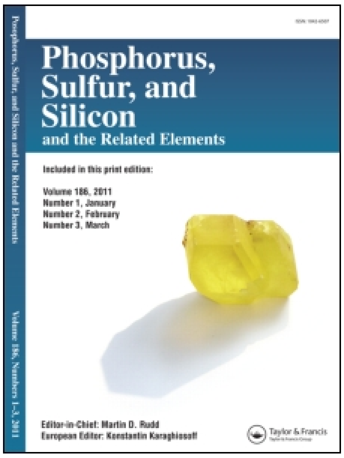

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Nizamov, Il'Yas S. , Kuznetzov, Vladislav A. and Batyeva, Elvira S.(1994) 'Dialkyl(Trimethylsilyl)-Tetrathiophosphates in Synthesis of Substituted Tetrathiophosphates', Phosphorus, Sulfur, and Silicon and the Related Elements, 90: 1, 249 — 257

To link to this Article: DOI: 10.1080/10426509408016409

URL: http://dx.doi.org/10.1080/10426509408016409

Phosphorus, Sulfur, and Silicon, 1994, Vol. 90, pp. 249–257
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DIALKYL(TRIMETHYLSILYL)-TETRATHIOPHOSPHATES IN SYNTHESIS OF SUBSTITUTED TETRATHIOPHOSPHATES

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(Received April 7, 1994)

Reactions of S,S'-dialkyl-S''-trimethylsilyl tetrathiophosphates with aldehydes, acetals, ortho ethers, aminals, thioacetals, bis(thiocyanato)methane, disulfides and alkyl halides resulted in the products of tetrathiophosphate structure.

Key words: S,S'-Dialkyl-S''-trimethylsilyl tetrathiophosphates; organic substances; substituted tetrathiophosphates.

INTRODUCTION

Over the past three years we have been involved in developing new synthetic routes for (1-alkylthio), (1-dialkylamino) and (1-alkoxy)alkyl derivatives of phosphorus (IV) thioacids in terms of phosphorus sulfides (P_4S_3 and P_4S_{10}) and Davy's and Lawesson's-like reagents with thioacids, aminals and acetals.[1–3] These compounds possess biological activity and may be used as intermediates for synthesizing organothiophosphorus products. In this article we used trimethylsilyl esters of dialkyltetrathiophosphoric acids as initial reagents for the synthesis of (1-trimethylsiloxy), (1-alkoxy), (1-dialkylamino), (1-alkylthio) and (1-thiocyanato)alkyl tetrathiophosphates.

RESULTS AND DISCUSSION

S-Trimethylsilyl esters of phosphorus (IV) thioacids have found an expanding application in synthetic organophosphorus chemistry.[4] The organothiophosphorus compounds were obtained in the reactions of S-trimethylsilyl dithiophosphates with aldehydes and ketones,[4,5] alkylene oxides,[6] organophosphorus compounds,[5,7] unsaturated carbonyl compounds,[5,8] nitroalkenes,[9] quinones,[10,11] isocyanates,[12,13] diimides,[14] and thionylimines.[15] On the other hand, trimethylsilyl tetrathiophosphates remained unknown previous to our investigations. We have recently developed a facile method of synthesizing dialkyl(trimethylsilyl)tetrathiophosphates on the basis of the reaction of tetraphosphorus decasulfide with trimethyl(alkylthio)silanes.[16] Meanwhile silyltetrathiophosphates containing a reactive S—Si bond

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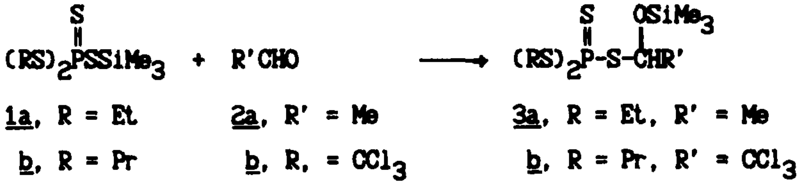
and a readily leaving trimethylsilyl group may result in products of tetrathiophosphate structure in addition and substitution reactions with organic compounds.

