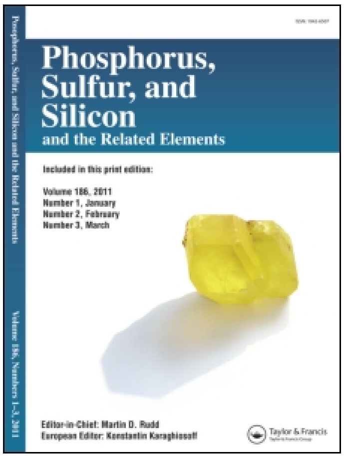

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Reactions of S-Silyl Esters of Tetracoordinated Phosphorus Thioacids with Acetals and Ortho Esters

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REACTIONS OF S-SILYL ESTERS OF TETRACOORDINATED PHOSPHORUS THIOACIDS WITH ACETALS AND ORTHO ESTERS

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The reactions of S-trimethylsilyl esters of dithiophosphoric, diamidodithiophosphoric, aryldithiophosphonic, aryltrithiophosphonic, and arylamidodithiophosphonic acids with diethyl acetal of benzaldehyde and ortho formiate and acetate were studied. On the basis of these studies, new derivatives of tetracoordinated phosphorus thioacids were obtained.

Keywords: Diethyl acetal of benzaldehyde; ortho acetate; ortho formiate; S-trimethylsilyl esters of tetracoordinated phosphorus thioacids

INTRODUCTION

S-Trimethylsilyl esters of tetracoordinated phosphorus thioacids contain the reactive S—Si bond and a readily leaving trimethylsilyl group. They have found an expanding application in synthetic organophosphorus chemistry. S-Trimethylsilyl esters of dithiophosphoric and tetrathiophosphoric acids are efficient intermediates for the synthesis of useful organothiophosphorus compounds.[1–3] The substitution reactions of S-trimethylsilyl O,O-dialkyldithiophosphates or S,S-bis(trimethylsilyl) trithiophosphonates with trialkylisocyanatostannane and its thioanalogue, trialkyl(dialkylamino)stannanes, trimethylbenzyl- or 4-vinylbenzylstannanes or trimethyl chlorostannane have been reported to result in S-trialkylstannyl dithiophosphates and bis(trimethylstannyl) trithiophosponates.[4,5] Organic compounds

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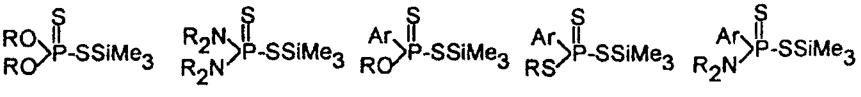
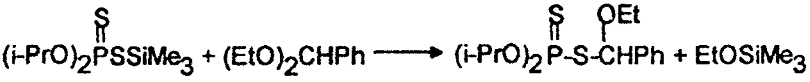
of geminal substituted structure such as acetals, ortho esters, and aminals possess rather high reactivity in the reactions with trimethylsilyl tetrathiophosphates.[3] Taking into account the facile occurence of the substitution reactions of trimethylsilyl tetrathiophosphates with acetals and ortho esters,[3] we have tried to extent these reactions to S-trimethylsilyl esters of dithiophosphoric, diamidodithiophosphoric, aryldithiophosphonic, aryltrithiophosphonic, and arylamidodithiophosphonic acids with the following formulae.



The formation of products of broad structural variations could be expected by the use of S-trimethylsilyl esters of tetracoordinated phosphorus thioacids.

RESULTS AND DISCUSSION

The reaction of S-trimethylsilyl O,O-diisopropyldithiophosphate **1a** with bis(ethoxy)phenylmethane **2** has been found to bring about the formation of S-(1-ethoxybenzyl) O,O-diisopropyldithiophosphate **3** and trimethyl(ethoxy)silane **4** at 20°C (Eq. 1, Tables I–V).



$$(i\text{-PrO})_2\overset{\overset{S}{\|}}{P}SSiMe_3 + (EtO)_2CHPh \longrightarrow (i\text{-PrO})_2\overset{\overset{S}{\|}}{P}\text{-}S\text{-}\overset{OEt}{\overset{|}{C}}HPh + EtOSiMe_3 \quad (1)$$

