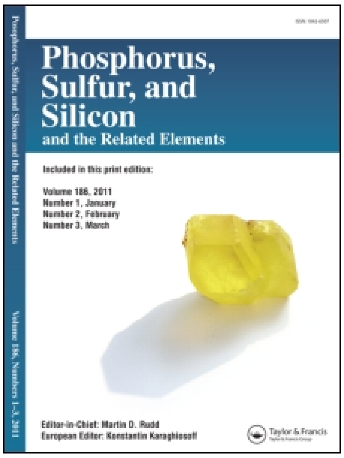

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REACTIONS OF TETRAPHOSPHORUS DECASULFIDE AND LAWESSON'S REAGENT WITH SILANES CONTAINING A FEW Si-O BONDS

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REACTIONS OF TETRAPHOSPHORUS DECASULFIDE AND LAWESSON'S REAGENT WITH SILANES CONTAINING A FEW Si-O BONDS

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The reactions of tetraphosphorus decasulfide and Lawesson's reagent with tetra-, tri- and dialkoxysilanes were studied. On the basis of these reactions, new S-silyl esters of phosphorus(V) thioacids have been prepared. The prepared compounds were identified by IR, ^{1}H, and ^{31}P NMR and mass spectra as well as elemental analyses.

Keywords: Tetraphosphorus decasulfide; Lawesson's reagent; silanes; organothiophosphorus compounds

INTRODUCTION

S-Triorganylsilyl and stannyl esters of phosphorus(V) thioacids with the P(S)SE (E = Si, Sn) structural fragment are well known to possess of practical use. Thus, S-trimethylsilyl dithiophosphates are thiation reagents for carbonyl compounds. [1] S-Trimethylsilyl esters of dithiophosphoric and tetrathiophosphoric acids are the efficient intermediates for the synthesis of useful organothiophosphorus compounds.[1,2] S-Triorganylstannyl dithiophosphates and tetrathiophosphates are used as pesticides and lubricant additives.[3,4] The reactions of tetraphosphorus decasulfide (P_4S_{10})

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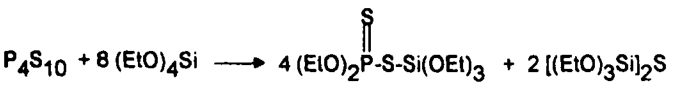
and 1,3,2,4-dithiadiphosphetane-2,4-disulfides with silicon(IV) and tin(IV) derivatives containing reactive E-X bonds (E = Si, Sn; X = O, S, N) such as heptamethyldisilazane,[5] trimethylsilylazide,[6] trimethylchlorosilane,[7] trimethyl(dialkylamino)silane,[8] bis(trimethylsilyl)sulfide, [8] bis(trimethylsilyl)acetamide,[9] bis(trimethylstannyl)sulfide,[10] trimethyl (alkoxy)silanes and trimethyl(alkylthio)silanes, trialkyl(alkoxy)stannanes and trialkyl(alkylthio)stannanes[11–13] result in S-triorganylsilyl and stannyl esters of phosphorus(V) thioacids. However, similar products with the P(S)SSi fragment were not obtained in the reactions of phosphorus sulfide (P_4S_{10}) with tetraphenoxysilane[14,15] and tetraalkoxysilanes.[15,16] Phosphorylation of tetraphenoxysilane by treatment with P_4S_{10} was reported to proceed under severe conditions (155–170°C, 12 h) with the formation of 4-hydroxyphenylphosphonic acid after hydrolysis of some unidentified precursor.[14,15] Trialkyl tetrathiophosphates,[16] trialkyl trithiophosphites, dialkylsulfides and alkylpolysiloxanes[17] have also been obtained in the reaction of P_4S_{10} with tetraalkoxysilanes at 160–170°C. These organothiophosphorus compounds seem to be secondary products and may be formed via the destruction of some initial products. We assumed that these initial products may include the P(S)SSi fragment similarly to the products formed in the reactions of P_4S_{10} with monoalkoxysilanes under mild conditions.[13] We decided to verify this idea and to study the reactions of tetraphosphorus decasulfide and 1,3,2,4-dithiadiphosphetane-2,4-disulfides with silanes containing a few Si-O bonds.

RESULTS AND DISCUSSION

We have reinvestigated the reaction of tetraphosphorus decasulfide **1** with tetraethoxysilane **2** at room temperature and obtained S-triethoxysilyl O,O′-diethyldithiophosphate **3** after stirring of the reaction mixture for 3 days (Reaction (1), Tables (I)-(V)).



$$P_4S_{10} + 8\,(EtO)_4Si \longrightarrow 4\,(EtO)_2\overset{S}{\overset{\|}{P}}\text{-}S\text{-}Si(OEt)_3 + 2\,[(EtO)_3Si]_2S \qquad (1)$$

1 **2** **3** **4**

Product **3** is a colorless liquid. It was purified by means of thin layer distillation (see Tables (I)-(V)). Reaction 1 was accompanied by the formation of bis(triethoxysilyl)sulfide **4**, which was easily removed from the reaction mixture by evaporation at reduced pressure. Its presence in the volatile distillation fractions was confirmed by use of ^1H NMR and mass spectra.

