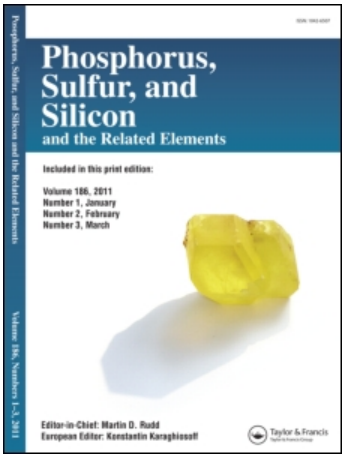

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REACTIONS OF TETRAPHOSPHORUS DECASULFIDE AND 2,4-BIS(ALKYLTHIO)-2,4-DITHIOXO-1,3,2λ⁵, 4λ⁵-DITHIADIPHOSPHETANES WITH DISULFIDES AND THIOACETALS

Il'yas S. Nizamov[a]; Lyubov' A. Al'metkina[a]; Gyuzel' G. Garifzyanova[a]; Elvira S. Batyeva[a]; Vladimir A. Al'fonsov[a]; Arkady N. Pudovik[a]
[a] A. E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, Kazan, Russia

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REACTIONS OF TETRAPHOSPHORUS DECASULFIDE AND 2,4-BIS(ALKYLTHIO)-2,4-DITHIOXO-1,3,2λ^5, 4λ^5-DITHIADIPHOSPHETANES WITH DISULFIDES AND THIOACETALS

IL'YAS S. NIZAMOV,† LYUBOV' A. AL'METKINA, GYUZEL' G. GARIFZYANOVA, ELVIRA S. BATYEVA, VLADIMIR A. AL'FONSOV and ARKADY N. PUDOVIK

A. E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, 420083 Kazan, Russia

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The reactions of tetraphosphorus decasulfide and 2,4-bis(4-alkylthio)-2,4-dithioxo-1,3,2λ^5, 4λ^5-dithiadiphosphetanes with disulfides and thioacetals were studied. The reactions were found to give some novel organothiophosphorus compounds.

Key words: Tetraphosphorus decasulfide; 2,4-bis(alkylthio)-2,4-dithioxo-1,3,2λ^5, 4λ^5-dithiadiphosphetanes; disulfides; thioacetals; organothiophosphorus compounds.

INTRODUCTION

A series of the reactions of anhydrides of thiophosphorus acids with organic compounds with mobile alkoxy-, alkylthio- and dialkylamino groups were previously investigated. These reactions were found to give some novel organothiophosphorus compounds. Thus phosphorus sesquisulfide, P_4S_3, reacts with dialkyl sulfides,[1] disulfides,[2–5] thioacetals,[4,5] thiobisamines,[6] sulfenamides[4,5] and aminals.[4,5] Lawesson's reagent and 2,4-bis(4-ethoxyphenyl)-2,4-dithioxo-1,3,2λ^5, 4λ^5-dithiadiphosphetane react with disulfides,[7] thioacetals,[7,8] acetals,[7,8] and ortho esters.[8] The reactions of tetraphosphorus decasulfide, P_4S_{10}, with ethers,[9] sulfides,[10] acetals,[11] ortho esters,[12,13] ortho thioesters[12] and thiobisamines[14] were studied. However the reactions of tetraphosphorus decasulfide with disulfides and thioacetals remained unknown. Besides the chemical behavior of disulfides and thioacetals also remained unknown in the reactions with homologues of Davy's reagent [2,4-bis(alkylthio)-2,4-dithioxo-1,3,2λ^5, 4λ^5-dithiadiphosphetanes].

RESULTS AND DISCUSSION

The disulfides are known to react with tetraphosphorus trisulfide, P_4S_3, to give trithiophosphite esters and tetrathiophosphate esters.[2–5] Taking this into consideration we would assume that the reactions of tetraphosphorus decasulfide with

†Author to whom correspondence should be addressed.

dialkyl disulfides will result in trialkyl tetrathiophosphates. On the other hand considering that the reactions of Lawesson's reagent with dialkyl disulfides proceed with the formation of phosphonotrithiolothioates with P—S—S—Alk bonds[7] we have assumed that the reaction of tetraphosphorus decasulfide with dialkyl disulfides should also lead to thiophosphates with the S—S thiol bond. We carried out the reaction of tetraphosphorus decasulfide 1 with dialkyl disulfides 2a–c in anhydrous toluene at 100–110°C for 1 h and actually obtained S,S'-dialkyl S", S"-alkyltetrathiolothionophosphates 3a–c (Equation 1, Method A).

$$P_4S_{10} + 6\,RS\text{-}SR \longrightarrow 4(RS)_2\overset{S}{\overset{\|}{P}}S\text{-}SR + \frac{1}{4}S_8 \qquad (1)$$

1 2a, R = Et 3a, R = Et
b, R = Pr-i b, R = Pr-i
c, R = Bu-i c, R = Bu-i

An S—S bridge bond is seen in the structure of 3a–c. The 3a–c were purified by column chromatography (see Experimental). The structures of 3a–c were established by IR (Table II), ^{1}H NMR (Table III), ^{31}P NMR (Table I), mass spectral data (Table IV), and microanalyses (Table I).

