and 16 which should be formed in accordance with the stoichiometry of Equation (4) were not isolated. The chemical ionization mass spectrum of the reaction mixture of 1 with the gem-diamine 12b exhibits the mass peak m/e 200 which may be attributed to the ion $[M + H]^+$ of dietylaminoiodide 17b.

It should be noted that the course of the reactions of 1 with disulfides 2, thioacetals 6, and aminals 12 in the presence of iodine (Equations (2–4)) and the yields of the products 3, 7 and 8, and 13 do not depend upon the sequence of mixing the reagent 1 and the organic substances, and iodine (see Experimental). This indicates that these reactions proceed via the formation of some kinetically unstable intermediates and result in thermodynamically stable products 3, 7 and 8, and 13.

Some assumptions may be made concerning the mechanism of destruction of 1 in reactions with disulfides 2, thioacetals 6 and aminals 12 due to the effect of iodine. The formation of final products proceeds under the conditions of the three component reactions. The promoting role of iodine may be both the initial interaction of iodine with organic substances and with phosphorus sulfide 1. The first case should lead in the case of reaction (2) to alkylsulfenyl iodide 5 (Equation (5)) which consequently reacts with 1.

$$\underset{\underline{2}}{RSSR} + 2\ I_2 \rightleftarrows 2\ \underset{\underline{5}}{RSI} \qquad (5)$$

In the chemical literature there is no information on the reaction of 1 with sulfenyl iodides. But organosulfenyl chlorides are known to react with 1 with the formation of organylchlorothiophosphites, organylchlorodithiophosphates and diorganylchlorotrithiophosphates.[7] The second case involves the addition of iodine to 1. It appears that β-diiodotetraphosphorus trisulfide 18a is the initial product of the reaction of 1 with iodine at 20°C in benzene or CS_2 solutions which is converted into its α-isomer 18b at 120–125°C.[8-10] Consequently the interaction of diiodide 18a with organic substances, e.g. disulfides, thioacetals and aminals may result in the formation of the same final organothiophosphorus products. To corroborate this assumption we carried out a series of model reactions of diiodide 18a with disulfides 2, thioacetals 6 and aminals 12 and in fact observed the formation of the same final products 4, 7 and 8, and 13, respectively. Thus, tetrathiophosphates 3c,d were obtained in the reaction of diiodide 18a with disulfides 2c,d in anhydrous benzene at 20°C for 1–3 h (Equation (6), Table I).

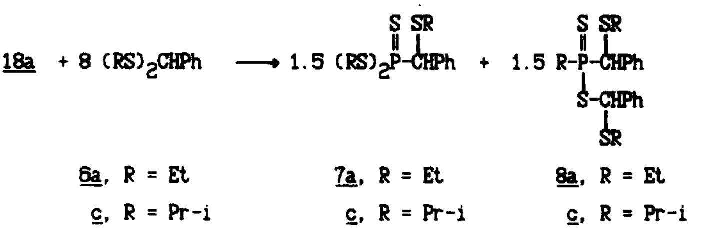


$$\underset{\underline{18a}}{\beta\text{-}P_4S_3I_2} + 7\ RSSR \longrightarrow 3\ (RS)_3P{=}S + [(RS)_3P] + [2\ RSI] \qquad (6)$$

2c, R = Pr; d, R = Et — 3c, R = Pr; d, R = Et — 4c, R = Pr; d, R = Et — 5c, R = Pr; d, R = Et

In this case (Equation (6)) the formation of sulfenyl iodides 5 was confirmed by the chemical ionization mass spectral analysis of the reaction mixture of 18a with disulfide 2c indicating the existence of the mass peak m/e 204 which corresponds to ion $[PrSI + 2H]^+$ (75%). However, trithiophosphites 4 in their distilled form were not isolated from the reaction mixtures.

The products of the (1-alkylthio)benzyl thionophosphonate structure 7a,c and 8a,c were isolated in the reaction of diiodide 18a with thioacetals 6a,c at 20°C for 5–7 h in benzene (Equation (7), Table I).