TABLE I Experimental data and yields of the products obtained

Initial Compounds Quantity, g (mmol)		*Reaction Conditions 20 °C, Time, h*		*Product Yield, g (%)*
1	2.7 (6.1)/**2** 10.0 (48.0)	30		**3** 8.4 (99)[a] /4.4 (52)[b]
1	2.0 (4.5)/**5a** 7.4 (36.2)	16		6a 2.5 (37)[a]/1.2 (18)[b]
1	1.6 (3.6)/**5b** 7.0 (28.6)	20		6b 3.7 (70)[b]
				7b 1.6 (48)[b]
12	10.0 (24.8)/**2** 10.3 (49.5)	3		**13a** 10.0 (49)[a]/7.5 (37)[b]
12	5.0 (12.3)/**8a** 7.0 (24.7)	16		**13b** 6.4 (53)[a]/4.7 (39)[b]
12	7.0 (17.3)/**8b** 6.9 (34.8)	5		**13c** 7.1 (51)[a]/5.7 (41)[b]
12	5.8 (14.4)/**5b** 7.0 (28.6)	5		**13d** 6.9 (54)[a]/3.5 (27)[b]
12	3.0 (7.4)/**5c** 4.0 (14.7)	5	5 mL PhH	**13d** 6.9 (54)[a]/3.5 (27)[b]

a. Yield of crude product.
b. Yield of isolated product.

TABLE II Physical, analytical and ^{31}P NMR spectral data of the products obtained

Prod.	*Bp, °C (mm Hg)*[a]	n_D^{20}	*Molecular Formula (Mol. mass)*	*Found(Calc.), %*		*^{31}P NMR, δ, ppm (C_6H_6)*
				Si	*P*	
3	100 (0.03)	1.4570	$C_{10}H_{25}O_5PS_2Si$	7.81	8.66	84.0
			(348.1)	(8.04)	(8.90)	
6a	130 (0.04)	1.4130	$C_{14}H_{33}O_3PS_2Si$	7.09	7.86	84.7
			(372.2)	(7.52)	(8.32)	
6b	140 (0.03)	1.5514	$C_{15}H_{19}O_3PS_2Si$	7.17	8.04	89.0
			(370.1)	(7.56)	(8.37)	
7b	146 (0.03)	1.6053	$C_{26}H_{26}O_2SSi$	12.46		
			(458.2)	(12.21)		
13a	90 (0.03)	1.5620	$C_{15}H_{19}O_3PS_2Si$	7.67	6.82	85.4
			(410.2)	(7.55)	(6.82)	
13b	140 (0.04)	1.4680	$C_{22}H_{33}O_4PS_2Si$	6.18	5.38	82.4

Prod.	*Bp, °C (mm Hg)*[a]	n_D^{20}	*Molecular Formula (Mol. mass)*	*Found(Calc.), %*		^{31}P *NMR, δ, ppm* (C_6H_6)
				Si	*P*	
			(484.2)	(6.40)	(5.78)	
13c	110 (0.03)	1.4919	$C_{16}H_{21}O_4PS_2Si$	7.38	6.66	87.6
			(400.1)	(7.74)	(6.99)	
13d	130 (0.03)	1.5540	$C_{21}H_{23}O_4PS_2Si$	6.27	5.66	84.7
			(446.1)	(6.94)	(6.27)	
13e	125 (0.03)	1.5635	$C_{23}H_{27}O_3PS_2Si$	6.35	5.46	84.4
			(447.2)	(6.53)	(5.90)	

a. Temperature of the thermal element of a thin layer distillation apparatus.

TABLE III IR spectral data of the products obtained

Prod.	ν, *cm*$^{-1}$
3	2980, 2930, 2895 ν (CH_3 as, s; CH_2 as, s); 1020 ν (PO-C); 970; 800; 680 ν (P=S); 660; 530, 480 ν (P-S, S-Si).
6a	2960, 2910, 2875 ν (CH_3 as, s; CH_2 as, s; CH); 1390, 1365 δ (Me_2C gem s); 1260 δ [CH_3(Si) s]; 1090; 1050; 1010 ν (PO-C); 880, 860 ρ [CH_3(Si)]; 800; 675 ν (P=S); 550 ν (P-S, S-Si).
6b	3070, 3050, 3030 ν (=C-H, Ar); 2940, 2830 ν (CH_3 as, s); 1590, 1430 ν (C=C, Ar); 1130; 1120; 1086; 1030 ν (PO-C); 820; 740; 730; 700; 663 ν (P=S); 528, 497 ν (P-S, S-Si).
13a	3090 ν (=C-H, Ar); 2985, 2940, 2905 ν (CH_3as, s; CH_2 as, s); 1600, 1510, 1450 ν (C=C, Ar); 1033 ν (PO-C); 675 ν (P=S, PS_2 as); 535 ν (P-S, PS_2 s, S-Si).
13b	3075, 3050, 3030 ν (=C-H, Ar); 2975, 2945, 2845, 2840 ν (CH_3 as, s; CH_2 as, s); 1592, 1500, 1465 ν (C=C, Ar); 1382, 1370 δ [$(CH_3)_2C$ reM s]; 980 ν (PO-C); 683 ν (P=S, PS_2 as); 520 ν (P-S, PS_2 s, S-Si).
13c	3070, 3050 ν (=C-H, Ar); 2945, 2970, 2845 ν (CH_3 as, s; CH_2 as, s); 1590, 1500 ν (C=C, Ar); 1035 ν (PO-C); 688 ν (P=S, PS_2 as); 535 ν (P-S, PS_2 s, S-Si).
13d	3070, 3050, 3005 ν (=C-H, Ar); 2940, 2840 ν (CH_3 as, s; CH_2 as, s); 1590, 1500, 1460 ν (C=C, Ar); 1035 ν (PO-C); 683 ν (P=S, PS_2 as); 530, 497 ν (P-S, PS_2 s, S-Si).
13e	3270, 3250, 3225, 3000 ν (=C-H, Ar); 2973, 2975, 2890, 2830 ν (CH_3 as, s; CH_2 as, s); 1600, 1500 ν (C=C, Ar); 1030 ν (PO-C); 684 ν (P=S, PS_2 as); 530, 500 ν (P-S, PS_2 s, S-Si).