We have found that the reaction of 1 with 2 is sensitive to reaction conditions. The trialkyl tetrathiophosphates 4 were formed when the reaction of 1 with 2 was subject to prolonged heating at 100°C or higher. Pure 3 decomposed during distillation in vacuum or when a thin layer distillation apparatus was used as well. The product 3a partially decomposed when handling during a long time (~4 months) in sealed tube at room temperature. Perhaps, the thermal instability of 3 is determined by the existence of an additional sulfur atom between the phosphorus atom and the alkylthio group. The decomposition of 3a–c may have occurred through the elimination of a sulfur atom to form 4a–c which were isolated (Equation 2).

$$(RS)_2\overset{S}{\overset{\|}{P}}S\text{-}SR \longrightarrow (RS)_3\overset{S}{\overset{\|}{P}} + \frac{1}{4}S_8 \qquad (2)$$

3a, R = Et 4a, R = Et
b, R = Pr-i b, R = Pr-i
c, R = Bu-i c, R = Bu-i

Some assumptions may be suggested concerning the mechanism of degradation of 1 due to the effect of 2 and formation of 3. Perhaps, the reaction of 1 with 2 is initiated by nucleophilic attack of the sulfur atom of the alkylthio group of 2 on the phosphorus atom of 1 and involves a succession of steps (Equation 3). Taking into account the ready formation of RS* radicals during decomposition of dialkyl disulfides in severe reaction conditions and short reaction time a radical pathway is possible. To corroborate this assumption we carried out the reaction of 1 with

TABLE I

Experimental, physical and analytical data of the products obtained

Prod.	Reaction conditions time (h)/temp. (°C) Methods of synthesis[a] A	B	Yield, % A	B	B.p.[d] °C (mm Hg) or mp (°C)[f]	R_f Value (eluant)	d_4^{20}	n_D^{20}	Molecular formula (Mol. mass)	Analytical data Found/Calc. (%) C	H	P	S	^{31}P NMR δ, ppm (solvent)
3a	1/100[e]	1/100	7[b]/4[c]	83[b]		0.90 (C_6H_6)	1.2800	1.5668	$C_6H_{15}PS_5$	25.64	5.32	10.89	57.09	98.0
									(278.0)	25.90	5.45	11.14	57.51	(CCl_4)
3b	1/100[e]		11[b]/5[c]			0.88 (C_6H_6)	1.1185	1.5918	$C_9H_{21}PS_5$	33.34	6.31	10.01	50.19	94.8
									(320.0)	33.75	6.62	9.68	49.95	(C_6D_6)
3c	1/100–110[e]	1.5/90	38[b]	59[b]		0.87 (C_6H_6)	1.0092	1.5253	$C_{12}H_{27}PS_5$	39.44	7.41	8.77	44.72	100.5
									(362.1)	39.77	7.57	8.55	44.15	(CCl_4)
7a	3/100	15/20	86[c]	62[b]/52[c]	130–140 (0.02)	0.82[h]	1.1498	1.6258	$C_{13}H_{21}PS_5$	42.51	5.50	8.74	43.14	88.4
									(368.0)	42.39	5.76	8.42	43.43	(CCl_4)
8a	3/100		8[c]		238–239 (MeCN)				$C_{20}H_{27}PS_6$ (490.1)	48.60 48.97	5.34 5.57	6.71 6.32	39.51 39.14	92.7 (MeCN)
7b	3.5/120–140	12/20	93[c]	48[c]	180–190 (0.02)		1.0016	1.5618	$C_9H_{33}PS_5$	50.59	7.23	6.89	35.26	90.5
									(452.2)	50.43	7.37	6.85	35.35	(C_6H_6)
8b	3.5/120–140		9[c]		219–220				$C_{26}H_{39}PS_6$	54.87	6.60	5.55	32.88	93.5
									(574.2)	54.34	6.86	5.39	33.41	(C_6H_6)
7c		15/20		36[b]/27[c]	163 (0.02)		1.2746	1.6504	$C_7H_{17}PS_5$	28.45	5.40	10.94	54.23	88.4
									(292.0)	28.77	5.88	10.61	54.74	(CCl_4)
7d		5/20		47[b]/35[c]	170–180 (0.03)		1.1772	1.6118	$C_9H_{21}PS_5$	33.56	6.20	9.88	49.56	90.2[g]
									(320.0)	33.75	6.63	9.68	49.66	
7e		5/20		60[b]/34[c]	175 (0.02)		1.0946	1.6354	$C_{15}H_{25}PS_5$	45.49	6.04	8.16	40.43	89.0[g]
									(396.1)	45.45	6.37	7.82	40.36	

[a]Methods of synthesis: A—the reaction of 1 with 2 or 6; B—the reaction of 5 with 2 or 6.
[b]Yield of crude product.
[c]Yield of isolated product.
[d]Temperature of the spiral of the thermal element of the thin layer distillation apparatus.
[e]Solvent: toluene.
[f]Solvent of recrystallization.
[g]Neat.
[h]Eluant: hexane-diethyl ether 1:1.