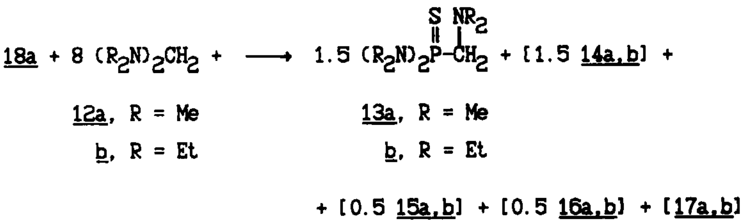
18a + 8 $(RS)_2CHPh$ ⟶ 1.5 $(RS)_2P(S)$–CH(SR)Ph + 1.5 R–P(S)(CH(SR)Ph)–S–CH(SR)Ph (7)

6a, R = Et; c, R = Pr-i — 7a, R = Et; c, R = Pr-i — 8a, R = Et; c, R = Pr-i

+ [0.5 9a,c] + [0.5 10a,c] + [5a,c] +

+ [11a,c]

Similarly the model reaction of diiodide 18a with aminals 12a,b results in the formation of the same diamidothionophosphonates 13a,b under mild conditions (20°C, benzene) (Equation (8), Table I).



$$\underline{18a} + 8\,(R_2N)_2CH_2 + \longrightarrow 1.5\,(R_2N)_2\overset{\overset{S}{\|}}{P}\text{-}\overset{\overset{NR_2}{|}}{C}H_2 + [1.5\ \underline{14a,b}] + + [0.5\ \underline{15a,b}] + [0.5\ \underline{16a,b}] + [\underline{17a,b}] \qquad (8)$$

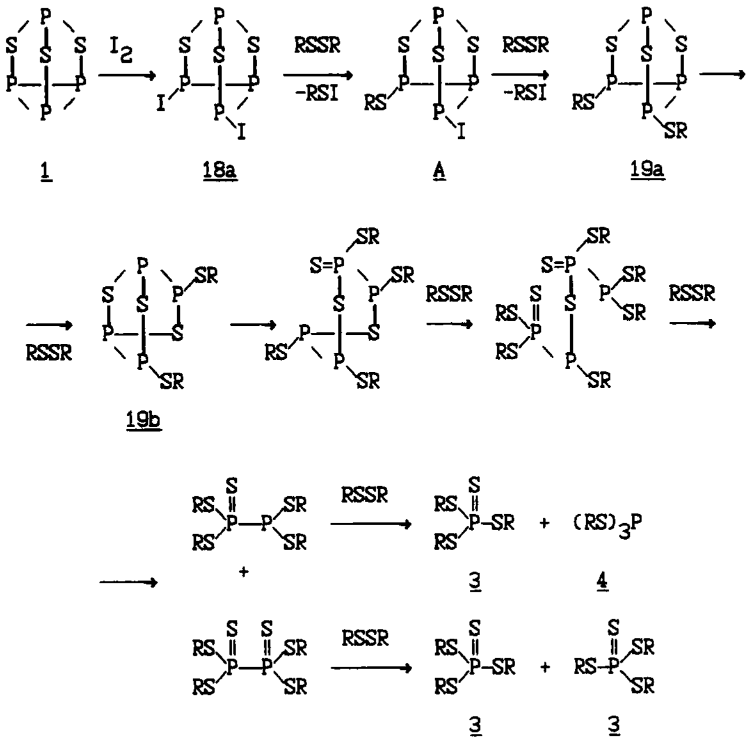
$\underline{12a}$, R = Me; $\underline{b}$, R = Et

$\underline{13a}$, R = Me; $\underline{b}$, R = Et

The same results were also obtained on the basis of the reactions of α-diiodotetraphosphorus trisulfide 18b with disulfides 2, thioacetals 6 and aminals 12 which resulted in the same products 3, 7 and 8, and 13 respectively.

It should be noted that the reactions of diiodides 18a,b with disulfides, thioacetals and aminals are of interest from the point of view of the study of the chemical behavior of β- and α-diiodides 18a,b. The substitution reactions of β- and α-$P_4S_3I_2$ 18a,b were previously studied with bis(trimethylstannyl)sulfide,[11] silver halides and pseudohalides,[12] amines[12] and thiols.[5]

Thus, a general scheme of the degradation of 1 due to the effect of disulfides 2 and the formation of final tetrathiophosphates 3 and trithiophosphites 4 can be conceived on the basis of the results of the reactions of phosphorus sulfide 1, and β- and α-diiodides 18a,b with disulfides 2 (Equation (9)).