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

Prod.	*CCl_4, δ, ppm, J, Hz*
3	1.25 (t, 9H, $\mathbf{CH_3}\mathrm{CH_2OSi}$, $^3J_{HH}$ 7.0); 1.42 (t, 6H, $\mathbf{CH_3}\mathrm{CH_2OP}$, $^3J_{HH}$7.0); 3.82 (q, 6H, $\mathrm{CH_3}\mathbf{CH_2}\mathrm{OSi}$, $^3J_{HH}$ 7.0); 4.07 (dq, 4H, $\mathrm{CH_3}\mathbf{CH_2}\mathrm{OP}$, $^3J_{HH}$ 7.0, $^3J_{PH}$ 11.0).
6a	0.15 (s, 6H, $\mathbf{CH_3}\mathrm{Si}$); 0.81 (d, 6H, $\mathbf{CH_3}\mathrm{CHCH_2OSi}$, $^3J_{HH}$ 7.0); 0.91 (d, 12H, $\mathbf{CH_3}\mathrm{CHCH_2OP}$, $^3J_{HH}$ 7.0); 1.57–1.59 (m, 1H, $\mathrm{CH_3}\mathbf{CH}\mathrm{CH_2OSi}$); 1.73–1.87 (m, 2H, $\mathrm{CH_3}\mathbf{CH}\mathrm{CH_2OP}$); 3.45 (dd, 4H, $\mathrm{CH_3CH}\mathbf{CH_2}\mathrm{OP}$, $^3J_{HH}$ 7.0, $^3J_{PH}$ 7.0); 3.83 (d, 2H, $\mathrm{CH_3CH}\mathbf{CH_2}\mathrm{OSi}$, $^3J_{HH}$ 7.0).
6b	4.38 (s, 3H, $\mathbf{CH_3}\mathrm{OSi}$); 4.83 (d, 6H, $\mathbf{CH_3}\mathrm{OP}$, $^3J_{PH}$ 18.0); 8.00–8.22 and 8.60–8.80 (two m, 10H, C_6H_5).
7b	4.39 (s, 3H, $\mathbf{CH_3}\mathrm{OSi}$); 7.83–8.12 (m, 12H, 3,4,5-$\mathrm{C_6}\mathbf{H_3}$); 8.47–8.73 (m (8H, $\mathbf{H_2}\mathrm{C_6}$).
13a	1.35 (t, 9H, $\mathbf{CH_3}\mathrm{CH_2OSi}$, $^3J_{HH}$ 7.0); 1.38 (t, 3H, $\mathbf{CH_3}\mathrm{CH_2OP}$, $^3J_{HH}$ 7.0); 3.35 (s, 3H, $\mathbf{CH_3}\mathrm{OC_6H_4}$); 4.00 (q, 6H, $\mathrm{CH_3}\mathbf{CH_2}\mathrm{OSi}$, $^3J_{HH}$7.0); 4.20 (dq, 2H, $\mathrm{CH_3}\mathbf{CH_2}\mathrm{OP}$, $^3J_{HH}$ 7.0, $^3J_{PH}$ 15.0); 6,73 (dd, 2H, 3,5-$\mathrm{H_2C_6}\mathbf{H_2}$, $^3J_{HH}$ 9.0, $^4J_{PH}$ 3.0); 6.20 (dd, 2H, 2,6-$\mathbf{H_2}\mathrm{C_6H_2}$, $^3J_{HH}$ 9.0, $^3J_{PH}$ 14.0).
13b	1.20 (d, 6H, $\mathbf{CH_3}\mathrm{CHOSi}$ $^3J_{HH}$ 7.0); 1.21 (d, 12H, $\mathbf{CH_3}\mathrm{CHOSi}$, $^3J_{HH}$ 7.0); 3.50 (s, 3H, $\mathbf{CH_3}\mathrm{OC_6H_4}$); 4.23–4.91 (m, 2H, $\mathrm{CH_3}\mathbf{CH}\mathrm{OSi}$; 1H, $\mathrm{CH_3}\mathbf{CH}\mathrm{OP}$); 6.58–6.63 (m, 2H, 3,5-$\mathrm{H_2C_6}\mathbf{H_2}$); 7.16–7.28 and 7.84- 7.87 (two m, 5H, $\mathrm{C_6}\mathbf{H_5}$); 7.86–7.99 (m, 2H, 2,6-$\mathbf{H_2}\mathrm{C_6H_2}$).
13c	0.84 (s, 6H, $\mathbf{CH_3}\mathrm{Si}$); 1.07 (d, 3H, $\mathbf{CH_3}\mathrm{OP}$, $^3J_{PH}$ 21.0); 3.40 (s, 3H, $\mathbf{CH_3}\mathrm{OC_6H_4}$); 7.02 (m, 2H, 3,5-$\mathrm{H_2C_6}\mathbf{H_2}$, $^3J_{HH}$ 9.0); 7.48 (m, 2H, 2,6- $\mathbf{H_2}\mathrm{C_6H_2}$, $^3J_{HH}$ 9.0).
13d	2.98 (d, 3H, $\mathbf{CH_3}\mathrm{OP}$, $^3J_{PH}$ 16.0); 3.33 (s, 3H, $\mathbf{CH_3}\mathrm{OC_6H_4}$ + 3H, $\mathbf{CH_3}\mathrm{OSi}$); 6.48 (dd, 2H, 3,5-$\mathrm{H_2C_6}\mathbf{H_2}$, $^3J_{HH}$ 9.0, $^4J_{PH}$ 3.0); 6.97–7.15 and 7.48–7.70 (two m, 10H, $\mathrm{C_6}\mathbf{H_5}$); 8.13 (dd, 2H, 2,6-$\mathbf{H_2}\mathrm{C_6H_2}$, $^3J_{HH}$ 9.0, $^3J_{PH}$ 14.0).
13e	1.06 (t, 3H, $\mathbf{CH_3}\mathrm{CH_2OSi}$, $^3J_{HH}$ 7.0); 1.09 (t, 3H, $\mathbf{CH_3}\mathrm{CH_2OP}$, $^3J_{HH}$ 7.0); 3 22 (s, 3H, $\mathbf{CH_3}\mathrm{OC_6H_4}$); 3.70 (q, 2H, $\mathrm{CH_3}\mathbf{CH_2}\mathrm{OSi}$, $^3J_{HH}$7.0); 3.91 (dq, 2H, $\mathrm{CH_3}\mathbf{CH_2}\mathrm{OP}$, $^3J_{HH}$ 7.0, $^3J_{PH}$ 23.0); 6.20–6.45 (m, 2H, 3,5- $\mathrm{H_2C_6}\mathbf{H_2}$); 6.73–6.93 and 7.30–7.58 (two m, 10H, $\mathrm{C_6}\mathbf{H_5}$); 7.58–7.81 (m, 2H, 2,6-$\mathbf{H_2}\mathrm{C_6H_2}$).