TABLE II

IR spectral data (cm^{-1}) of the products obtained

Prod.	C—H[a], Ar	CH_3[a] as, s; CH_2[a] as, s	C═C,[a] Ar	δ (CH_3 as, CH_2 s)	δ[$(CH_3)_2C$ gem s]	ω, $\tau(CH_2)$	P═S,[a] PS_2[a] as	PS_2[a] s, P—SC[a]
3a		2970, 2930, 2875, 2850		1453, 1379		1260	693	535, 503
3b		2985, 2972, 2935, 2877		1453, 1420	1380, 1368	1260	690	548, 530, 515
3c		2965, 2935, 2900, 2876		1468, 1430	1388, 1370	1260	693	548, 535, 525, 505
7a	3065, 3035	2975, 2935, 2878	1590, 1498	1452		1265	700 680	560, 526
8a[b]	3090, 3060, 3030			1599, 1495			695	
7b	3070, 3035	2965, 2935, 2915, 2879	1560, 1498	1460	1390, 1370	1262	705	526, 515
8b[b]	3090, 3040		1600, 1495				692	
7a		2970, 2930, 2875		1380			693	545, 530
7d		2970, 2930, 2877		1450	1385, 1370	1265	682	545, 580
7e	3070, 3035	2970, 2934, 2878	1598, 1498	1456	1382, 1370	1267	685	530, 515

[a]Valence vibrations.
[b]In vaseline oil.