It was interesting to compare the reactivity of silyl dithiophosphates[4–15] and that of silyltetrathiophosphates in the addition reactions. The reaction of O,O′-dialkyl-S-trimethylsilyl dithiophosphates with aldehydes and ketones under mild conditions was reported to result in O,O′-dialkyl-S-(1-trimethylsiloxy)alkyl dithiophosphates.[4–15] We assumed that the corresponding silyltetrathiophosphates should easily add themselves to the C═O bond of aldehydes. Indeed, we have found that dialkyl(trimethylsilyl)tetrathiophosphates 1a,b react with aldehydes 2a,b at 10–20°C with the formation of S,S′-dialkyl-S″-(1-trimethylsiloxy)alkyl tetrathiophosphates 3a,b (Equation 1, and Tables I–III).



$$(RS)_2\overset{\overset{S}{\|}}{P}SSiMe_3 + R'CHO \longrightarrow (RS)_2\overset{\overset{S}{\|}}{P}\text{-}S\text{-}\overset{\overset{OSiMe_3}{|}}{C}HR' \qquad (1)$$

1a, R = Et 2a, R′ = Me 3a, R = Et, R′ = Me

b, R = Pr b, R, = CCl$_3$ b, R = Pr, R′ = CCl$_3$

TABLE I

Experimental, physical and analytical data of the products obtained

Initial cpd.		Prod.	Reaction conditions temp. (°C)/time (h)	Yield[a] (%) crude/isolated	B.p.[d] °C (mm Hg)	d_4^{20}	n_D^{20}	Molecular formula (Mol. mass)	Analytical data Found/Calc. (%) C	H	P	S	^{31}P NMR δ, ppm (solvent)
1a,	2a	3a[e,g]	10/2	80[b]/20[c]	120 (0.02)	1.1172	1.5483	$C_9H_{23}OPS_4Si$	32.01	6.52	9.60	38.67	87.2
								(334.1)	32.33	6.95	9.27	38.28	(C_6H_6)
1b,	2b	3b[f]	20/4	95[b]/69[c]	140 (0.02)	1.2044	1.5452	$C_{11}H_{24}Cl_3OPS_4Si$	28.30	4.88	6.84	27.03	93[h]
								(465.6)	28.35	5.21	6.65	27.47	
1a,	4a	5a	20/12	46[c]	165 (0.02)	1.1237	1.5754	$C_{13}H_{21}OPS_4$	43.27	6.35	9.12	35.91	89.6
								(352.1)	44.31	6.03	8.80	36.32	(C_6H_6)
1a,	4b	5b	20/1	87[b]/69[c]	160 (0.02)	1.1388	1.4513	$C_9H_{21}O_2PS_4$	33.52	6.89	10.27	39.44	90.3
								(320.1)	33.74	6.63	9.68	39.95	(C_6H_6)
1a,	7a	8a[k]	100/1	90[b]		1.2031	1.5901	$C_7H_{18}NPS_4$	30.22	6.55	11.24	46.36	98.5
								(275.0)	30.54	6.61	11.26	46.50	(C_6H_6)
1a,	7b	8b[l]	90-100/1	86[b]/48[c]	170 (0.02)		1.5672	$C_{13}H_{30}NPS_4$	43.58	8.66	7.95	35.30	101[h]
								(359.2)	43.44	8.44	8.62	35.60	
1a,	10	11[i]	100-160/13	62[b]/55[c]	170 (0.02)		1.6609	$C_7H_{17}PS_5$	29.12	5.96	10.55	54.12	88.4
								(292.0)	28.77	5.88	10.61	54.74	(CCl_4)
1a,	13	14[g,m]	100-110/6	59[b]/29[c]	150 (0.02)	1.3397	1.6758	$C_8H_{12}NPS_5$	25.83	4.21	10.86	55.08	90.6
								(288.9)	24.92	4.19	10.72	55.32	(C_6H_6)
1c,	19b	20b[j]	100/2	88[b]/45[c]	130 (0.02)		1.5402	$C_{12}H_{27}PS_4$	44.01	8.52	9.60	37.90	93.1
								(330.1)	43.62	8.26	9.38	38.74	(C_6H_6)

[a] Yield of crude/isolated product.

[b] Yield of crude product.

[c] Yield of isolated product.

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

[e] Analytical data: Found, % : Si 8.57. Calc., % : 8.38.

[f] Analytical data: Found, % : Cl 28.43; Si 6.47. Calc., % : Cl 22.87; Si 6.01.

[g] Solvent for reaction: toluene.

[h] Neat.

[i] Reference 12: b.p. 163°C (0.02 mm Hg), n_D^{20} 1.6504.

[j] Solvent for reaction: benzene.

[k] Analytical data: Found, % : N 5.96. Calc., % : N 5.09.

[l] Analytical data: Found, % : N 3.80. Calc., % : N 3.90.

[m] Analytical data: Found, % : N 4.50. Calc., % : N 4.85.