TABLE V Mass spectral data of the products obtained

Prod.	*i-C_4H_{10}, m/e (I_{rel}, %)*
3[a]	215 $[M + 2H - 3EtO]^+$ (31); 154 $[M + H - S - Si(OEt)_3]^+$ (42).
3[b]	185 $[M - Si(OEt)_3]^+$. (50); 153 $[M - S - Si(OEt)_3]^+$. (40).
6a[a]	242 $[M + H - Si(OBu\text{-}i)Me_2]^+$(13).
6a[b]	357 $[M - Me]^+$ (12).
7a[a]	280 $[M + H - Me]^+$ (12).
6b[b]	278 $[M - Ph - Me]^+$. (12); 246 $[M - 3MeO - S]^+$. (22).
7b[b]	458 $[M]^+$. (67); 412 $[M - MeO - Me]^+$. (100).
13a[a]	396 $[M + H - Me]^+$ (32), 276 $[M + 2H - Si(OEt)_3]^+$ (10).

Prod.	*i-C_4H_{10}, m/e (I_{rel}, %)*
13b[a]	263 [M + H – 2Pr-i – OPr-i – Ph]$^+$(60).
13b[b]	469 [M – Me]$^+$. (10); 441 [M – Pr -i]$^+$. (15); 338 [M – 2Pr-i – OPr-i]$^+$. (10), 441 [M – Pr -i]$^+$. (15).
13c[b]	235 [M + 2H – SiPh(OMe)$_2$]$^+$(72).
13c[a]	385 [M – Me]$^+$. (10); 201 [M – S – SiPh(OMe)$_2$]$^+$. (100).
13d[a]	234 [M + H – Si(OMe)Ph$_2$]$^+$(30).
13d[b]	201 [M – S – Si(OMe)Ph$_2$]$^+$. (100).
13e[a]	249 [M + 2H – 2OEt – 2Ph]$^+$ (55).249 [M + 2H – 2OEt – 2Ph]$^+$ (55).
13e[b]	459 [M – Me]$^+$. (16).