TABLE III

^{1}H NMR spectral data of the products obtained

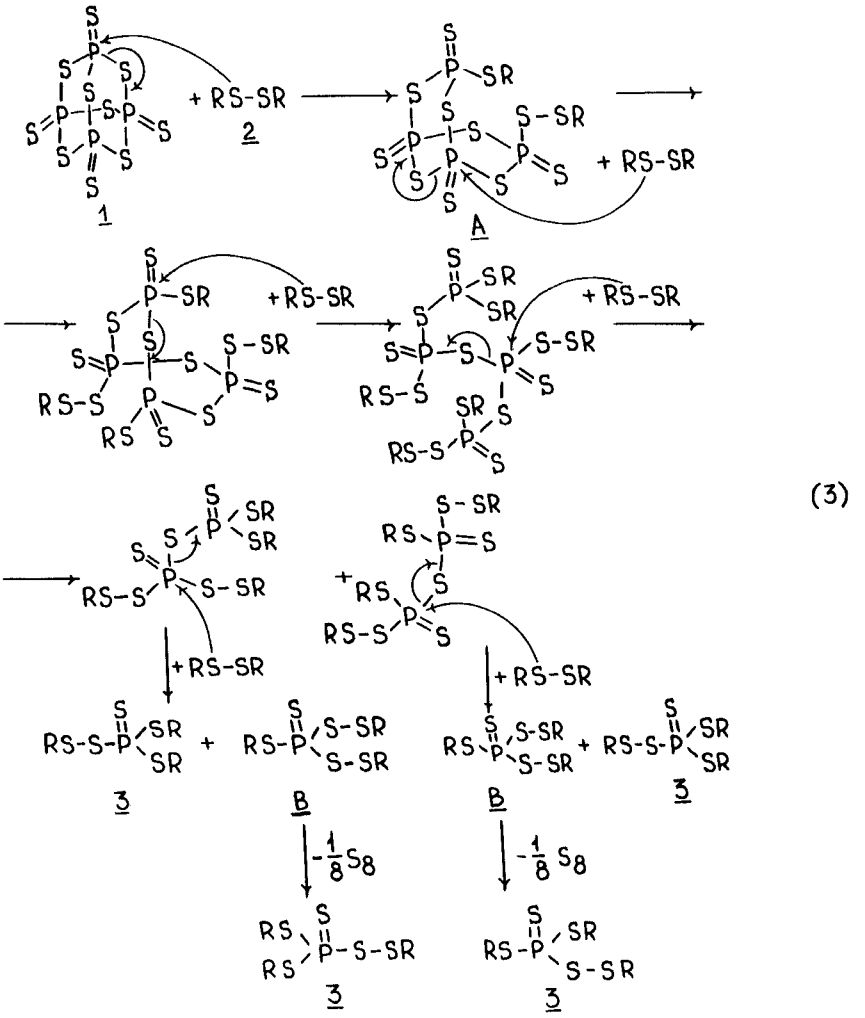
Prod.	CCl_4, δ, ppm, J, Hz
3a	1.37 (t, 3H, $\underline{CH_3}CH_2SS$, $^3J_{H-H}$ 7.5); 1.41 (t, 6H, $\underline{CH_3}CH_2SP$, $^3J_{H-H}$ 7.5); 2.78 (q, 2H, $CH_3\underline{CH_2}SS$, $^3J_{H-H}$ 7.5); 3.02 (dq, 4H, $CH_3\underline{CH_2}SP$, $^3J_{H-H}$ 7.5, $^3J_{P-H}$ 17.0.
3b	1.33 (t, 6H, $\underline{CH_3}CHSS$, $^3J_{H-H}$ 6.5); 1.40 (t, 12H, $\underline{CH_3}CHSP$, $^3J_{H-H}$ 6.5); 2.58–3.77 (m, 3H, $CH_3\underline{CH}SP$, $CH_3\underline{CH}SS$).
3c	1.03 (d, 6H, $\underline{CH_3}CHCH_2SS$, $^3J_{H-H}$ 6.5); 1.04 (d, 12H, $\underline{CH_3}CHSP$, $^3J_{H-H}$ 6.5); 1.58–2.22 (m, 3H, $CH_3\underline{CH}CH_2$); 2.52 (d, 2H, $CH\underline{CH_2}SS$, $^3J_{H-H}$ 6.5); 2.83 (dd, 4H, $CH\underline{CH_2}SP$, $^3J_{H-H}$ 6.5, $^3J_{P-H}$ 15.0).
7a	1.20 (t, 3H, $\underline{CH_3}CH_2SCH$, $^3J_{H-H}$ 7.5); 1.39 (t, 6H, $\underline{CH_3}CH_2SP$, $^3J_{H-H}$ 7.5); 2.49 (q, 2H, $CH_3\underline{CH_2}SCH$, $^3J_{H-H}$ 7.5); 2.95 (dq, 4H, $CH_3\underline{CH_2}SP$, $^3J_{H-H}$ 7.5, $^3J_{P-H}$ 18.0), 5.42 (d, 1H, $\underline{CH}P$, $^3J_{P-H}$ 11.0); 7.18–7.49 (m, 5H, $C_6\underline{H_5}$).
8a[a]	1.21 (t, 6H, $\underline{CH_3}CH_2SCHS$, $^3J_{H-H}$ 7.4); 1.26 (t, 3H, $\underline{CH_3}CH_2SP$, $^3J_{H-H}$ 7.4); 2.38 (q, 4H, $CH_3\underline{CH_2}SCHS$, $^3J_{H-H}$ 7.4); 2.29–2.47 (m, 2H, $CH_3\underline{CH_2}SP$), 5.07 (d, 2H, $\underline{CH}SP$, $^3J_{P-H}$ 7.5); 7.37–7.57 (m, 10H, $C_6\underline{H_5}$).
7b	0.84 (d, 6H, $\underline{CH_3}CHCH_2SCH$, $^3J_{H-H}$ 6.5); 1.00 (d, 12H, $\underline{CH_3}CHCH_2SP$, $^3J_{H-H}$ 6.5); 1.65–2.08 (m, 3H, $CH_3\underline{CH}CH_2$); 2.35 (d, 2H, $CH_3CH\underline{CH_2}SCH$, $^3J_{H-H}$ 6.5); 5.30 (d, 1H, $\underline{CH}P$, $^3J_{P-H}$ 15.0); 6.95–7.37 (m, 5H, $C_5\underline{H_5}$).
7c	1.39 (t, 3H, $\underline{CH_3}CH_2SCH_2S$, $^3J_{H-H}$ 7.2); 1.48 (t, 6H, $\underline{CH_3}CH_2SP$, $^3J_{H-H}$ 7.2); 2.79 (q, 2H, $CH_3\underline{CH_2}SCH_2S$, $^3J_{H-H}$ 7.2); 3.04 (dq, 4H, $CH_3\underline{CH_2}SP$, $^3J_{H-H}$ 7.2, $^3J_{P-H}$ 17.5); 4.10 (d, 2H, $S\underline{CH_2}SP$ $^3J_{P-H}$ 10.0).
7d	1.12 (d, 6H, $\underline{CH_3}CHCH_2S$, $^3J_{H-H}$ 6.5); 1.39 (t, 3H, $\underline{CH_3}CH_2SCH_2$, $^3J_{H-H}$ 7.2); 1.48 (t, 3H, $\underline{CH_3}CH_2SP$, $^3J_{H-H}$ 7.2); 1.77–2.30 (m, 1H, $\underline{CH}CH_2SP$); 2.77 (q, 2H, $CH_3\underline{CH_2}SCH_2S$, $^3J_{H-H}$ 7.2); 2.90 (dd, 2H, $CH_3CH\underline{CH_2}SP$, $^3J_{H-H}$ 6.5, $^3J_{P-H}$ 15.0); 2.60–3.38 (m, 2H, $CH_3\underline{CH_2}SP$); 4.11 (d, 2H, $S\underline{CH_2}SP$, $^3J_{P-H}$ 10.0).
7e[b]	0.97 (d, 6H, $\underline{CH_3}CHCH_2$, $^3J_{H-H}$ 6.5); 1.15 (t, 3H, $\underline{CH_3}CH_2SCH$, $^3J_{H-H}$ 7.0); 1.31 (t, 3H, $\underline{CH_3}CH_2SP$, $^3J_{H-H}$ 7.0); 2.80 (q, 2H, $CH_3\underline{CH_2}SCHS$, $^3J_{H-H}$ 7.0); 2.24–3.22 (m, 4H, $CH_3\underline{CH_2}SP$, $CH_3CH\underline{CH_2}SP$); δ_1 5.30 (d, 1H, $\underline{CH}SP$, $^3J_{P-H}$ 12.5); δ_2 5.35 (d, 1H, $\underline{CH}SP$, $^3J_{P-H}$ 12.5); 7.28–7.52 (m, 5H, $C_6\underline{H_5}$).