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

TABLE I Experimental Data and Yields of the Products Obtained

Initial compounds Quantity (g (mmol))	Reaction conditions Temp. (°C) Time (h)	Product Yield (g (%))
1a 4.6 (16.1)/**2** 2.9 (16.1)	20/3	**3** 4.1 (89)[a]/3.5 (63);[b] **4** 0.9 (47)[c]
1a 4.6 (16.1)/**5a** 2.4 (16.2)	20/4	**6a** 2.7 (53)[a]/2.3 (45);[b] **4** 1.0 (53)[c]
1b 5.0 (15.9)/**5b** 2.6 (16.0)	20/0.5	**6b** 4.3 (75)[a]/2.9 (51);[b] **4** 1.4 (74)[c]
7 5.0 (16.0)/**5a** 2.4 (16.2)	20/1	**8a** 4.3 (78)[a]/1.8 (33)[b]
7 4.5 (14.4)/**5b** 2.3 (14.2)	20/3	**8b** 3.8 (75)[a]/2.7 (53);[b] **4** 0.9 (53)[c]
9a 3.3 (9.9)/**5a** 1.5 (10.1)	20/3	**10a** 2.9 (81)[a]/1.1 r (31);[b] **4** 1.0 (83)[c]
9b 5.0 (13.8)/**5b** 2.2 (13.6)	20/1	**10b** 3.8 (68)[a]/1.8 (32);[b] **4** 0.9 (56)[c]
11a 9.5 (27.1)/**5b** 4.4 (27.1)	70/2	**12a** 6.0 (56)[a]/5.1 (48);[b] **4** 2.3 (72)[c]
11b 5.0 (13.7)/**5b** 2.2 r (13.6)	20/1	**12b** 4.7 (84)[a]/3.2 (57);[b] **4** 1.3 (81)[c]
13 4.0 (11.5)/**5a** 1.7 (11.5)	20/1	**14** 4.1 (95)[a]/2.7 (63);[b] **4** 1.0 (71)[rc]

[a] Yield of crude product.

[b] Yield of product isolated by means of a thin layer distillation.

[c] Yield of product isolated by distillation.

TABLE II Physical, Analytical, and ^{31}P NMR Spectral Data of Products Obtained

Product	B.p. (°C) (mm Hg)[a]	n_D^{20}	Molecular formula (mol. mass)	Found/(calc.), % P	Found/(calc.), % S	^{31}P NMR, δ (ppm (C_6H_6))
3	130 (0.05)	1.5225	$C_{15}H_{25}O_3PS_2$ (348.2)	8.69 8.90	18.02 18.36	90.7
6a	100 (0.06)	1.4873	$C_{11}H_{25}O_4PS_2$ (316.2)	9.93 9.80	20.21 20.22	91.1
6b	110–115 (0.03)	1.5670	$C_{14}H_{31}O_4PS_2$ (358.2)	8.67 8.65	17.54 17.85	91.4
8a	100 (0.03)	1.5052	$C_{13}H_{31}N_2O_2PS_2$ (342.2)	9.06 9.05	18.88 18.68	93.9
8b	120–125 (0.04)		$C_{14}H_{33}N_2O_2PS_2$ (356.2)	8.60 8.69	17.70 17.95	93.9
10a	160–165 (0.03)	1.5355	$C_{15}H_{25}O_4PS_2$ (364.2)	8.47 8.50	15.17 17.56	94.1
10b	155–160 (0.03)	1.5639	$C_{18}H_{31}O_4PS_2$ (406.2)	7.34 7.62	16.16 15.74	94.9
12a	135–140 (0.03)	1.5065	$C_{16}H_{27}O_3PS_3$ (394.2)	7.50 7.86	24.66 24.33	77.9
12b	145 (0.03)	1.6090	$C_{17}H_{29}O_3PS_3$ (408.2)	7.93 7.59	23.15 23.50	78.4
14	130 (0.03)	1.5530	$C_{16}H_{28}NO_3PS_2$ (377.2)	8.09 8.21	17.12 16.95	94.9

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

It is noteworthy that acetal **2** takes part in reaction **1** via the cleavage of only one O—C bond under mild conditions used. Compound **3** was formed as a liquid in high yield (89%). S-Benzyldithiophosphate 3 was isolated by use of a thin layer distillation. Ethoxysilane **4** was easily removed from the reaction mixtures by evaporation at reduced pressure (see Experimental). It was purified by a subsequent distillation.

The ^{31}P NMR spectrum of S-benzyldithiophosphate **3** (Table II) shows a singlet at δ 90.7 ppm. This resonance is shifted toward low field in comparison with the ^{31}P NMR data of initial *S*-trimethylsilyl dithiophosphate **1a** (δ 86 ppm). Substitution of the trimethylsilyl group by the benzyl one in the molecule of the derivative of dithiophosphoric acid was confirmed by the data of the ^{1}H NMR spectra of **3** (Table IV). While a signal of the trimethylsilyl group[4,5] in the range of δ 0.05–0.08 is absent it reveals the characteristic doublet of the methine proton of the benzyl group at δ 6.21 ppm ($^3J_{HH}$ 10.0 Hz). A band at ν 700 cm^{-1} in the IR spectrum of **3** (Table III) is assigned to the P=S valence vibrations showing a shift to higher frequency with respect to the initial **1a**