TABLE II

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

Prod.	CH_3[a] as, s; CH_2[a] as, s	δ (CH_3 as, s), δ (CH_2)	ω, τ (CH_2)	P=S,[a] PS_2[a] as	P-S,[a] PS_2[a] s
3a[e,f]	2985, 2933, 2905, 2878			692	530
3b[e,f]	2968, 2935, 2905, 2860			690	533
5a[d]	2983, 2932, 2910, 2880	1458, 1398	1265	658	526, 515
5b	2980, 2932, 2910, 2878	1460	1267	660	530, 516
8a[b]	2965, 2930, 2880	1463, 1415	1260	666	568, 513
8b	2970, 2870, 2815	1463, 1382, 1365	1265	665	570, 550
14[c]	2975, 2930, 2878, 2825	1453, 1379	1260	691	535
20b	2965, 2935, 2910, 2878	1468, 1437, 1389, 1370	1260	690	535, 510

[a] Valence vibrations.

[b] Valence vibrations ν 2760 cm^{-1} $N(CH_3)_2$.

[c] Valence vibrations ν 2038 cm^{-1} $S-C\equiv N$.

[d] Valence vibrations ν 3070, 3030 cm^{-1} C-H, Ar; ν 1600, 1495 cm^{-1} C=C, Ar.

[e] Deformation vibrations δ 1260-1263 cm^{-1} [$CH_3(Si)$ s].

[f] Valence vibrations ν 1040-1060 cm^{-1} C-O (Si).

TABLE III

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

Prod.	CCl_4, δ, ppm, J, Hz
3a	0.43 (s, 9H, $\underline{CH_3}Si$), 1.47 (t, 6H, $\underline{CH_3}CH_2$, $^3J_{H-H}$ 7.5), 1.88 (d, 3H, $\underline{CH_3}CHSP$, $^3J_{H-H}$ 7.5), 2.90 (dq, 4H, $CH_3\underline{CH_2}SP$, $^3J_{H-H}$ 7.5, $^3J_{P-H}$ 23.0), 3.90-4.70 (m, 1H, $CH_3\underline{CH}SP$).
3b	0.42 (s, 9H, $\underline{CH_3}Si$), 1.17 (t, 6H, $\underline{CH_3}CH_2CH_2$, $^3J_{H-H}$ 7.0), 1.85 (dt, 4H, $CH_3CH_2\underline{CH_2}SP$, $^3J_{H-H}$ 7.0, $^3J_{P-H}$ 2.0), 2.72-3.25 (m, 4H, $CH_3\underline{CH_2}CH_2SP$), 5.76 (d, 1H, $\underline{CH}SP$, $^3J_{P-H}$ 14.0).
5a	1.23 (t, 3H, $\underline{CH_3}CH_2O$, $^3J_{H-H}$ 7.0), 1.37 (t, 6H, $\underline{CH_3}CH_2S$, $^3J_{H-H}$ 7.0), 2.73 (dq, 4H, $\underline{CH_3}CH_2SP$, $^3J_{H-H}$ 7.0, $^3J_{P-H}$ 17.0), 5.48 (s, 1H, $\underline{CH}SP$, $^3J_{H-H}$ 7.0), 7.13-7.48 (m, 5H, $C_6\underline{H_5}$).
5b	1.34 (t, 6H, $\underline{CH_3}CH_2O$, $^3J_{H-H}$ 7.0), 1.37 (t, 6H, $\underline{CH_3}CH_2SP$, $^3J_{H-H}$ 7.0), 2.67 (dq, 4H, $CH_3\underline{CH_2}SP$, $^3J_{H-H}$ 7.0, $^3J_{P-H}$ 2.0), 4.13 (q, 4H, $CH_3\underline{CH_2}OCHS$, $^3J_{H-H}$ 7.0), 5.25 (d, 1H, $\underline{CH}SP$, $^3J_{P-H}$ 12.0).
8a	1.47 (t, 6H, $\underline{CH_3}CH_2S$, $^3J_{H-H}$ 7.5), 2.35 (s, 6H, $\underline{CH_3}N$), 2.86 (d, 2H, $N\underline{CH_2}SP$, $^3J_{P-H}$ 17.0), 2.88 (dq, 4H, $CH_3\underline{CH_2}SP$, $^3J_{H-H}$ 7.0, $^3J_{P-H}$ 20.0).
8b[a]	1.07 (d, 12H, $\underline{CH_3}CHCH_2S$, $^3J_{H-H}$ 6.6), 1.43 (t, 6H, $\underline{CH_3}CH_2N$, $^3J_{H-H}$ 7.2), 3.06 (d, 2H, $N\underline{CH_2}SP$, $^3J_{P-H}$ 7.1), 2.00-3.67 (m, $CH_3\underline{CH}CH_2SP$, $CH_3CH\underline{CH_2}SP$, $CH_3\underline{CH_2}N$).