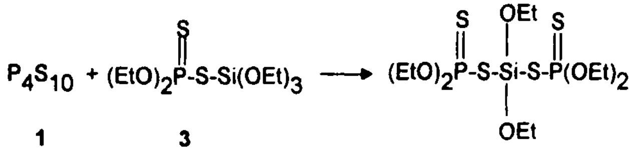
a. Chemical ionization, 100 eV.

b. Electron impact, 70 eV

The ^{31}P NMR signal of **3** appears as a singlet (δ 84.0 ppm in benzene solution) in the same region as for S-trimethylsilyl diethyl- or diisopropyldithiophosphates (δ 86–89 ppm) obtained previously.[13] It is noteworthy, that mainly one ethoxy group of tetraethoxysilane **2** takes part in the reaction with **1** under the mild conditions used. We observed signals in the ^{1}H NMR spectrum of **3** due to the protons of various ethoxy groups attached to the phosphorus and to the silicon atoms. One of two triplets, present in the ^{1}H NMR spectrum of **3** in C_6D_6 solution (Table (IV)), in the range of δ 1.25 ppm is due to the methyl protons of three ethoxy groups at the silicon atom $\underline{CH_3}CH_2OSi$ ($^3J_{HH}$ 7.0 Hz). The similar protons of two ethoxy groups at the phosphorus atom $\underline{CH_3}CH_2OP$ resonats at δ 1.42 ppm ($^3J_{HH}$ 7.0 Hz). Integral intensity ratio of these two triplets is 3 : 2. The methylene protons of three ethoxy groups at the silicon atom $CH_3\underline{CH_2}OSi$ appear as a quartet at δ 3.82 ppm. Whereas, a doublet of quartets at δ 4.07 ppm has been assigned to the similar methylene protons of two ethoxy groups at the phosphorus atom $CH_3\underline{CH_2}OP$ ($^3J_{PH}$ 11.0 Hz) of **3**.

Bands of strong intensity presented in the range of ν 1020 cm^{-1} in the IR spectra of **3** (Table III) is due to the PO-C valence vibrations, such as that found for S-trimethylsilyl O,O′-diethyldithiophosphate (cf. ν (PO-C) 1020 cm^{-1}).[13] S-Triethoxysilyl O,O′-diethyldithiophosphate **3** is rather moisture sensitive. The hydrolysis of **3** brought about by exposure to the open air during 2–3 h involves the cleavage of the S-Si bond and results in the appearance of a band at ν 2450 cm^{-1} which was assigned to the valence vibrations of the PS-H bond of free dithiophosphoric acids[18].

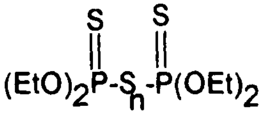
The rupture of the S-Si bond of **3** in conditions of recording of electron impact mass spectra was observed by the presence of the mass peak m/e 185 of the ion $[M - Si(OEt)_3]^+$. (Table (V)). In spite of the fact that the reaction 1 was performed under mild conditions some secondary products were also observed by use of mass spectrometry, however in minor quantities. The mass peaks m/e 489 and 490 which were present in the chemical ionization mass spectra of the crude reaction mixture of **1** with **2** may be attributed to the molecular ions $[M + H]^+$ and $[M + 2H]^+$ (20%), respectively, of bis(O,O-diethyldithiophosphato) diethoxysilane **A** (calculated molecular mass M of **A** is 488). Product **A** may be formed via the interaction of the initial product **3** with phosphorus sulfide **1** (Reaction (2)).



$$P_4S_{10} + (EtO)_2\overset{S}{\overset{\|}{P}}\text{-S-}Si(OEt)_3 \longrightarrow (EtO)_2\overset{S}{\overset{\|}{P}}\text{-S-}\underset{OEt}{\overset{OEt}{Si}}\text{-S-}\overset{S}{\overset{\|}{P}}(OEt)_2 \qquad (2)$$

1 **3** **A**

Some secondary products of desilylation of the initial product **3** were also found by mass spectra. Thus, the chemical ionization mass spectra of the crude reaction mixture of **1** with **2** also indicates the mass peak m/e 340 that is considered to be tetraethylpyrotrithiophosphate **B** $[M + 2H]^+$ (5%) (calculated molecular mass of **B** is 338). Moreover, there are the mass peaks m/e 371, 403 and 433 in the chemical ionization mass spectra of the crude reaction mixture of **1** with **2**; those are considered to be pyroperthiophosphates **C, D** and **E** as the products of addition of one, two and three sulfur atoms to the compound **B** $[M + H]^+$.