(9)

Perhaps, the reactions of 1 with disulfides 2 in the presence of iodine is initiated by the addition of iodine to 1 and involves breaking of the P—P bond of the basal fragment of 1 and the formation of adduct 18a.[10,11] The consequent substitution reaction of 18a with disulfides 2 may result in intermediate A and β-bis(alkylthio)tetraphosphorus trisulfide 19a. The β-isomer 19a undergoes a skeletal rearrangement to give the α-isomer 19b[5] which then reacts with disulfides 2 to form final tetrathiophosphates 3 and trithiophosphites 4 via a succession of steps (Equation (9)). Similar compounds α-$P_4S_3(SR)_2$ (where R = Et, Ph) were previously obtained by the reaction of α-diiodide 18b with ethanethiol and mercury (II) bis(phenylsulfide) respectively in the presence of a base.[5]

Besides the alkyldiiodothiophosphites and dialkyliododithiophosphites may be formed along with tetrathiophosphates 3 and trithiophosphites 4 in the reactions of 1 or 18a,b with disulfides 2. Thus, in the chemical ionization mass spectrum of the reaction mixture of diiodide 18a with the disulfide 2c there is the mass peak m/e 361 which may be attributed to the ion $[PrSPI_2 + H]^+$ (13%). Together with the signals of products 3c and 4c the weak signals at δ_P 179.5 and 163.4 ppm (in benzene solution) were also observed in the ^{31}P NMR spectra of both reaction mixtures of phosphorus sulfide 1 with disulfide 2c and β-diiodide 18a with disulfide 2c. These signals may be attributed to phosphorus triiodide (PI_3) (Reference 13: the ^{31}P NMR spectrum of PI_3 δ_P 178 ppm) and dipropyliododithiophosphites, $(PrS)_2PI$, respectively. To corroborate this assumption we carried out model reaction of authentic phosphorus triiodide with propanethiol and *i*-butanethiol in benzene. The ^{31}P NMR spectra in benzene solution show the signals at δ_P 179.4 and 164.5 ppm in the case of propyl mercaptan and at δ_P 180.9, 173.7 and 165.6 ppm in the case of *i*-butanethiol. The signals at δ_P 164.5 and 165.6 ppm may be attributed to dialkyliododithiophosphites (Equation (10)). We also observed the formation of

$$2\,PI_3 + 3\,RSH \longrightarrow RSPI_2 + (RS)_2PI + 3\,HI \qquad (10)$$

trithiophosphites 4 in this model reaction (Equation (11)) (the NMR ^{31}P spectra of 4b (C_6H_6) δ_P: 118.0 ppm and of 4c (C_6H_6) δ_P: 117.2 ppm (Reference 13: δ_P 118.4 ppm).

$$PI_3 + 3\,RSH \longrightarrow (RS)_3P + 3\,HI \qquad (11)$$

4b, R = Bu-i
c, R = Pr

Dialkyliododithiophosphites are likely to be secondary products and may be formed via the substitution reaction of trithiophosphites 4 formed as intermediates in the reactions (2) and (6) with sulfenyliodides 5 (Equation (12)).

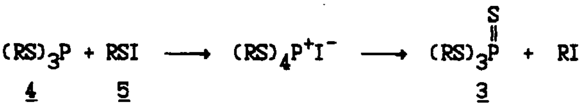
$$\underset{4}{(RS)_3P} + \underset{5}{RSI} \longrightarrow (RS)_2PI + \underset{2}{RSSR} \qquad (12)$$

A similar formation of dialkylchlorodithiophosphites and dialkyl disulfides was previously described in the substitution reaction of trialkyltrithiophosphites with sulfenyl chlorides.[14]

The alternative direction of the reaction of 4 with 5 with the formation of 3

(Arbuzov rearrangement, (Equation (13)) may be a reason of the decrease of the amount of 4 in the reactions (2) and (6).

Thus, we have developed an efficient method of promoting the reactions of tetraphosphorus trisulfide with organic compounds by involving iodine in the reaction mixtures.



$$\underset{\mathbf{4}}{(RS)_3P} + \underset{\mathbf{5}}{RSI} \longrightarrow (RS)_4P^+I^- \longrightarrow \underset{\mathbf{3}}{(RS)_3\overset{S}{\overset{\|}{P}}} + RI \quad (13) \qquad (13)$$

EXPERIMENTAL

^{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%). ^{1}H NMR spectra were run on a Varian T-60 (60 MHz) spectrometer in CCl_4. IR spectra were obtained in a KBr pellet with an UR-20 infrared spectrophotometer. Mass spectra (electron impact, 70 eV; chemical ionization, 100 eV) were obtained on a M 80 B Hitachi chromato mass spectrometer.