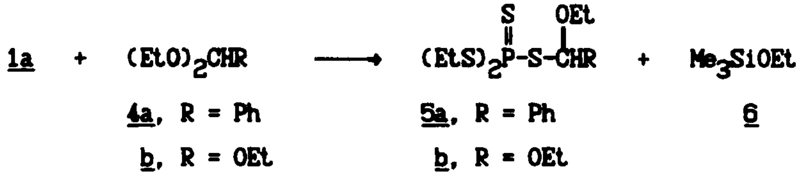
TABLE III (*Continued*)

Prod.	CCl_4, δ, ppm, J, Hz
14[a]	1.25 (t, 6H, $\underline{CH_3}CH_2S$, $^3J_{H-H}$ 7.2), 2.94 (dq, 4H, $CH_3\underline{CH_2}SP$, $^3J_{H-H}$ 7.0, $^3J_{P-H}$ 17.0), 3.80 (d, 2H, $NCS\underline{CH_2}SP$, $^3J_{P-H}$ 16.0).
20b	0.47 (t, 3H, $\underline{CH_3}CH_2CH_2CH_2S$, $^3J_{H-H}$ 5.5), 1.13 (d, 12H, $\underline{CH_3}$-$CHCH_2S$, $^3J_{H-H}$ 7.0), 1.48-2.44 (m, 4H, $CH_3\underline{CH_2CH_2}CH_2S$; 2H, $CH_3\underline{CH}CH_2SP$), 2.90 (dd, 4H, $CH_3CH\underline{CH_2}SP$, $^3J_{H-H}$ 7.0, $^3J_{P-H}$ 16.0), 2.71-3.17 (m, 2H, $CH_3CH_2CH_2\underline{CH_2}SP$).

[a] In C_6D_6.

The structure of the products 3a,b have been established by IR (Table II). ^1H NMR (Table III), ^{31}P NMR (Table I) spectral data and microanalyses (Table I). It should be emphasized that formally 3 are the products of the insertion of the C=O group of 2 into the S—Si bond of 1. However, 3b was partially decomposed when a thin layer distillation apparatus was used. The driving forces of the smooth addition reaction of 1 with 2 are the oxygenophilicity of a silicon atom (the difference in the Si—O and the Si—S bond energy values is ~34 kcal/mol[17]) and the high nucleophilicity of the PS_2 group. The electronwithdrawing effect of P=S group facilitates the cleavage of the Si—S bond of 1 that should promote the substitution reaction as well. Thus, we have introduced 1 into the substitution reactions of a trimethylsilyl group with derivatives of acetal structure of carbonyl compounds such as acetals, ortho ethers, aminals, thioacetals and bis(thiocyanato)methane.

1,1-Bis(ethoxy)-1-phenylmethane 4a and orthoformic ether 4b were found to react with 1a with an exothermic effect and smooth formation of S,S′-diethyl-S″-(1-ethoxy)benzyl and S,S′-diethyl-S″-bis(1-ethoxy)benzyl tetrathiophosphates 5a,b (Equation 2, Tables I–IV).



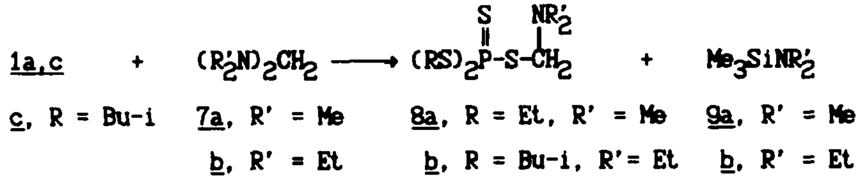
$$\underline{1a} + (EtO)_2CHR \longrightarrow (EtS)_2\overset{S}{\overset{\|}{P}}\text{-}S\text{-}\overset{OEt}{\overset{|}{C}}HR + Me_3SiOEt \qquad (2)$$

$\underline{4a}$, R = Ph $\quad$ $\underline{5a}$, R = Ph $\quad$ $\underline{6}$

$\underline{b}$, R = OEt $\quad$ $\underline{b}$, R = OEt

This substitution reaction of 1 with ethoxy derivatives 4a,b (Equation 2) is followed by the formation of trimethyl(ethoxy)-silane 6, which is easily given off by the reaction mixture. It should be noted that this reaction is a convenient preparative method for synthesizing products of (1-alkoxy)substituted alkyltetrathiophosphates under mild conditions.