TABLE III IR Spectral Data of the Products Obtained

Product	ν, cm^{-1}
3	3090, 3065, 3030 ν (=C—H, Ar); 2980, 2938, 2880, 2825 ν (CH_3 as, s; CH_2 as, s; CH); 1598, 1580, 1492 ν (C=C, Ar); 1455 ν (CH_3 as); 1487, 1477 δ [$(CH_3)_2C$ gem s]; 1310 ν (C=C, Ar); 1180, 1105, 980 ν (C—O—C as, s); 700 ν (P=S); 650, 615 ν [(P)S—C]; 540, 515 ν (P—S)
6a	2979, 2930, 2877 ν (CH_3 as, s; CH_2 as, s, CH); 1470, 1451 δ (CH_3 as, CH_2); 1386, 1376 δ [$(CH_3)_2C$ gem s]; 1264 ω, τ (CH_2); 980 ν ((P)O—C), ν (O—C); 860, 781 δ (PO_2 as, s); 656 ν (P=S); 547 ν (P—S)
6b	2960, 2930, 2887 ν (CH_3 as, s; CH_2 as, s); 1465, 1453, 1380 δ (CH_3 as, CH_2); 1260 ω, τ (CH_2); 1022 ν [(P)O—C]; 950 ν (OC—C); 850, 780 δ (PO_2 as, s); 690 ν (P=S); 552, 530 ν (P—S)
8a	2980, 2935, 2880 ν (CH_3 as, s; CH_2 as, s); 1450, 1430, 1380 δ (CH_3 as, CH_2); 1210, 1175 ν (C—N—C as); 1025 ν (P—N—C as); 950 ν [(N)C—C]; 713 ν (P=S); 642 ν (P—N—C as); ν (P—S); ν (C—S); δ (PN_2); 535 δ (CNC)
8b	3070, 3040 ν (=C—H, Ar); 2985, 2970, 2935, 2900 ν (CH_3 as, s; CH_2 as, s; CH); 1600, 1508, 1480 ν (C=C, Ar); 1450 δ (CH_3 as, CH_2); 1310, 1298 ν (C=C, Ar); 1260 ω, τ (CH_2); 1050, 1030, 1010 ν (O—C, (P)O—C); 950 ν (OC—C); 852 ν [P—O(C)]; 700 ν (P=S); 645, 630 ν (C—S); 543 ν (P—S)
10a	3070, 3040 ν (=C—H, Ar); 2985, 2970, 2935, 2900 ν (CH_3 as, s; CH_2 as, s; CH); 1600, 1508, 1480 ν (C=C, Ar); 1450 δ (CH_3 as, CH_2); 1310, 1298 ν (C=C, Ar); 1260 ω, τ (CH_2); 1050, 1030, 1010 ν (O—C, (P)O—C); 950 ν (OC—C); 852 ν [P—O(C)]; 700 ν (P=S); 645, 630 ν (C—S); 543 ν (P—S)
10b	3065, 3030 ν (=C—H, Ar); 2960, 2930, 2880 ν (CH_3 as, s; CH_2 as, s; CH); 1592, 1500, 1470 ν (C=C, Ar); 1450 ν (CH_3 as, s; CH_2); 1390, 1370 δ [$(CH_3)_2C$ gem s]; 1310, 1296 ν (C=C, Ar); 1260 ω, τ (CH_2); 1050, 1010, 1005 ν [(P)O—C, O—C]; 960 ν (OC—C); 850 ν [P—O(C)]; 700 ν (P=S); 647, 627 ν (C—S); 545 ν (P—S)
12a	3070, 3010 ν (=C—H, Ar); 1590, 1498, 1460, 1380 δ (CH_3 as, CH_2); 1310, 1295 ν (C=C, Ar); 1260 ω, τ (CH_2); 690 ν (P=S); 622 ν (C—S); 593, 512 ν (P—S)
12b	3070, 3010 ν (=C—H, Ar); 2965, 2930, 2870, 2844 ν (CH_3 as, s; CH_2 as, s; CH); 1595, 1500, 1463 ν (C=C, Ar); 1450, 1440, 1410 δ (CH_3 as, CH_2); 1384, 1369 δ [$(CH_3)_2C$ gem s]; 1310, 1298 ν (C=C, Ar); 1031 ν (O—C); 950 ν (OC—C); 692 ν (P=S); 623 ν (C—S); 543, 510 ν (P—S)
14	3090, 3075, 3010 ν (=C—H, Ar); 2980, 2935, 2900, 2880, 2840 ν (CH_3 as, s; CH_2 as, s); 1598, 1505, 1463 ν (C=C, Ar); 1440 δ (CH_3 as, CH_2); 1310, 1297 ν (C=C, Ar); 1260 ω, τ (CH_2); 1183 ν (C—N—C as); 1030 ν (O—C, P—N—C as); 950 ν [(N)C—C]; 688 ν (P=S); 625 ν (C—S); 540 ν (P—S)

(ν P=S 654 cm^{-1}). The mass peak m/e 348 was observed by examination of the electron impact mass spectrum of **3**; it may be attributed to its molecular ion (Table V).