Tri-i-propyl-tetrathiophosphate 3a. *Typical Procedure*: The mixture of 1 (1.7 g, 7.7 mmol) and 2a (7.0 g, 46.6 mmol) was stirred at 180–200°C for 4.5 h. The mixture was evaporated at reduced pressure (0.1 and 0.02 mm Hg) at 50°C for 2 h and gave crude 3a (5.2 g, 77%). Distillation of the residue gave pure 3a (4.3 g, 64%), b.p. 107–109°C (0.05 mm Hg), n_D^{20} 1.5662. The ^{31}P NMR spectrum (C_6H_6) δ_P: 86.9 ppm. Mass spectrum (chemical ionization, 100 eV), m/e (I_{rel}, %): 289 $[M + H]^+$ (45). (Reference 15: b.p. 123–125°C (0.3 mm Hg); reference 1: n_D^{20} 1.5653, the ^{31}P NMR spectrum δ_P: 86.5 ppm).

Similarly 1 (3.8 g, 17.3 mmol) and 2b (18.4 g, 103.3 mmol) (reaction conditions: 180–200°C, 8 h) produced crude 3b (10.0 g, 58%) and distilled 3b (7.6 g, 44%), b.p. 133–134°C (0.03 mm Hg), n_D^{20} 1.5556. The ^{31}P NMR spectrum (C_6H_6) δ_P: 92.9. Mass spectrum (electron impact, 70 eV), m/e (I_{rel}, %): 330 $[M]^+$ (45) (Reference 16: 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 β-Tetraphosphorus Trisulfide 1 *with Dipropyl Disulfide* 2c *in the Presence of Iodine. Typical Procedure*: Compound 1 (3.6 g, 16.4 mmol) was added portionwise to a stirred solution of iodine (4.2 g, 33.1 mg-atom) in 10 ml of anhydrous benzene at 20°C and stirring was continued for 1.5 h at 20°C. Compound 2c (17.2 g, 114.6 mmol) was slowly added dropwise with stirring at 20°C to the mixture obtained and stirring was continued for 6 h at 20°C. The mixture was filtered. The filtrate was evaporated under vacuum (10 and 0.06 mm Hg). Distillation of the residue gave pure 3c (10.4 g, 74%), b.p. 126–128°C (0.05 mm Hg), n_D^{20} 1.5889. The ^{31}P NMR spectrum (C_6H_6): δ_P 91.8 ppm. Mass spectrum (chemical ionization, 100 eV), m/e (I_{rel}, %): 289 $[M + H]^+$ (45) (Reference 15: 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 1 (4.0 g, 18.2 mmol) and 2b (22.7 g, 127.5 mmol) in the presence of iodine (4.6 g, 36.2 mg-atom) in 10 mL of benzene gave distilled 3b (17.6 g, 98%) and 4b (1.8 g, 33%), b.p. 58°C (0.03 mm Hg). The ^{31}P NMR spectrum (C_6H_6) of 4b: δ_P 117.8 ppm. Mass spectrum (chemical ionization, 100 eV), m/e (I_{rel}, %): 299 $[M + H]^+$ (45).