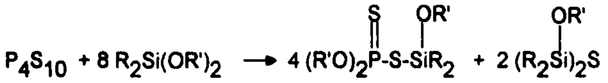


$$(EtO)_2\overset{S}{\overset{\|}{P}}\text{-}S_n\text{-}\overset{S}{\overset{\|}{P}}(OEt)_2$$

n = 1 (**B**); n = 2 (**C**); n = 3 (**D**); n = 4 (**E**)

Similar chemical behavior should be expected in the case of other silanes containing a few Si-O bonds. Thus, we have found that

O,O-diisobutyl dimethylsilane **5a** and O,O-dimethyl diphenylsilane **5b** react with P_4S_{10} at room temperature to form S-(alkoxy)diorganylsilyl O,O-dialkyldithiophosphates **6a,b** (Reaction (3), Tables (I)-(V)).



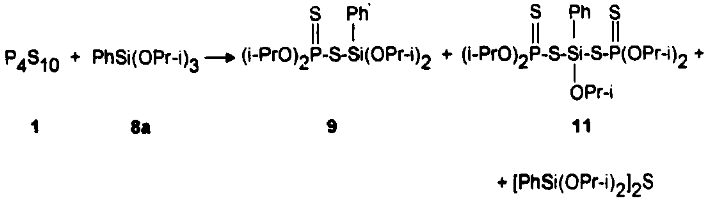
$$P_4S_{10} + 8\,R_2Si(OR')_2 \longrightarrow 4\,(R'O)_2\overset{S}{\overset{\|}{P}}\text{-}S\text{-}\overset{OR'}{\overset{|}{Si}}R_2 + 2\,(R_2\overset{OR'}{\overset{|}{Si}})_2S \qquad (3)$$

1 **5a**, R = Me, R' = Bu-i **6a**, R = Me, R' = Bu-i **7a**, R = Me, R' = Bu-i

b, R = Ph, R' = Me **b**, R = Ph, R' = Me **b**, R = Ph, R' = Me

S-Silyldithiophosphates **6a,b** were formed as liquids and were isolated from the reaction mixtures by use of a thin layer distillations (see Tables (I)-(V)). Disilylsulfide **7b** was contained in a heavy volatile distillation fraction (see Experimental). The electron impact mass spectrum of **7b** shows the mass peaks m/e 458 and 412 those may be attributed to its molecular ion $[M]^{+}$. and ion $[M - Me - MeO]^{+\cdot}$, respectively (calculated molecular mass M of **7b** is 458.1). In the ^1H NMR spectrum of **7b** in CCl_4 solution the CH_3O protons appear as a singlet in the range of δ 4.39 ppm, while the phenyl protons appear as two multiplets at δ 7.83–8.12 ppm (12H, 3,4,5-$C_6\mathbf{H}_3$ and 8.47–8.73 ppm (8H, $\mathbf{H}_2C_6$). The chemical ionization mass spectrum of disilylsulfide **7a** reveals the mass peak m/e 280 corresponding to the ion $[M + H - Me]^+$ (calculated molecular mass M of **7a** is 294.2).

We have found that the reaction of P_4S_{10} with O,O,O-triisopropyl phenylsilane **8a** proceeds at room temperature. The ^{31}P NMR spectrum of the crude reaction mixture **1** and **8a** shows two signals at δ 84.6 and 81.1 ppm in the integral intensity ratio ~ 1 : 1. These resonances may be assigned to S-(O,O-diisopropyl)phenylsilyl O,O-diisopropyldithiophosphate **9** and bis (diisopropyldithiophosphoryl) (O-isopropyl)phenylsilane **11** (Reaction (4)).

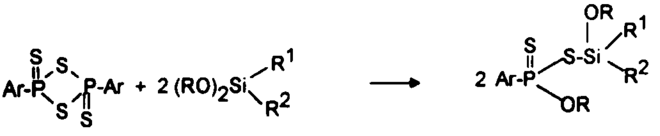


$$P_4S_{10} + PhSi(OPr\text{-}i)_3 \longrightarrow (i\text{-}PrO)_2\overset{S}{\overset{\|}{P}}\text{-}S\text{-}\overset{Ph}{\overset{|}{Si}}(OPr\text{-}i)_2 + (i\text{-}PrO)_2\overset{S}{\overset{\|}{P}}\text{-}S\text{-}\underset{OPr\text{-}i}{\underset{|}{\overset{Ph}{\overset{|}{Si}}}}\text{-}S\text{-}\overset{S}{\overset{\|}{P}}(OPr\text{-}i)_2 + [PhSi(OPr\text{-}i)_2]_2S \qquad (4)$$

1 **8a** **9** **11**

However, we were not successful to separate products **9, 10** and **11** by means of a thin layer distillation, followed by numerous common vacuum distillations. Their formation circumstantially was confirmed by mass spectral data. Thus, the mass peaks m/e 393, 527 and 283, observed in the electron impact mass spectra of the crude reaction mixture (reaction (4)), are due to the ions $[M - Pr\text{-}i]^{+\cdot}$ of silyldithiophosphate **9**, $[M - 2S]^{+\cdot}$ of bis(dithiophosphoryl)silane **11** and $[M - Ph - 2\ i\text{-}PrO]^{+\cdot}$ of disilylsulfide **10**, respectively (calculated molecular masses M of **9, 11** and **10** are 436, 590 and 478, respectively).