We have found that S-trimethylsilyl O,O-dialkyldithiophosphates **1a**,**b** react with ortho formiate **5a** and ortho acetate **5b** to form S-(1,1-diethoxyalkyl) O,O-dialkyldithiophosphates **6a**,**b** and

TABLE IV ^1H NMR Spectral Data of the Products Obtained

Product	$CDCl_3$, δ, ppm, J, Hz
3	1.32 (t, 3H, $\underline{CH}_3CH_2OC$, $^3J_{HH}$ 7.0); 1.42 (d, 12H, $(\underline{CH}_3)_2CHOP$, $^3J_{HH}$ 6.0); 3.75 (q, 2H, $CH_3\underline{CH}_2OC$, $^3J_{HH}$ 6.0); 4.51–5.11 (m, 2H, $(CH_3)_2\underline{CH}OP$); 6.21 (d, 1H, $\underline{CH}SP$, $^3J_{PH}$ 10.0); 7.18–7.60 and 7.75–8.00 (two m, 5H, $C_6\underline{H}_5$)
6a	1.38 (t, 6H, $(\underline{CH}_3CH_2O)_2C$, $^3J_{HH}$ 7.0); 1.41 (d, 12H, $[(\underline{CH}_3)_2CHO]_2P$, $^3J_{HH}$ 7.0); 2.81 (q, 4H, $(CH_3\underline{CH}_2O)_2C$, $^3J_{HH}$ 7.0); 3.18 (d, 1H, $\underline{CH}SP$, $^3J_{PH}$ 8.0); 4.41–5.26 (m, 2H, $[(CH_3)_2\underline{CH}O]_2P$)
6b	0.95 (t, 6H, $(\underline{CH}_3CH_2CH_2CH_2O)_2P$, $^3J_{HH}$ 7.0); 1.40 (t, 6H, $(\underline{CH}_3CH_2O)_2C$, $^3J_{HH}$ 7.0); 1.43–2.07 (m, 3H, $\underline{CH}_3SP$; 8H, $(CH_3\underline{CH}_2CH_2CH_2O)_2P$); 2.68–3.25 (m, 4H, $(CH_3\underline{CH}_2O)_2C$; 4H, $(CH_3CH_2\underline{CH}_2\underline{CH}_2O)_2P$)
8a	1.10 (t, 6H, $(\underline{CH}_3CH_2O)_2C$, $^3J_{HH}$ 7.0); 1.28 (t, 12H, $[(\underline{CH}_3CH_2)_2N]_2P$, $^3J_{HH}$ 7.0); 3.23 (q, 4H, $(CH_3\underline{CH}_2O)_2C$, $^3J_{HH}$ 7.0); 3.51 (d, 1H, $\underline{CH}SP$, $^3J_{PH}$ 8.0); 3.87 (d, q, 8H, $[(CH_3\underline{CH}_2)_2N]_2P$, $^3J_{HH}$ 7.0, $^3J_{PH}$ 15.0)
8b	1.14 (t, 12H, $[(\underline{CH}_3CH_2)_2N]_2P$, $^3J_{HH}$ 7.0); 1.31 (t, 6H, $(\underline{CH}_3CH_2O)_2C$, $^3J_{HH}$ 7.0); 2.07 (s, 3H, $\underline{CH}_3CS$); 3.00 (d, q, 8H, $[(CH_3\underline{CH}_2)_2N]_2P$, $^3J_{HH}$ 7.0, $^3J_{PH}$ 23.0); 3.28 (q, 4H, $(CH_3\underline{CH}_2O)_2C$, $^3J_{HH}$ 7.0)
10a	1.24 (t, 3H, $\underline{CH}_3CH_2OP$, $^3J_{HH}$ 7.0); 1.40 (t, 3H, $\underline{CH}_3CH_2OC_6H_4$, $^3J_{HH}$ 7.0); 1.44 (t, 6H, $(\underline{CH}_3CH_2O)_2C$, $^3J_{HH}$ 7.0); 2.76 (d, q, 2H, $CH_3\underline{CH}_2OP$, $^3J_{HH}$ 7.0, $^3J_{PH}$ 15.0); 4.01 (q, 4H, $(CH_3\underline{CH}_2O)_2C$, $^3J_{HH}$ 7.0); 4.15 (q, 2H, $(CH_3\underline{CH}_2$ OC_6H_4, $^3J_{HH}$ 7.0); 4.53 (d, 1H, $\underline{HC}SP$, $^3J_{PH}$ 10.0); 6.89 (d. d, 2H, 3,5-$H_2C_6\underline{H}_2$, $^3J_{HH}$ 9.0, $^4J_{PH}$ 2.5); 7.61 (d. d, 2H, 2,6-$\underline{H}_2C_6H_2$, $^3J_{HH}$ 9.0, $^3J_{PH}$ 13.0)