Reaction of β-Tetraphosphorus Trisulfide 1 *with Phenylbis(ethylthio)methane* 6a *in the Presence of Iodine*. Iodine (1.7 g, 13.4 mg-atom) was added portionwise to a stirred suspension of 1 (1.5 g, 6.8 mmol) in 5 mL of anhydrous benzene for 0.5 h at 20°C. Thioacetal 6a (10.1 g, 47.6 mmol) was added dropwise with stirring at 20°C to the mixture obtained and stirring was continued for 3 h at 20°C. The mixture was filtered. The filtrate was evaporated at reduced pressure (10 and 0.02 mm Hg). Multiple distillation of the residue on a thin layer distillation apparatus gave trithiophosphonate 7a (2.0 g, 59%) at 150–155°C (0.02 mm Hg), n_D^{20} 1.6319. The ^{31}P NMR spectrum (C_6H_6) δ_P: 93.4 ppm. Mass spectrum (chemical ionization, 100 eV), m/e (I_{rel}, %): 337 $[M + H]^+$ (10) (Reference 1: b.p. 130–150°C (0.002 mm Hg) (thin layer distillation apparatus), n_D^{20} 1.6315, the ^{31}P NMR spectrum (neat) δ_P: 94 ppm). Dithiophosphonate 8a (1.8 g, 41%) was also obtained, b.p. 220°C (0.02 mm Hg) (thin layer distillation apparatus), n_D^{20} 1.6424. The ^{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 (0.9 g, 4.1 mmol), thioacetal 6b (7.7 g, 28.7 mmol) and iodine (1.0 g, 7.9 mg-atom) in 10 mL of benzene (reaction conditions: 20°C, 4h) gave pure trithiophosphonate 7b (2.0 g, 77%), b.p. 130–140°C (0.02 mm Hg) (thin layer distillation apparatus), n_D^{20} 1.5929. The ^{31}P NMR spectrum (C_6H_6) δ_P: 94.8 ppm. ^1H NMR spectrum (CCl_4, δ, ppm, J, Hz): 0.94 (d, 6H, $\underline{CH}_3CHCH_2SC$, $^3J_{H-H}$ 6.0); 1.02 (d, 12H, $\underline{CH}_3CHCH_2SP$, $^3J_{H-H}$ 6.0); 1.67–2.49 (m, 3H, $CH_3\underline{CH}CH_2SP$; $CH_3\underline{CH}CH_2SC$); 2.40 (d, 2H, $CH_3CH\underline{CH}_2SC$, $^3J_{H-H}$ 6.0); 2.82 (dd, 4H, $CH_3CH\underline{CH}_2SP$, $^3J_{H-H}$ 6.0, $^3J_{P-H}$ 16.4); 4.17 (d, 1H, $\underline{CH}P$, $^2J_{P-H}$ 12.0); 7.08–7.42 (m, 5H, $C_6\underline{H}_5$). IR spectrum (ν, cm^{-1}): 3090, 3065, 3030 ν (=C—H, Ar); 2960, 2930, 2872 ν (CH_3 as, s; C—H); 1600, 1496 ν (C=C, Ar); 1463 δ (CH_3 as); 1389, 1370 δ [$(CH_3)_2C$ gem s]; 699 ν (P=S), ν (PS_2 as); 650 ν (C—S); 530 ν (PS_2 s), ν (P—SC), ν (P—CS). Mass spectrum (chemical ionization, 100 eV), m/e (I_{rel}, %): 421 $[M + H]^+$ (14), 178 $[M + H - BuS - Bu - 3S]^+$ (100); (electron impact, 70 eV), m/e (I_{rel}, %): 331 $[M - BuS]^{+\cdot}$ (45); 274 $[M - BuS - Bu]^{+\cdot}$ (5); 241 $[M - BuS - Bu - S]^{+\cdot}$ (19). Found, %: C 54.06; H 7.71; P 7.61; S 30.78. $C_{19}H_{33}PS_4$. Calc., %: C 54.26; H 7.93; P 7.37; S 30.44.

Reaction of β-Tetraphosphorus Trisulfide 1 with Bis-(dimethylamino)metane 12a in the Presence of Iodine. Typical Procedure: The solution of iodine (3.8 g, 29.9 mg-atom) in 10 mL anhydrous benzene was added dropwise to a stirred suspension of 1 (3.3 g, 15.0 mmol) in 5 mL of benzene for 20 min at 20°C. Aminal 12a (12.2 g, 119.5 mmol) was added dropwise with stirring at 20°C to the mixture obtained and stirring was continued for 8.5 h at 20°C. The mixture was filtered. Distillation of the filtrate by means of thin layer distillation gave thionophosphonate 13a (2.8 g, 60%) at 90–100°C (0.02 mm Hg), n_D^{20} 1.5115. The ^{31}P NMR spectrum (C_6H_6) δ_P: 81.1 ppm. Mass spectrum (electron impact, 70 eV), m/e (I_{rel}, %): 209 $[M]^{+\cdot}$ (46), 194 $[M - Me]^{+\cdot}$ (100), 149 $[M - NMe_2 - Me]^{+\cdot}$ (8).

Similarly 1 (2.5 g, 11.4 mmol), aminal 12b (14.4 g, 91.0 mmol) and iodine (2.9 g, 22.9 mg-atom) gave thionophosphonate 13b (1.5 g, 30%), b.p. 100–110°C (0.02 mm Hg) (thin layer distillation apparatus), n_D^{20} 1.5033. The ^{31}P NMR spectrum (C_6H_6) δ_P: 76.9 ppm (Reference 1: b.p. 113–115°C (0.07 mm Hg), n_D^{20} 1.5041, the ^{31}P NMR spectrum (neat) δ_P: 77 ppm).