We have previously found that the Lawesson's reagent **12** reacts with monoalkoxy trimethylsilanes under mild conditions to form S-trimethylsilyl O-alkyl-4-methoxyphenyldithiophosphonates. [19] The products of similar structure could be expected in the reaction of **12** with silanes, containing a few Si-O bonds. In fact, we have shown, that tetraethoxysilane **2**, O,O,O-trisopropyl phenylsilane **8a**, O,O,O-trimethyl phenylsilane **8b**, O,O-dimethyl diphenylsilane **5b** and O,O-diethyl diphenylsilane **5c** react with **12** to form S-(O-alkylsilyl) O-alkyl-4-methoxyphenyldithiophosphonates **13a-e** (Reaction (5), Tables (I)-(V)).



(5)

12

2, $R = Et, R^1 = R^2 = OEt$

8a, $R = Pr\text{-}i, R^1 = OPr\text{-}i, R^2 = Ph$

8b, $R = Me, R^1 = OMe, R^2 = Ph$

5b, $R = Me, R^1 = R^2 = Ph$

5c, $R = Et, R^1 = R^2 = Ph$

13a, $R = Et, R^1 = R^2 = OEt$

13b, $R = Pr\text{-}i, R^1 = OPr\text{-}i, R^2 = Ph$

13c, $R = Me, R^1 = OMe, R^2 = Ph$

13d, $R = Me, R^1 = R^2 = Ph$

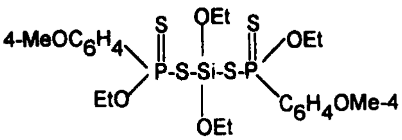
13e, $R = Et, R^1 = R^2 = Ph$

$Ar = 4\text{-}MeOC_6H_4$

It is noteworthy, that the thermal stability of S-silyldithiophosphonates **13**, containing the P-C bonds, is rather higher than that of the corresponding S-silyldithiophosphates **3** and **6** with the P-O bonds. Thus, products **13a-e** were purified by use of a thin layer distillations without thermal destructions (see Tables (I)-(V)). In the ^1H NMR spectrum of **13a** (Table

(IV)) the methylene protons of the ethoxy group attached to the phosphorus atom appear as a characteristic doublet of quartets at δ 4.20 ppm with $^3J_{PH}$ 15.0 Hz ($^3J_{HH}$ 7.0 Hz). Whereas, a quartet at δ 4.00 ppm with $^3J_{HH}$ 7.0 Hz has been attributed to the similar methylene protons of three ethoxy groups remaining at the silicon atom. Integral intensity ratio of these proton groups is 1 : 3. In all cases the methoxy protons of the 4-methoxyphenyl groups of **13** appear as singlets in the range of δ 3.22–3.40 ppm that has been assigned to the formation of **13b-e** as unique thiophosphorylation products and no secondary products.

The structure of **13** was also confirmed by mass spectral data of distilled **13b-e** and crude reaction mixtures of reaction 6. It should be emphasized that the electron impact mass spectra of **13** exhibit the characteristic formation of ions via the elimination of methyl or isopropyl groups from the molecules of **13**. Thus, **13a, 13b, 13c** and **13e** reveal the mass peaks m/e 396 $[M + H - Me]^+$, 441 $[M - Pr\text{-}i]^{+\cdot}$, 385 $[M - Me]^{+\cdot}$ and 459 $[M - Me]^{+\cdot}$, respectively, in their mass spectra (their calculated molecular masses M are 410.2, 484.2, 400.1 and 474.2, respectively). Thus, the alkoxysilanes **8a, 8b, 5b** and **5c**, containing two or three alkoxy groups, react with the Lawesson's reagent **12** with the participation of only one alkoxy group under mild conditions. The exception of this rule was found in the case of tetraethoxysilane **2** and its reaction with **12**. Thus, the mass peaks m/e 597 and 568 observed in the mass spectra of a distilled fraction of **13a** may be assigned to the ions $[M\text{-}Me]^{+\cdot}$ and $[M + H - OEt]^+$, respectively, of bis(O-ethyl-4-methoxyphenyldithiophosphonato) diethoxysilane **F** (calculated molecular mass M of **F** is 612.1). The compound **F** seems to be a product of the interaction of **13a**, containing three rather reactive Si-O bonds, with the Lawesson's reagent.



F

Thus, as we expected, the phosphorylation of silanes, containing a few Si-O bonds, with phosphorus sulfide **1** and the Lawesson's reagent **12** under mild conditions proceeds with the formation of compounds with the

P(S)S-Si structural fragment similarly to the reactions with monoalkoxysilanes.[13] In some cases reactions are complicated by the thiophosphorylation, sulfuration and desilylation processes. Thiophosphorylation of alkoxysilanes with a few Si-O bonds with the Lawesson's reagent, containing stable P-C bonds, proceeds more readily than that with tetraphosphorus decasulfide.