10b	1.02 (d, 6H, $(\underline{CH}_3)_2CHCH_2OP$, $^3J_{HH}$ 7.0); 1.22 (s, 3H, $\underline{CH}_3CS$); 1.38 (t, 3H, $\underline{CH}_3CH_2OC_6H_4$, $^3J_{HH}$ 7.0); 1.43 (t, 6H, $(\underline{CH}_3CH_2O)_2C$, $^3J_{HH}$ 7.0); 1.67–2.25 (m, 1H, $(CH_3)_2\underline{CH}CH_2OP$); 2.73 (d. d, 2H, $(CH_3)_2CH\underline{CH}_2OP$, $^3J_{HH}$ 7.0, $^3J_{PH}$ 14.0); 3.89 (q, 2H, $CH_3\underline{CH}_2OC_6H_4$, $^3J_{HH}$ 7.0); 4.06 (q, 4H, $(CH_3\underline{CH}_2O)_2C$, $^3J_{HH}$ 7.0); 6.88 (d. d, 3,5-$H_2C_6\underline{H}_2$, $^3J_{HH}$ 9.0, $^4J_{PH}$ 3.0); 7.78 (d. d, 2H, 2,6-$\underline{H}_2$ C_6H_2, $^3J_{HH}$ 9.0, $^3J_{PH}$ 13.0)
12a	0.77 (t, 3H, $\underline{CH}_3CH_2CH_2SP$, $^3J_{HH}$ 7.0); 1.11 (t, 6H, $(\underline{CH}_3CH_2O)_2C$, $^3J_{HH}$ 7.0); 1.21–1.79 (m, 2H, $CH_3\underline{CH}_2CH_2SP$; 3H, $\underline{CH}_3CS$); 2.48 (q, 4H, $(CH_3\underline{CH}_2O)_2C$, $^3J_{HH}$ 7.0); 2.76 (d. t, 2H, $CH_3CH_2\underline{CH}_2SP$, $^3J_{HH}$ 7.0, $^3J_{PH}$ 22.4); 3.71 (s, 3H, $\underline{CH}_3OC_6H_4$); 6.88 (d. d, 2H, 3,5-$H_2C_6\underline{H}_2$, $^3J_{HH}$ 9.0, $^4J_{PH}$ 3.0); 7.84 (d. d, 2H, 2,6-$\underline{H}_2C_6H_2$, $^3J_{HH}$ 9.0, $^3J_{PH}$ 15.0)
12b	0.97 (d, 6H, $(\underline{CH}_3)_2CHCH_2SP$, $^3J_{HH}$ 7.0); 1.30 (t, 6H, $(\underline{CH}_3CH_2O)_2C$, $^3J_{HH}$ 7.0); 1.46 (s, 3H, $\underline{CH}_3CS$); 1.57–2.13 (m, 1H, $(CH_3)_2\underline{CH}CH_2SP$); 2.80 (d. d, 2H, $(CH_3)_2CH\underline{CH}_2SP$, $^3J_{HH}$ 7.0, $^3J_{HH}$ 14.0); 3.05 (q, 4H, $(CH_3\underline{CH}_2O)_2C$, $^3J_{HH}$ 7.0); 3.84 (s, 3H, $\underline{CH}_3OC_6H_4$); 6.94 (d. d, 2H, 3,5-$H_2C_6\underline{H}_2$, $^3J_{HH}$ 9.0, $^4J_{PH}$ 3.0); 7.95 (d. d, 2H, 2,6-$\underline{H}_2C_6H_2$, $^3J_{HH}$ 9.0, $^3J_{PH}$ 14.0)
14	1.23 (t, 6H, $(\underline{CH}_3CH_2O)_2C$, $^3J_{HH}$ 7.0); 1.43 (t, 6H, $[(\underline{CH}_3CH_2)_2N]_2P$, $^3J_{HH}$ 7.0); 2.76 (q, 4H, $(CH_3\underline{CH}_2O)_2C$, $^3J_{HH}$ 7.0); 3.40 (d. q, 4H, $[(CH_3\underline{CH}_2)_2N]_2P$, $^3J_{HH}$ 7.0, $^3J_{PH}$ 5.0); 3.84 (s, 3H, $\underline{CH}_3OC_6H_4$); 4.13 (d, 1H, $\underline{CH}SP$); 6.93 (d. d, 3,5-$H_2C_6\underline{H}_2$, $^3J_{HH}$ 9.0, $^4J_{PH}$ 3.0); 7.84 (d. d, 2H, 2,6-$\underline{H}_2C_6H_2$, $^3J_{HH}$ 9.0, 2H, $^3J_{PH}$ 13.5)