Aminals have proved to be less reactive as regards 1. Thus, S,S′-dialkyl-S″-(1-N,N′-dialkylamino)methyl tetrathiophosphates 8a,b were isolated from the reaction of 1a,c with bis(dialkylamino)methanes 7a,b when heated for 1 h at 90–100°C (Equation 3, Tables I–IV).



$$\underline{1a,c} + (R'_2N)_2CH_2 \longrightarrow (RS)_2\overset{\overset{\displaystyle S}{\|}}{P}\text{-}S\text{-}\overset{\overset{\displaystyle NR'_2}{|}}{CH_2} + Me_3SiNR'_2 \qquad (3)$$

$\underline{c}$, R = Bu-i; $\underline{7a}$, R' = Me; $\underline{b}$, R' = Et; $\underline{8a}$, R = Et, R' = Me; $\underline{b}$, R = Bu-i, R' = Et; $\underline{9a}$, R' = Me; $\underline{b}$, R' = Et

Along with 8a,b trimethyl(dialkylamino)silanes 9a,b were formed in the reaction of 1a,c with 7a,b (Equation 3). However, we have failed to isolate 8a in a purely distilled form, as it decomposed even when a thin layer distillation apparatus was used.

The substitution reaction of 1a with bis(ethylthio)methane 10 proceeds under

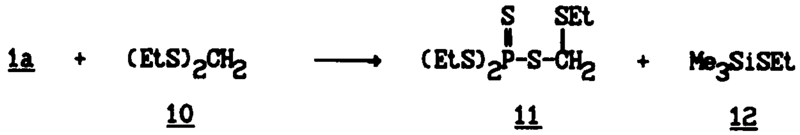
TABLE IV
Mass spectral data of the products obtained

Prod.	$i\text{-}C_4H_{10}$, m/e (I_{rel})
5a[a]	307 $[M - Et]^{+\cdot}$ (10), 275 $[M - Et - S]^{+\cdot}$ (10).
5b[a]	259 $[M - EtS]^{+\cdot}$ (100), 153 $[M - S - SCH(OEt)_2]^{+\cdot}$ (20), 135 $[M - (EtS)_2PS_2]^{+\cdot}$ (90).
5b[b]	185 $[M + H - (EtO)_2CH]^{+}$ (5), 107 $[M + H - (EtS)_2PS]^{+}$ (25).
8a[a]	275 $[M]^{+\cdot}$ (10), 260 $[M - Me]^{+\cdot}$ (10), 246 $[M - Et]^{+\cdot}$ (40), 217 $[M - CH_2NMe_2]^{+\cdot}$ (100), 185 $[M - SCH_2NMe_2]^{+\cdot}$ (50), 159 $[M - 2Et - CH_2NMe_2]^{+\cdot}$ (5), 156 $[M - Et - CH_2NMe_2]^{+\cdot}$ (100), 153 $[M - S - SCH_2NMe_2]^{+\cdot}$ (100), 124 $[M - Et - S - CH_2NMe_2]^{+\cdot}$ (20), 98 $[M - 2EtS - CH_2NMe_2]^{+\cdot}$ (20), 63 $[M - 2EtS - SCH_2NMe_2]^{+\cdot}$ (100).
8b[a]	275 $[M - CNEt_2]^{+\cdot}$ (5), 147 $[M - 2H - (SBu\text{-}i)_2 - S]^{+\cdot}$ (10), 116 $[M - 2H - (i\text{-}BuS)_2PS]^{+\cdot}$ (5).
8b[b]	331 $[M + H - Et]^{+}$ (25), 185 $[M + H - Bu - S - CH_2NEt_2]^{+}$ (60), 153 $[M + H - SBu\text{-}i - SCH_2NMe_2]^{+}$ (35).
11[a]	292 $[M]^{+\cdot}$ (100), 263 $[M - Et]^{+\cdot}$ (100), 217 $[M - CH_2SEt]^{+\cdot}$ (20), 185 $[M - SCH_2SEt]^{+\cdot}$ (85), 153 $[M - S - SCH_2SEt]^{+\cdot}$ (100).
11[b]	232 $[M + H - SEt]^{+}$ (20), 186 $[M + H - SCH_2SEt]^{+}$ (70).
14[a]	263 $[M - CN]^{+\cdot}$ (100), 217 $[M - CH_2NCS]^{+\cdot}$ (15), 185 $[M - S - CH_2NCS]^{+\cdot}$ (82).
14[b]	157 $[M + H - EtS - CH_2NCS]^{+}$ (65).
20b[a]	185 $[M - Bu - SBu]^{+\cdot}$ (50).
20b[b]	331 $[M + H]^{+}$ (100), 274 $[M + H - Bu]^{+}$ (90), 218 $[M + 2H - 2Bu]^{+}$ (100), 153 $[M - SBu - SBu]^{+}$ (30).