[a] In CD_3CN.

[b] The mixture of diastereosiomers.

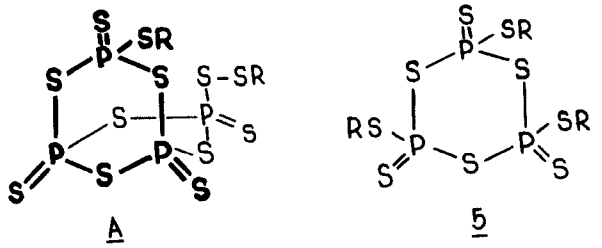
2a,b under UV irradiation at 35–45° and observed the formation of 3a,b. In accordance with Equation 3 the reaction should involve the formation of hexathiophosphates B which decompose resulting in 3 with the elimination of a sulfur atom. This assumption is confirmed by the chemical ionization mass spectral analysis of a crude reaction mixture of 1 and 2a indicating the existence of the mass peak m/e 311 which corresponds to S-ethyl S′,S′,S″,S″-bis(ethyl)pentathiolothionophosphate B. Along with the signal of 3a with δ 98.0 ppm a weak signal with δ 105.5 ppm was also observed in the ^{31}P NMR spectra of the reaction mixture, which may be attributed to B. In Table V the ^{31}P NMR spectral data of various tetra-, penta- and hexathiophosphates are listed. The increase of the amount of sulfur atoms in molecules of thiophosphates (from 4 via 3 to B) results in a decrease of the chemical shifts.

We assumed that during the initial steps of the destruction process of 1 (Equation 3) an intermediate A may be formed. The structural fragment of A may be similar to that of 2,4-bis(alkylthio)-2,4-dithioxo-1,3,2λ^5, 4λ^5-dithiadiphosphetanes 5 in their trimer form (drawing 1). Intermediates 5 in their dimer form may be formed in accordance with Equation 3.



(3)

Consequently the interaction of 5 with 2 may be used as a model reaction of some intermediate processes of degradation of 1 and formation of 3. As we expected the counter-reaction of 5a,b with 2a,c at 90–100°C for 1–1.5 h had been found to



DRAWING I

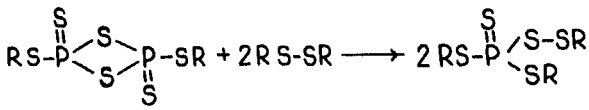
TABLE IV
Mass spectral data of the products obtained

Prod.	i-C_4H_{10}, m/e (I_{rel})
3a[a]	279 $[M + H]^+$ (45), 247 $[M + H - S]^+$ (100), 218 $[M + H - EtS]^+$ (30), 185 $[M + H - EtS_2]^+$ (30), 154 $[M + H - EtS_3]^+$ (30).
3b[a]	321 $[M + H]^+$ (30), 278 $[M + H - Pr\text{-}i]^+$ (10), 246 $[M + H - SPr\text{-}i]^+$ (10), 214 $[M + H - S_2Pr\text{-}i]^+$ (95), 203 $[M + H - SPr\text{-}i - Pr\text{-}i]^+$ (10), 171 $[M + H - S_2Pr\text{-}i - Pr\text{-}i]^+$ (10), 139 $[M + H - S_2Pr\text{-}i - SPr\text{-}i]^+$ (80).
3c[b]	362 $[M]^+$ (100), 330 $[M - S]^+$ (20), 273 $[M - SBu\text{-}i]^+$ (25), 241 $[M - S_2Bu\text{-}i]^+$ (80).
3c[a]	185 $[M + H - S_2Bu\text{-}i]^+$ (100), 153 $[M + H - S_3Bu\text{-}i_2]^+$ (30).
7a[b]	368 $[M]^+$ (10).
7a[a]	337 $[M + H - S]^+$ (10), 279 $[M + H - SEt - SEt]^+$ (10).
8a[b]	246 $[M - SEt - SC(SEt)HPh]^+$ (55), 213 $[M - H - SEt - SC(SEt)HPh]^+$ (10), 181 $[M - H - SEt - S - SC(SEt)HPh]^+$ (15), 169 $[M - SC(SEt)HPh - SEt - Ph]^+$ (10), 151 $[M - EtSP(S)SC(SEt)HPh]^+$ (10), 124 $[M - SC(SEt)HPh - SC(SEt)HPh]^+$ (100).
7b[a]	340 $[M + H - Bu\text{-}i - Bu\text{-}i]^+$ (10), 123 $[M + H - Bu\text{-}i - (i\text{-}BuS)_2PS_2]^+$ (70).
7b[b]	274 $(M - H - SBu\text{-}i - SBu\text{-}i]^+$ (10), 179 $[M - SBu\text{-}i - SBu\text{-}i - PS_2]^+$ (100).
8b[b]	274 $[M - H - SBu\text{-}i - SC(SBu\text{-}i)HPh]^+$ (10).
7c[b]	292 $[M]^+$ (30), 263 $[M - Et]^+$ (25), 231 $[M - SEt]^+$ (35), 185 $[M - SCH_2SEt]^+$ (30), 153 $[M - S - SCH_2SEt]^+$ (100).
7d[a]	321 $[M + H]^+$ (90), 292 $[M + H - Et]^+$ (100), 264 $[M + H - Bu\text{-}i]^+$ (50).
7d[b]	320 $[M]^+$ (30), 259 $[M - SEt]^+$ (30), 231 $[M - SBu\text{-}i]^+$ (50), 170 $[M - SEt - SBu\text{-}i]^+$ (55).
7e[a]	397 $[M + H]^+$ (60), 368 $[M + H - Et]^+$ (100), 340 $[M + H - Bu\text{-}i]^+$ (10), 312 $[M + 2H - Bu\text{-}i - Et]^+$ (10), 279 $[M + H - SBu\text{-}i - Et]^+$ (10).