TABLE V Mass Spectral Data of the Products Obtained

Product	i-C_4H_{10}, m/e (I_{rel}, %)
3[a]	348 $[M]^{+\cdot}$ (1); 333 $[M-Me]^{+\cdot}$ (1); 319 $[M-Et]^{+\cdot}$ (1); 316 $[M-S]^{+\cdot}$ (1); 305 $[M-Pr\text{-}i]^{+\cdot}$ (1); 303 $[M-OEt]^{+\cdot}$ (7); 289 $[M-OPr\text{-}i]^{+\cdot}$ (2)
6a[a]	316 $[M]^{+\cdot}$ (1); 273 $[M-Pr\text{-}i]^{+\cdot}$ (0.4); 256 $[M-Pr\text{-}i-H]^{+\cdot}$ (0.7); 242 $[M-Et-EtO]^{+\cdot}$ (18); 228 $[M-Pr\text{-}i-EtO]^{+\cdot}$ (2)
6b[a]	358 $[M]^{+\cdot}$ (2); 343 $[M-Me]^{+\cdot}$ (1); 329 $[M-Et]^{+\cdot}$ (1); 269 $[M-Bu-S]^{+\cdot}$ (1)
6b[b]	328 $[M+2H-S]^{+}$ (1); 314 $[M+H-EtO]^{+}$ (1); 302 $[M+H-Bu]^{+}$ (100)
8a[a]	313 $[M-Et]^{+\cdot}$ (3); 297 $[M-EtO]^{+\cdot}$ (5); 270 $[M-Et_2N]^{+\cdot}$ (1)
8a[b]	282 $[M+H-EtO-S]^{+}$ (1); 226 $[M+H-EtO-Et_2N]^{+}$ (1)
8b[a]	356 $[M]^{+\cdot}$ (0.1); 324 $[M-S]^{+\cdot}$ (1); 341 $[M-Me]^{+\cdot}$ (1); 327 $[M-Et]^{+\cdot}$ (1); 311 $[M-OEt]^{+\cdot}$ (2); 298 $[M-2\ Et]^{+\cdot}$ (7); 284 $[M-Et_2N]^{+\cdot}$ (1); 282 $[M-OEt-Et]^{+\cdot}$ (1)
10a[a]	364 $[M]^{+\cdot}$ (18); 363 $[M-H]^{+\cdot}$ (45); 349 $[M-Me]^{+\cdot}$ (13); 332 $[M-S]^{+\cdot}$ (2); 335 $[M-Et]^{+\cdot}$ (1); 319 $[M-OEt]^{+\cdot}$ (31)
10a[b]	365 $[M+H]^{+}$ (15)
10b[a]	406 $[M]^{+\cdot}$ (0.2); 391 $[M-Me]^{+\cdot}$ (2); 377 $[M-Et]^{+\cdot}$ (1); 349 $[M-Bu\text{-}i]^{+\cdot}$ (7); 333 $[M-OBu\text{-}i]^{+\cdot}$ (1); 289 $[M-CMe(OEt)_2]^{+\cdot}$ (1)
10b[b]	375 $[M+H-S]^{+}$ (3)
12b[a]	408 $[M]^{+\cdot}$ (1); 376 $[M-S]^{+\cdot}$ (1); 379 $[M-Et]^{+\cdot}$ (1); 369 $[M-OEt]^{+\cdot}$ (1)
12b[b]	394 $[M+H-Me]^{+}$ (1)
14[a]	377 $[M]^{+\cdot}$ (0.2); 362 $[M-Me]^{+\cdot}$ (0.4); 348 $[M-Et]^{+\cdot}$ (0.4); 345 $[M-S]^{+\cdot}$ (1); 332 $[M-EtO]^{+\cdot}$ (1); 287 $[M-2\ EtO]^{+\cdot}$ (0.2)

[a] Chemical ionization, 100 eV.

[b] Electron impact, 70 eV.

trimethyl(ethoxy)silane **4** (Eq. 2, Tables I–V).

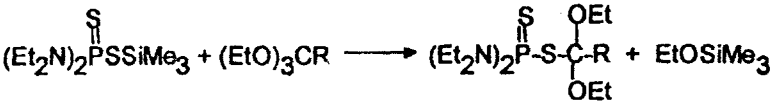
$$(RO)_2\overset{S}{\overset{\|}{P}}SSiMe_3 + (EtO)_3CR' \longrightarrow (RO_2\overset{S}{\overset{\|}{P}}\text{-}S\text{-}\underset{OEt}{\overset{OEt}{C}}\text{-}R' + EtOSiMe_3 \qquad (2)$$