[a] Electron impact, 70 eV.

[b] Chemical ionization, 100 eV.

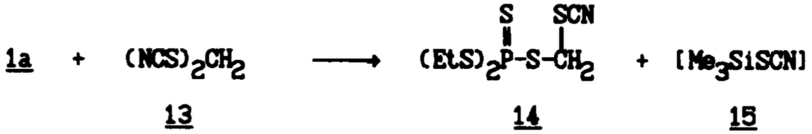
more severe conditions (100–160°C, 13h) and leads to the formation of S,S′-diethyl-S″-(1-ethylthio)methyl tetrathiophosphate 11 and trimethyl(ethylthio)silane 12 (Equation 4, Tables I–IV).



$$\underline{1a} + \underset{\underline{10}}{(EtS)_2CH_2} \longrightarrow \underset{\underline{11}}{(EtS)_2\overset{S}{\overset{\|}{P}}\text{-}S\text{-}\overset{SEt}{\overset{|}{C}}H_2} + \underset{\underline{12}}{Me_3SiSEt} \qquad (4)$$

It should be noted that we previously obtained 11 by the reaction of 2,4-bis(ethylthio)-2,4-dithioxo-1,3,2λ^5, 4λ^5-dithiadiphosphetane with thioacetal 10.[2] The physical and spectral data of 11 (Equation 4) were identical with those of 11 obtained in Reference 2.

Similarly the reaction of bis(thiocyanato)methane 13 with 1a results in the formation of S,S′-diethyl-S″-(1-thiocyanato)methyl tetrathiophosphate 14 at 100–110°C for 6 h (Equation 5, Tables I–IV).

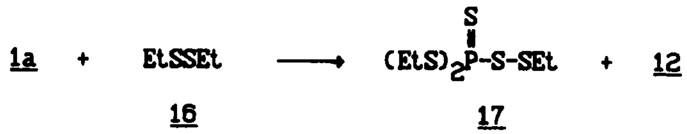


$$\underline{1a} + \underset{\underline{13}}{(NCS)_2CH_2} \longrightarrow \underset{\underline{14}}{(EtS)_2\overset{S}{\overset{\|}{P}}\text{-}S\text{-}\overset{SCN}{\overset{|}{C}}H_2} + \underset{\underline{15}}{[Me_3SiSCN]} \qquad (5)$$

As shown in the analysis of 14 by the electron impact mass spectral method there is a mass peak m/e 263. This may be attributed to the cation-radical $[(EtS)_2P(S)S—CH_2—S]^{+\cdot}$ i.e. $[M—CN]^{+\cdot}$ (100% of relative intensity). This fact lends support to the (1-thiocyanato)methyl tetrathiophosphate structure of 14 and not to the (1-isothiocyanato)methyl tetrathiophosphate structure.

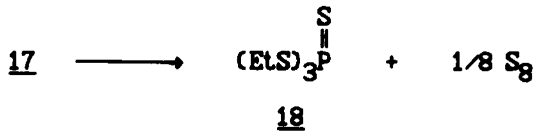
In these reactions (Equations 2–5) the reactivity of the compounds of acetal structure towards 1 decreases in the series: acetals ≈ ortho ethers > aminals > bis(thiocyanato)methane > thioacetals. Perhaps, this reactivity series is due to the fact that the formation of the C—O bond in (1-alkoxy)alkyl derivatives 5a,b is more favourable as compared to those of the C—N and the C—S bonds of 8, 11 and 14, respectively. This correlates with the calculated energy values of these bonds (bond energy values of the C—O, the C—N and the C—S bonds are 84.0, 69.7 and 62.0 kcal/mol, respectively[18]).

We have attempted to find the application of range of these substitution reactions. A series of reagents feasible for the substitution of a trimethylsilyl group was supplemented by compounds containing S—S and C—Hlg bonds such as dialkyl disulfides and alkyl halides. Thus, the reaction of diethyl disulfide 16 with 1a proceeds under severe conditions (150–170°C) and requires prolonged heating (18 h). This reaction (Equation 6) results in the initial formation of S,S′-diethyl-S″,S″-ethyltetrathiolothionophosphate 17 and thiosilane 12.