[a]Chemical ionization, 100 eV.
[b]Electron impact, 70 eV.

bring about the same 3a,c we have obtained due to the reaction of 1 with 2a,c (Equation 4, Method B, Table I).

It should be noted that the physical and spectral data of 3a,c were identical with those of 3a,c obtained in the course of the reaction of 1 with 2a,c (Equation 1). In this case one of the alkylthio groups is attached to the phosphorus atom and the other alkylthio group is attached via a sulfur atom. It should be emphasized that formally 3 are the products of the insertion of monomeric unit, $RSPS_2$, of 5 into the S—S bond of 2. Unfortunately in this case (Equation 4) the 3a,c were also unstable during distillation and 4a,c were also isolated in distilled form from the reaction mixture.



(4)

5a, R = Et 2a, R = Et 3a, R = Et
b, R = Bu-i c, R = Bu-i c, R = Bu-i

TABLE V

^{31}P NMR spectral data of 3, 4 and B

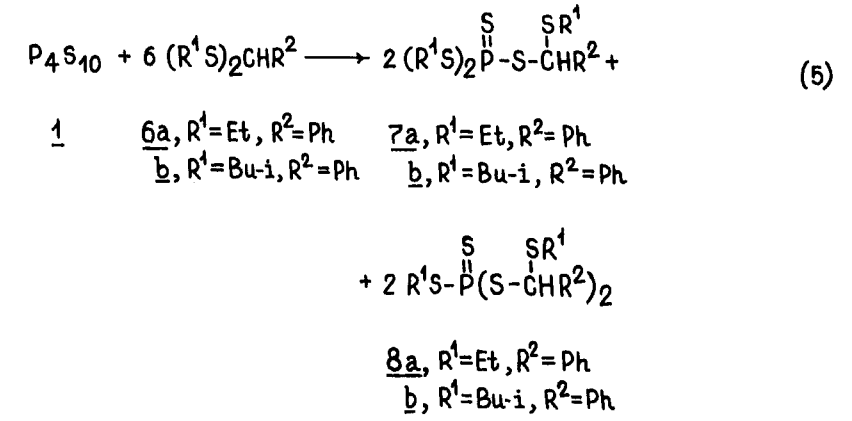
Compounds R	No.	δ, ppm, (C_6H_6) Et a	Pr-i b	Bu-i c
$(RS)_3P{=}S$	4	90.5	86.5	92.8
$(RS)_2P(S)SR$	3	98.0	94.8	100.5
$RSP(SSR)_2$ (S)	B	105.5	103.9	106.8

As shown in the analysis of the reaction mixture of 1 with 2a by the electron impact mass spectral method there is a mass peak m/e 156. This may be attributed to cation-radical $[EtSPS_2]^{+\cdot}$ which is the monomeric unit of 5a. The electron impact mass spectrum of pure authentic 5a shows the same mass peak of ion $[EtSPS_2]^{+\cdot}$ m/e 156 as well. Consequently 1,3,2,4-dithiadiphosphetanes like 5 (in their monomeric, dimeric or trimeric forms) may be formed during several steps of the degradation process of 1 due to the effect of 2. But on the other hand we cannot rule out that this mass peak (m/e 156) in the mass spectrum of the reaction mixture of 1 and 2a to be due only to a fragment of the product 3a. Nevertheless the structure of 3 is confirmed by this counter-reaction (Equation 4).

However we consider that, perhaps, the reaction of 1 with 2 proceeds via more complicated route than we could have imagined. Thus the chemical ionization mass spectrum of the reaction mixture of 1 and 2a also indicates the existence of mass peaks m/e 123, 155, 187 and 218 which may be attributed to EtSSEt (2a) and other diethyl polysulfides (EtS_3Et, EtS_4Et and EtS_5Et, respectively). These polysulfides may be formed either during the degradation of 1 or by the reaction of 2a with elemental sulfur formed under reaction conditions.