EXPERIMENTAL

The ^{31}P NMR spectra were recorded with a Bruker MSL 400 (162 MHz) instrument in C_6H_6. The ^{1}H NMR spectra were taken on a Bruker MSL-400 (400 MHz) spectrometer and a Varian T-60 (60 MHz) spectrometer in C_6D_6 or CCl_4. The IR spectra were obtained with a Bruker IFS 113v and an UR-20 infrared spectrophotometers. Mass spectra (EI, 70 eV; CI, 100 eV) were determined on an M 80 B Hitachi chromatomass spectrometer.

Reaction of Tetraphosphorus Decasulfide 1 with Tetraethoxysilane 2. Typical Procedure

Compound **1** (2.7 g, 6.1 mmol) was added portionwise under dry argon with stirring at 20°C to **2** (10.0 g, 48.0 mmol), and stirring was continued for 30 h at 20°C. The mixture was filtered. The filtrate was evaporated at reduced pressure (0.08 mm Hg) at 50°C for 2 h to give crude **3** (8.4 g, ~ 99%). Pure product **3** (4.4 g, 52%) was isolated from the residue by means of a thin layer distillation at 100°C (0.03 mm Hg) (See Tables (I) -(V)).

Products **6a** and **13a-d** were obtained similarly (See Tables (I)-(V)). The reaction of **12** with **5c** was carried out in the suspension of 5 mL of anhydrous benzene.

Reaction of Tetraphosphorus Decasulfide 1 with O,O-Dimethyl Diphenylsilane 5b

The mixture of **1** (1.6 g, 3.6 mmol) and **5b** (97.0 g, 28.6 mmol) was stirred at 20°C for 20 h and filtered. The filtrate was evaporated under vacuum (0.1 and 0.08 mm Hg) at 40°C for 2 h. Product **6b** (3.7 g, 70%) was isolated from the residue by means of a thin layer distillation at 140°C (0.03 mm Hg) (See Tables (I)-(V)). Compound **7b** (1.6 g, 48%) was obtained in the less volatile distillation fraction (See Tables (I), (II), (IV) and (V)).

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References

[1] R. A. Cherkasov, G. A. Kutyrev and A. N. Pudovik, *Tetrahedron*, **41**, 2567 (1985).

[2] I. S. Nizamov, V. A. Kuznetzov and E. S. Batyeva, *Phosphorus, Sulfur, and Silicon*, **90**, 249 (1994).

[3] J. L. Lefferts, K. C. Molloy, J. J. Zuckerman, I. Haiduc, C. Guta, D. Ruce, *Inorg. Chem.*, **19**, 1662 (1980) and references therein.

[4] B. P. Singh, G. Srivastava, R. C. Mehrotra, *J. Organomet. Chem.*, **171**, 35 (1979).

[5] W. Zeiss, H. Henjes, D. Lux, W. Schwarz, H. Hess, *Z. Naturforsch., B : Anorg. Chem., Org. Chem.*, **34B**, 1334 (1979).

[6] H. W. Roesky, M. Dietl, *Angew. Chem.*, **85**, 454 (1973).

[7] A. Borkowsky, *Dissertation*, Universität Köln (1989).

[8] H. W. Roesky and G. Remmers, *Z. Anorg. Allg. Chem.*, **431**, 221 (1977).

[9] I. S. Nizamov, L. A. Al'metkina, E. S. Batyeva, V. A. Al'fonsov and A. N. Pudovik, *Izv. Akad. Nauk SSSR., Ser. Khim.*, 2164 (1991).

[10] J. Hahn and T. Nataniel, *Z. Anorg. Allg. Chem.*, **543**, 7 (1986).

[11] I. S. Nizamov, V. A. Kuznetzov, E. S. Batyeva and V. A. Al'fonsov, *Izv. Akad. Nauk., Ser. Khim.*, 2457 (1992).

[12] I. S. Nizamov, V. A Kuznetzov, E. S. Batyeva, V. A. Al'fonsov and A. N. Pudovik, *Heteroatom Chem.*, **4**, 379 (1993).

[13] I. S. Nizamov, V. A. Kuznetzov, E. S. Batyeva, V. A. Al'fonsov and A. N. Pudovik, *Phosphorus, Sulfur and Silicon.*, **79**, 179 (1993).

[14] V. K. Kuskov and G. F. Bebich, *Dokl. Akad. Nauk SSSR*, **136**, 354 (1961).

[15] V. K. Kuskov, Ya. A. Pentin and T. B. Yershova, *Zh. Obshch. Khim.*, **33**, 3544 (1963).

[16] V. S. Blagoveshchensky, S. N. Kudrjavtseva and Yu. N. Mitrokhina, *Vestnik Mosk. Univ., Ser. 2. Khimiya*, **24**, 68 (1968).

[17] J. H. J. Coetzee and S. Norval, *J. S. Afr. Chem. Inst.*, **25**, 92 (1972); *Chem. Abstr.*, **77**, 113340u (1972).

[18] R. R. Shagidullin, L. I. Vachugova and L. V. Avvakumova, *Izv. Akad. Nauk., Ser. Khim.*, 2820 (1979).

[19] I. Nizamov, V. Al'fonsov and E. Batyeva, *Phosphorus, Sulfur and Silicon*, **109–110**, 453 (1996).