Reaction of β-Diiodotetraphosphorus Trisulfide 18a with Dipropyl Disulfide 2c. Typical Procedure: Disulfide 2c (12.0 g, 79.9 mmol) was added dropwise to a stirred suspension of diiodide 18a (5.4 g, 11.4 mmol) in 15 mL of anhydrous benzene with dry argon at 20°C and stirring was continued for 1 h at 20°C. The mixture was filtered. The filtrate was evaporated under vacuum (10 and 0.03 mm Hg). Distillation of the residue gave tetrathiophosphate 3c (7.8 g, 81%).

Similarly diiodide 18a (6.6 g, 13.9 mmol) and disulfide 2d (11.9 g, 97.4 mmol) in 15 mL of benzene (reaction conditions: 20°C, 3 h) gave tetrathiophosphate 3d (9.0 g, 87%), b.p. 135–136°C (10 mm Hg), n_D^{20} 1.6205. The ^{31}P NMR spectrum (C_6H_6) δ_P: 90.5 ppm. Mass spectrum (electron impact, 70 eV), m/e (I_{rel}, %): 246 $[M]^{+\cdot}$ (40) (Reference 15: b.p. 124–125°C (1.5 mm Hg), n_D^{20} 1.6201, the ^{31}P NMR spectrum δ_P: 91.7 ppm).

Reaction of β-Diiodotetraphosphorus Trisulfide 18a with Phenylbis(ethylthio)methane 6a. Typical Procedure: Diiodide 18a (5.6 g, 11.8 mmol) was added portionwise to a stirred solution of thioacetal 6a (17.5 g, 82.5 mmol) in 5 mL of anhydrous benzene for 2 h at 20°C. The mixture was filtered. The filtrate was evaporated at reduced pressure (10 and 0.02 mm Hg). Multiple distillation of the residue with a thin layer distillation apparatus gave trithiophosphonate 7a (3.6 g, 60%) and dithiophosphinate 8a (1.9 g, 25%).

Similarly diiodide 18a (4.7 g, 9.9 mmol) and thioacetal 6c (16.6 g, 69.2 mmol) in 5 mL of benzene (reaction conditions: 20°C, 7 h) gave trithiophosphonate 7c (3.6 g, 64%), b.p. 150°C (0.02 mm Hg) (thin layer distillation apparatus), n_D^{20} 1.6028. The ^{31}P NMR spectrum (C_6H_6) δ_P: 92.7 ppm. Mass spectrum (chemical ionization, 100 eV), m/e (I_{rel}, %): 379 $[M + H]^+$ (56), 304 $[M + H - PrS]^+$ (5), 272 $[M + H - PrS - S]^+$ (13), 186 $[M + H - PrS - Pr - Pr - S]^+$ (15) (Reference 1: n_D^{20} 1.6031, the ^{31}P NMR spectrum (neat) δ_P: 92 ppm). Dithiophosphinate 8c (1.1 g, 16%) was also isolated, b.p. 200°C (0.02 mm Hg) (thin layer distillation apparatus), n_D^{20} 1.6090. The ^{31}P NMR spectrum (C_6H_6) δ_P: 85.5 ppm. Mass spectrum (chemical ionization, 100 eV), m/e (I_{rel}, %): 469 $[M + H]^+$ (5) (Reference 1: n_D^{20} 1.6177, the ^{31}P NMR spectrum (neat) δ_P: 85 ppm.).

Reaction of β-Diiodotetraphosphorus Trisulfide 18a with Bis(dimethylamino)methane 12a. Typical Procedure: Diiodide 18a (4.8 g, 10.1 mmol) was added portionwise to stirred solution of aminal 12a (8.3 g, 81.3 mmol) in 5 mL of anhydrous benzene for 2 h at 20°C and stirring was continued for 2 h at 20°C. The mixture was filtered. The filtrate was evaporated under vacuum (10 and 0.02 mm Hg). Distillation of the residue with a thin layer distillation apparatus gave diamidothionophosphonate 13a (1.3 g, 41%).

Similarly diiodide 18a (4.2 g, 8.9 mmol) and aminal 12b (11.2 g, 70.8 mmol) in 5 mL benzene (reaction conditions: 20°C, 2 weeks) gave diamidothionophosphonate 13b (1.6 g, 41%).

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