We have previously shown that the phosphorus sesquisulfide, P_4S_3, reacts with thiocetals to form the products of (1-alkylthio)alkyl thionophosphonate structure.[4,5] We have also found that the reaction of Lawesson's-like reagents with thioacetals proceeds with the formation of alkyl(1-alkylthioalkyl) arylphosphonotrithioates with an aldehyde fragment, $R{-}\underset{|}{\overset{|}{C}}{-}H$, in their composition.[7] The formation of products of (1-alkylthio)alkyl thionophosphate structure could be expected in the reaction of 1 with thioacetals. Indeed we have found that the interaction of 1 with thioacetals 6a,b at 100–140°C for 3–3.5 h results in S,S′-dialkyl S″-(1-alkylthio)benzyl tetrathiophosphates 7a,b and S-alkyl S′,S′-bis(1-alkylthiobenzyl) tetrathiophosphates 8a,b (Equation 5, Method A, Tables I–IV).

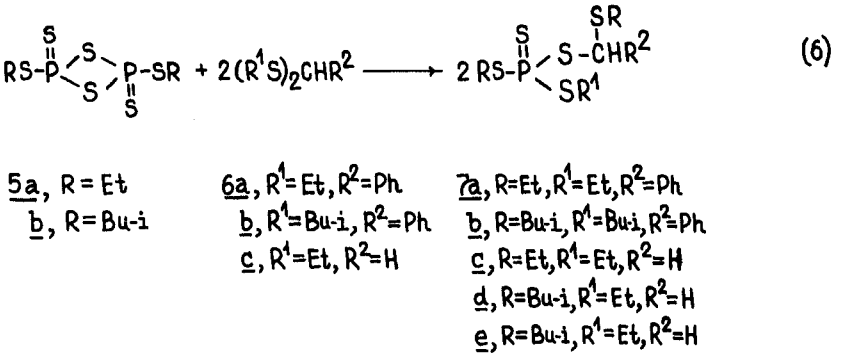
As we expected 7 and 8 involve an aldehyde fragment, $R{-}\underset{|}{\overset{|}{C}}{-}H$, in their com-



(5)

position. Unlike 3 the products 7 and 8 are stable compounds. In spite of the existence of a mixture of products 7 and 8 in the reaction mixture they are easily isolated. The products 8 are solids and are recrystallized from organic solvents (Table I and Experimental). The products 7 were purified by thin layer distillation or by column chromatography.

The mechanism of formation of 7 and 8 is assumed to be similar to that suggested for 3. If so 7 can be formed in the reaction of 6 with 5. Indeed this approach enabled us to obtain 7a,b through the reaction of 5a,b with 6a,b under mild conditions (20°C, 5–15 h) (Equation 6, Method B, Tables I–IV).



(6)

The physical and spectral data of 7a,b were identical to those of 7a,b obtained by the reaction of 1 with 6a,b (Equation 5). It should be noted that in this case formally 7 are also the products of the insertion of the monomeric unit, $RSPS_2$, of 5 into the C—S bond of thioacetals 6. Thus this counter-reaction (Equation 5) substantiates the structure of 7.

We extended this convenient method to the reaction of 5 with 6c (Reaction 6). We carried out the reactions of 6c with 5a and 5b, and 6a with 5b and obtained (1-alkylthio)alkyl tetrathiophosphates 7c, 7d and 7e, respectively under mild conditions (20°C, 5–15 h) (Equation 6, Method B, Tables I–IV). When using the products 5 and 6 with different alkylthio groups at 5 and 6, and substituents at the

1-carbon atom of 6 (e.g., 5b and 6a) we obtain the product 7 as a mixture of diastereoisomers (e.g., 7e) (Tables I and III), there being two asymmetrical centres (phosphorus atom and 1-carbon atom of the aldehyde fragment, R—C—H, in the molecule of 7e). Unlike the reaction of phosphorus sulfide 1 with 6 compounds 7 are the only organothiophosphorus products in the reaction mixture of 5 with 6. It is noteworthy that the reactivity of 5 towards 6 is higher than that of 1.

EXPERIMENTAL

^{31}P NMR spectra were recorded with a Bruker MSL-400 (162 MHz) and a Bruker CXP-100 (36.5 MHz) spectrometer to external H_3PO_4 (85%). ^1H NMR spectra were run on a Varian T-60 (60 MHz) spectrometer in CCl_4 with $(Me_3Si)_2O$ as an internal reference and on a Bruker WM 250 (250 MHz) spectrometer in CD_3CN. IR spectra were obtained in KBr with a UR-20 infrared spectrophotometer. Mass spectra (electron impact, 70 eV; chemical ionization, 100 eV) were determined on a M 80 B Hitachi chromato mass spectrometer.