1a, R = Pr-i **5a**, R' = H **6a**, R = Pr-i, R' = H **4**

b, R = Bu **b**, R' = Me **b**, R = Bu, R' = Me

Reaction 2 is exothermic and occurs at room temperature during 4 h. Ortho esters **5a**,**b** also react with the participation of one of O—C bonds under mild conditions. Two ethoxy groups remained attached to the α-carbon atom of the S-alkyl group. Bis(ethoxy)alkyl dithiophosphates **6a**,**b** formed in reaction 2 were obtained in 45 and 75% yields respectively. Compounds **6a**,**b** are colorless liquids and were purified by means of thin layer distillations. The ^{31}P NMR spectra of **6a**,**b** (Table II) show singlets in the range of δ 91.1–91.4 ppm. These resonances appear in practically the same region as that for **3**. As we can see, the ^{31}P NMR spectral signals of **3** and **6a**,**b** reveal no significant change when the number of alkoxy groups at the α-carbon atom of the S-alkyl group is increased. The ^{1}H NMR and IR spectra of bis(ethoxy)alkyl dithiophosphate **6a**,**b** show characteristic features similarly to monoethoxybenzyl dithiophosphate **3**. The electron impact mass spectrum of **6b** exhibits the mass peak m/e 358 due its molecular ion $[M]^+$ (Table V).

In continuation of a study of the reactivity of the S—Si bond of S-silyl esters of tetracoordinated phosphorus thioacids, we have tried to extend these substitution reactions to S-silyldiamidodithiophosphates. We have developed a new method for synthesizing S-(diethoxy) alkyl bis(diethylamido)dithiophosphates **8a**,**b** by the reaction of S-trimethylsilyl bis(diethylamido)dithiophosphate **7** with ortho esters **5a**,**b** (Eq. 3, Tables I–V).



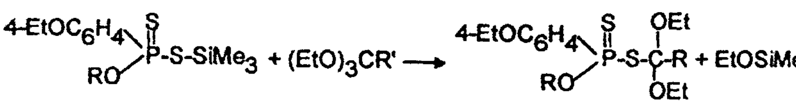
$$(Et_2N)_2P(=S)SSiMe_3 + (EtO)_3CR \longrightarrow (Et_2N)_2P(=S)\text{-}S\text{-}C(OEt)_2\text{-}R + EtOSiMe_3 \qquad (3)$$

7 **5a**, R = H **8a**, R = H **4**

b, R = Me **b**, R = Me

Reaction 3 proceeds at room temperature. We have not observed an exothermic effect in this reaction. When dialkoxy groups at the phosphorus atom were exchanged by the dialkylamido groups, the reactivity of S-silyl diamidodithiophosphates decreased slightly. In spite of this, diamidodithiophosphates **8a**,**b** were obtained with 75–78 yields. The ^{31}P nuclei of **8a**,**b** resonate in practically the same region (δ 93.9 ppm) as observed in **6a**,**b**. We have observed a mass peak m/e 356 in the electron impact mass spectrum of **8b** that may be assigned to its molecular ion $[M]^+$ (Table V).

Thus, the high phosphorylating ability S-silyl dithiophosphates and S-silyl diamidodithiophosphates have been elucidated by reactions 1–3. The rather high reactivity of organothiophosphorus compounds containing the S—Si bond was also shown with the behavior of S-silyl esters of dithiophosphonic acids. Thus, the substitution reactions of S-trimethylsilyl O-alkyl-4-ethoxyphenyldithiophosphonates **9a**,**b** wirth ortho esters **5a**,**b** at 20°C for 1–3 h yielded S-(1,1-diethoxy)alkyl diamidodithiophosphates **10a**,**b** and trimethyl(ethoxy)silane **4** (Eq. 4, Tables I–V).



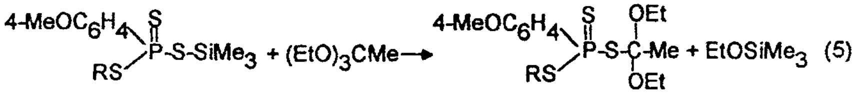
$$4\text{-}EtOC_6H_4(RO)P(=S)\text{-}S\text{-}SiMe_3 + (EtO)_3CR' \longrightarrow 4\text{-}EtOC_6H_4(RO)P(=S)\text{-}S\text{-}C(OEt)_2\text{-}R + EtOSiMe_3 \qquad (4)$$

9a, R = Et **5a**, R' = H **10a**, R = Et, R' = H **4**

b, R = Bu-i **b**, R' = Me **b**, R = Bu-i, R' = Me

The formation of **10b** was accompanied by an exothermic effect. Compounds **10a**,**b** were purified by the use of a thin layer distillations. The thermal stability of **10a**,**b** containing the strong P—C bond are rather higher than that of **8a**,**b**. The ^{31}P NMR spectra of **10a**,**b** in benzene solutions show singlets at δ 94.1 and 94.9 ppm (Table II). The ^{1}H NMR spectrum of **10a** in $CDCl_3$ solution (Table IV), reveals three triplets (δ 1.24, 1.40, and 1.44 ppm) of the methyl protons of the $\underline{CH_3}CH_2OP$, $\underline{CH_3}CH_2OC_6H_4$ and $(\underline{CH_3}CH_2O)_2C$ groups, respectively ($^3J_{HH}$ 7.0 Hz). The mass peaks m/e 364 and 406 observed in the mass spectra of **10a** and **10b**, respectively, are due to their molecular ions $[M]^+$ (Table V).