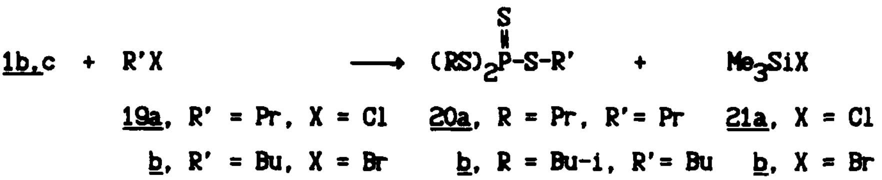
$$\underline{1a} + \underset{\underline{16}}{EtSSEt} \longrightarrow \underset{\underline{17}}{(EtS)_2\overset{S}{\overset{\|}{P}}\text{-}S\text{-}SEt} + \underline{12} \qquad (6)$$

It is of interest that 17 was earlier obtained in the reaction of 16 with tetraphosphorus decasulfide and the ethyl homoloque of Davy's reagent.[2] Thus, the substitution reactions of 1 with thioacetal 10 and disulfide 16 act as counter syntheses of substituted tetrathiophosphates 11 and 17. However, 17 is an unstable compound as in the case of the reaction of P_4S_{10} with 16[2] and decomposes during prolonged heating or distillation under vacuum with the formation of triethyl tetrathiophosphate 18 (Equation 7, Tables I–IV).



$$\underline{17} \longrightarrow \underset{\underline{18}}{(EtS)_3\overset{\overset{S}{\|}}{P}} + 1/8\ S_8 \qquad (7)$$

The trialkyl tetrathiophosphates 20a,b were also obtained in the reaction of 1b,c with alkyl halides 19a,b (Equation 8).



$$\begin{array}{llll} \underline{1b,c} + R'X & \longrightarrow (RS)_2\overset{\overset{S}{\|}}{P}\text{-}S\text{-}R' & + & Me_3SiX \\ \underline{19a},\ R' = Pr,\ X = Cl & \underline{20a},\ R = Pr,\ R' = Pr & & \underline{21a},\ X = Cl \\ \underline{b},\ R' = Bu,\ X = Br & \underline{b},\ R = Bu\text{-}i,\ R' = Bu & & \underline{b},\ X = Br \end{array} \qquad (8)$$

In spite of the severe reaction conditions (100–160°C, 2–5 h) (Equation 8) this approach made it possible for us to obtain trialkyl tetrathiophosphates with mixed alkyl substituents (e.g. 20b).

Thus, we have developed new methods for synthesizing (1-trimethylsiloxy), (1-alkoxy), (1-dialkylamino), (1-alkylthio) and (1-thiocyanato)alkyl tetrathiophosphates, trialkyl pentathiophosphates and trialkyl tetrathiophosphates on the basis of the addition and substitution reactions of silyltetrathiophosphates.

EXPERIMENTAL

^{31}P NMR spectra were recorded with a Bruker MSL-400 (162 MHz), a Bruker CXP-100 (36.5 MHz), and a non-serial NMR KGU-4 (10.2 MHz) spectrometer, reference external H_3PO_4 (85%). ^1H NMR spectra were run on a Varian T-60 (60 MHz) spectrometer in CCl_4 with C_6H_6 or $(Me_3Si)_2O$ as internal references and on a Bruker WM-250 (250 MHz) spectrometer in C_6D_6. IR spectra were obtained in KBr pellet with an UR-20 spectrophotometer. Mass spectra (electron impact, 70 eV; chemical ionization, 100 eV) were determined on a M 80 B Hitachi chromato mass spectrometer.

S,S'-Dipropyl-S''-(1-trimethylsiloxy)-2,2,2-trichloroethyl tetrathiophosphate 3b: *Typical Procedure.* Compound 2b (7.9 g, 53.5 mmol) was slowly added dropwise with stirring at 20°C under a dry argon atmosphere to 1b (17.0 g, 53.4 mmol) and stirring was continued for 4 h at 20°C. The mixture was evaporated at reduced pressure (0.05 mm Hg) at 40°C for 1 h and gave crude 3b (23.6 g, 95%). Pure 3b (17.3 g, 69%) was isolated from the residue by means of thin layer distillation (see Table I–IV).

The product 3a was obtained similarly (reaction in toluene, see Table I).

S,S'-Diethyl-S"-bis(1-ethoxy)methyl tetrathiophosphate 5b; *Typical Procedure.* Compound 4b (5.2 g, 35.2 mmol) was added dropwise with stirring at 20°C to 1a (10.2 g, 35.2 mmol) and stirring was continued for 2 h at 20°C. The mixture was evaporated under vacuum (0.1 and 0.02 mm Hg) at 50°C for 2 h and gave crude 5b (9.8 g, 87%). Pure 5b (7.8 g, 69%) was isolated from the residue by means of thin layer distillation (see Table I–IV). The distillation of the volatile fractions resulted in 6 (3.8 g, 90%), b.p. 74–76°C, n_D^{20} 1.3749. (Reference 19: b.p. 75.7°C, n_D^{20} 1.3742).