S,S'-Diethyl S'',S''-ethyltetrathiolothionophosphate 3a; *Typical Procedure. (Method A).* The mixture of 1 (5.9 g, 13.3 mmol) and 2a (9.8 g, 80.2 mmol) in 10 ml of anhydrous toluene was stirred at 100°C for 1 h. The mixture was filtered. The solvent was removed from the filtrate at reduced pressure (0.02 mmHg) at 40°C for 2 h. Removal of the volatile materials from the residue resulted in crude 3a (1.1 g, 7%). The latter was chromatographed on a silica gel column with benzene as an eluant and yielded pure 3a (0.66 g, 4%) (Physical, analytical and spectral data are listed in Tables I–IV).

The products 3b,c were obtained similarly (Tables I–IV).

Method B. The mixture of 5a (10.0 g, 32.2 mmol) and 2a (7.9 g, 64.7 mmol) was stirred at 100°C for 1 h. The mixture was filtered. The solvent was removed from the filtrate at reduced pressure (0.02 mmHg) at 40–50°C for 2 h. The residue is crude 3a (14.9 g, 83%) (its physical and spectral data are identical with those of 3a obtained by Method A).

The product 3c is obtained similarly.

Triethyl tetrathiophosphate 4a; *Typical Procedure (Method A).* Similarly to the preparation of 3a (Method A) from 1 (4.8 g, 10.8 mmol) and 2a (7.9 g, 64.6 mmol) yielded a residue. The distillation of the residue gave 4a (0.6 g, 5%), b.p. 112°C (0.02 mmHg), n_D^{20} 1.6130, ^{31}P NMR spectrum (C_6H_6, 162 MHz) δ: 90.5 ppm. Mass spectrum (chemical ionization, 100 eV): m/e 247 $[M + H]^+$ (100%). (Reference 15: b.p. 124–125°C (1.5 mm Hg), ^{31}P NMR spectrum δ: 91.7 ppm).

The product 4b (yield 10%) is obtained similarly (b.p. 123°C (0.02 mm Hg), n_D^{20} 1.5655, ^{31}P NMR spectrum (C_6H_6) δ: 86.5 ppm.

The product 4c (yield 73%) is obtained similarly (b.p. 136–137°C (0.02 mm Hg), n_D^{20} 1.5549, ^{31}P NMR spectrum (C_6H_6) δ: 92.8 ppm. Mass spectrum (Chemical ionization, 100 eV): m/e 331 $[M + H]^+$ (10%).

Method B. Similarly to the preparation of 3a (Method B) the interaction of 5a (10.0 g, 33.2 mmol) and 2a (7.9 g, 64.7 mmol) yielded a residue. It was distilled and gave 4a (6.7 g, 42%).

The product 4c (yield 47%) is obtained similarly.

S,S'-Diethyl S''-(1-ethylthio)benzyl tetrathiophosphate 7a *and S-ethyl S',S''-bis(1-ethylthiobenzyl)-tetrathiophosphate* 8a. *Typical Procedure (Method A). a.* The mixture of 1 (10.9 g, 24.6 mmol) and 6a (31.7 g, 147.6 mmol) was stirred at 100°C for 3 h. The mixture was evaporated under vacuum (0.02 mm Hg) at 50°C for 3 h. The residue was kept at ~20°C for 0.5 month. The precipitate was filtered and recrystallized from MeCN. Yield of 8a (2.0 g, 8%) (Tables I–IV). Thin layer distillation of the filtrate resulted in 7a (14.2 g, 86%) (Tables I–IV).

b. Similarly 1 (0.8 g, 1.8 mmol) and 6a (2.3 g, 10.8 mmol) gave a residue after evaporation under vaccum. It was chromatographed on a silica gel column with 1:1 hexane-ether as an eluant and yielded pure 7a (0.6 g, 50%) (Tables I–IV).

The products 7b and 8b were obtained similarly (Tables I–IV).

S,S'-Diethyl S"-(1-ethylthio)benzyl tetrathiophosphate 7a; *Typical Procedure* (*Method B*). The mixture of 5a (10.0 g, 32.3 mmol) and 6a (13.7 g, 64.6 mmol) was stirred at 20°C for 15 h. The mixture was filtered. The filtrate was evaporated under vacuum (0.02 mm Hg) at 50°C for 2 h. Product 7a was isolated from the residue by means of thin layer distillation (its physical and spectral data are identical with those of 7a obtained by Method A).

The products 7b–e were obtained similarly (Tables I–IV).

Influence of UV irradiation on the reaction of tetraphosphorus decasulfide 1 *with disulfide* 2a. *Typical Procedure.* The mixture of 1 (1.0 g, 2.25 mmol) and 2a (1.65 g, 1.35 mmol) was irradiated by UV light at 35–37°C for 1 h. The mixture was filtered. Removal of the volatile materials from the filtrate resulted in crude 3a (0.4 g, 165).

Similarly 1 (3.0 g, 6.8 mmol) and 2b (6.1 g, 40.6 mmol) (reaction conditions: 45°C, 1 h) gave crude 3b (0.4 g, 5%).

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