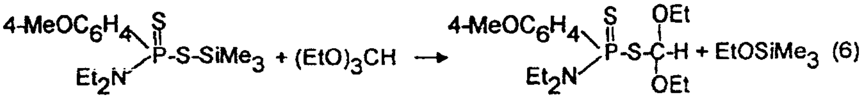
It is considered of interest to compare the reactivity of ortho esters toward S-silyl esters of aryldithiophosphonic and aryltrithiophosphonic acids. We have shown that S-trimethylsilyl S-alkyl-4-methoxyphenyltrithiophosphonates **11a**,**b** react with ortho acetate **5b** at room temperature for 2 h to give S-(1,1-diethoxy)ethyl S-alkyl-4-methoxyphenyltrithiophosphonates **12a**,**b** and trimethyl(ethoxy)silane **4** (Eq. 5, Tables I–V).



11a, R = Pr **5b** **12a**, R = Pr **4**
b, R = Bu-i **b**, R = Bu-i

The reaction of S-silyl trithiophosphonate **11b** with ortho acetate **5b** is exothermic. The ^{31}P NMR spectra of **12a**,**b** in benzene solutions reveal the signals at δ 77.9 and 78.4 ppm, respectively (Table II). These resonances are within the common region attributed to esters of aryltrithiophosphonic acids containing the $P(S)(SR)_2$ structural fragment.[6] Bands at ν 692–688 cm^{-1} in the IR spectra of **12a**,**b** (Table III) are assigned to the P=S valence vibrations showing a shift to lower frequency with respect to derivatives of dithiophosphonic acids **10a**,**b** (ν P=S 700 cm^{-1}). The mass peak m/e 408 was found in the electron impact mass spectrum of **12b**; it may be attributed to its molecular ion $[M]^+$ (Table V).

In development of our approach, we have managed to involve S-trimethylsilyl ester of diethylamido 4-methoxyphenyltrithiophosphonic acid **13** in the reaction with ortho formiate **5a** (Eq. 6, Tables I–V).



13 **5a** **14** **4**

S-(Diethoxy)methyl diethylamido 4-methoxyphenyltrithiophosphonate **14** and trimethyl-(ethoxy)silane **4** were formed with an exothermic effect, as depicted in Eq. 6. The ^{31}P chemical shift value of **14** (δ 94.9 ppm) is shifted to low field with respect to that of trithiophosphonates **12a**,**b** (δ 77.9 and 78.4 ppm). The ^{1}H NMR spectrum of **14** in $CDCl_3$ solution (Table IV) shows the characteristic doublet of doublets at δ 3.40 ppm due the methylene protons of the diethylamino groups attached to the phosphorus atom $[(CH_3\underline{CH_2})_2N]_2P$ ($^3J_{HH}$ 7.0 Hz, $^3J_{HH}$ 15.0 Hz). The peak of the molecular ion (m/e 377 $[M]^+$) was observed by use of the electron impact mass spectrum of **14** (Table V).

Thus, the above substitution reactions of S-trimethylsilyl esters of tetracoordinated phosphorus thioacids with diethyl acetal of benzaldehyde and ortho esters proceed under mild conditions with the participation of only one O—C bond. The reactions studied are of interest from the point of view of preparative organophosphorus chemistry.

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 $CDCl_3$. The IR spectra were obtained with an UR-20 infrared spectrophotometer. Mass spectra (EI, 70 eV; CI, 100 eV) were determined on a M 80 B Hitachi chromatomass spectrometer.

Reaction of S-Trimethylsilyl O,O-Diisopropyldithiophosphate 1a with Bis(ethoxy)phenylmethane 2

Compound **2** (2.9 g, 16.1 mmol) was added dropwise under dry argon with stirring at 20°C to 4.6 g (16.1 mmol) of **1a**, and stirring was continued for 3 h at 20°C. The mixture was evaporated at reduced pressure (0.5 and then 0.06 mm Hg) at 40°C for 2 h with the use of a trap cooled by liquid nitrogen to give crude **3** (4.1 g, 89%). Pure **3** (3.5 g, 63%) was isolated from the residue by means of a thin layer distillation (see Tables I–V). Distillation of the content of the liquid nitrogen trap gave trimethyl(ethoxy)silane **4** (0.9 g, 47%), b.p. 75–76°C, n_D^{20} 1.3753 (cf. lit.[7]: b.p. 75.7°C, n_D^{20} 1.3742).

Products **6a**,**b**, **8a**,**b**, **10a**,**b**, **12a**,**b**, and **14** were obtained similarly (see Tables I–V).

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