The product 5a was obtained similarly.

S,S'-Di-i-butyl-S"-(1-diethylamino)methyl tetrathiophosphate 8b. *Typical Procedure.* The mixture of 1c (8.4 g, 24.3 mmol) and 7b (3.8 g, 24.0 mmol) was stirred at 90°C for 1 h. The mixture was evaporated at reduced pressure (0.1 and 0.07 mm Hg) at 40°C for 2 h and gave crude 8b (7.7 g, 86%). Pure 8b (4.2 g, 48%) was isolated from the residue by means of thin layer distillation (see Table I–IV). The distillation of the volatile fractions resulted in 9b (1.8 g, 51%), b.p. 126–128°C, n_D^{20} 1.4096. Mass spectrum (chemical ionization, 100 eV), m/e (I_{rel}, %): 147 $[M + 2H]^+$(16). (Reference 19: b.p. 126.8–127.1°C (738 mm Hg), n_D^{20} 1.4109).

The product 8a in crude form was obtained similarly and 9a (2.8 g, 57%) was also isolated from the volatile fractions, b.p. 116–118°C, n_D^{20} 1.4250. Mass spectrum (electron impact, 70 eV), m/e (I_{rel}, %): 117 $[M]^{+\cdot}$(10). (Reference 19: b.p. 121°C. (734 mm Hg), n_D^{20} 1.4244).

S,S'-Diethyl-S"-(1-ethylthio)methyl tetrathiophosphate 11. The mixture of 1a (6.0 g, 20.7 mmol) and 10 (2.8 g, 20.6 mmol) was stirred at 100°C for 1 h. Additional amounts of 10 (2.8 g) was added to the mixture, stirring was continued for 5 h at 140–160°C. The addition of 10 (2.8 g) was repeated (140–160°C, 7 h). The mixture was evaporated under vacuum (0.02 mm Hg) at 40°C for 2 h and gave crude 11 (3.7 g, 62%). Pure 11 (3.3 g, 55%) was isolated from the residue by means of thin layer distillation (its physical and spectral data are identical with those of 11 obtained in Reference 12, Table I). The distillation of the volatile fractions gave 12 (1.0 g, 36%), b.p. 128–130°C, n_D^{20} 1.4509. Mass spectrum (electron impact, 70 eV), m/e (I_{rel}, %): 134 $[M]^{+\cdot}$(50). (Reference 19: b.p. 130°C, n_D^{20} 1.4512).

The product 14 (reaction in toluene) was obtained similarly to the preparation of 8b.

Triethyl tetrathiophosphate 18. The mixture of 1a (8.4 g, 29.0 mmol) and 16 (3.5 g, 28.6 mmol) in 10 mL anhydrous toluene was stirred at 160°C for 6 h. Additional amounts of 16 (3.5 g) was added to the mixture and stirring was continued for 6 h at 150–170°C. The addition of 16 (3.5 g) was repeated (150–170°C, 6 h). The distillation of the mixture gave 18 (3.4 g, 48%), b.p. 113°C (0.02 mm Hg), n_D^{20} 1.6208. ^{31}P NMR spectrum (C_6H_6): δ 90.5 ppm. Mass spectrum (chemical ionization, 100 eV), m/e (I_{rel}, %): 331 $[M + H]^+$ (30). (Reference 20: b.p. 124–125°C (1.5 mm Hg), n_D^{20} 1.6201. ^{31}P NMR spectrum: δ 91.7 ppm).

Tripropyl tetrathiophosphate 20a. *Typical Procedure.* The mixture of 1b (8.0 g, 25.2 mmol) and 19a (2.0 g, 25.5 mmol) was stirred at 160°C for 5 h. The mixture was evaporated at reduced pressure (0.02 mm Hg) at 50°C for 2 h and gave crude 20a (5.1 g, 70%). Distillation of the residue gave pure 20a (1.9 g, 26%), b.p. 86–88°C (0.02 mm Hg), n_D^{20} 1.5882. ^{31}P NMR spectrum (C_6H_6): δ 92.2 ppm. Mass spectrum (electron impact, 70 eV), m/e (I_{rel}, %): 289 $[M]^{+\cdot}$(75). (Reference 20: b.p. 140–142°C (1.8–2 mm Hg), n_D^{20} 1.5885. ^{31}P NMR spectrum δ 92.5 ppm).

The product 20b (reaction in benzene) was obtained similarly.

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