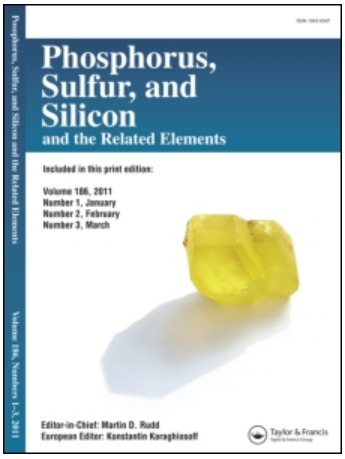

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REACTIONS OF 2,4-BIS(4-ALKOXYPHENYL)-2,4- DITHIOXO-1,3,2λ⁵,4λ⁵-DITHIADIPHOSPHETANES WITH DISULFIDES. NEW DATA ON REACTIONS WITH THIOACETALS AND ACETALS

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REACTIONS OF 2,4-BIS(4-ALKOXYPHENYL)-2,4-DITHIOXO-1,3,2λ^5,4λ^5-DITHIADIPHOSPHETANES WITH DISULFIDES. NEW DATA ON REACTIONS WITH THIOACETALS AND ACETALS

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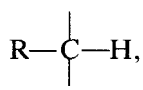
Lawesson's reagent reacts with dialkyl disulfides to form S,S-alkyl-S'-alkyl (4-methoxyphenyl) phosphonotrithiolothionoates with P—S—S—Alk bonds. The reactions of 2,4-bis(4-alkoxyphenyl)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetanes with thioacetals and acetals were reinvestigated and were shown to give trithio- and dithiophosphonates including an aldehyde fragment in their composition.

Key words: 2,4-Bis(4-alkoxyphenyl)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetanes, Lawesson's reagent, disulfides, thioacetals, acetals.

INTRODUCTION

2,4-Bis(4-alkyl or aryl substituted)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetanes, in particular the Lawesson's reagent, **LR**, are known to be very efficient thiation reagents for different substrates and for the synthesis of heterocyclic organothiophosphorus compounds.[1–4] Their reactions with alcohols, thiols, amines, oximes, esters, ortho esters, acetals, thioacetals, epoxides, and benzenesulfenyl chloride were also studied.[1,5–8] However the chemical behaviour of organic disulfides remained unknown in the reactions with Lawesson's reagent. Moreover the reactions of **LR** with acetals and thioacetals are reported to yield organothiophosphorus compounds with no aldehyde fragment,



in their composition.[7]

RESULTS AND DISCUSSIONS

Such an electrophile as benzenesulfenyl chloride is known to react with **LR** to give S,S-phenyl (4-methoxyphenyl) phosphonochloridodithiolothionoate,[8] in which the phenyl substituent is attracted to the phosphorus atom via the S—S bridge bond. We assumed that the reaction of **LR** with dialkyl disulfides should lead to thio-

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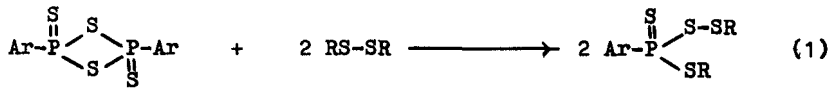
phosphonates with the S—S thiol bond as well. In fact we have found that **LR 1** reacts with dialkyl disulfides **2a,b** in anhydrous toluene at 120–130°C for 40–60 min to result in S,S-alkyl-S'-alkyl (4-methoxyphenyl) phosphonotrithiolothionoates **3a,b** (Equation 1).



(1)

1, Ar = 4-$MeOC_6H_4$ **2a**, R = Et **3a**, R = Et

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

The structures of the products **3a,b** have been established by IR (Table II), ^1H NMR (Table III), ^{31}P NMR spectroscopy and by mass spectral data and microanalyses (Table I). In the ^1H NMR spectrum of **3a** the $\underline{CH_3}CS$ protons appear as two triplets in the region of δ_1 1.17 ppm and δ_2 1.32 ppm with $^3J_{H\text{-}H}$ 7.2 Hz (6H), while the $C\underline{CH_2}SP$ protons appear as a multiplet in the region of 2.45–2.85 ppm (2H) and the $C\underline{CH_2}SS$ protons appear as a quartet at 2.85 ppm with $^3J_{H\text{-}H}$ 7.2 Hz (2H), the $\underline{CH_3}O$ protons appear as a singlet at 3.75 ppm (3H), the 3,5-$H_2C_6\underline{H_2}$ protons appear as double doublets at 6.83 ppm with $^3J_{H\text{-}H}$ 9.0 Hz, $^4J_{P\text{-}H}$ 4.5 Hz (2H), and the 2,6-$\underline{H_2}C_6H_2$ protons appear as double doublets at 7.85 ppm with $^3J_{H\text{-}H}$ 9.0 Hz, $^3J_{P\text{-}H}$ 15.0 Hz. The ^{31}P NMR spectrum of **3a** (neat) reveals a resonance at 85 ppm. The chemical ionization mass spectrum of **3a** shows a mass peak of the ion $[M + H]^+$ m/e 325.

The reaction of **LR** with thioacetals in xylene at 110°C or 140°C was reported[7] to result in dialkyl 4-methoxyphenylphosphonotrithioates, isolated by column chromatography. Their ^{31}P NMR spectra show signals at 77.3–77.4 ppm.[7,9] If we compare these data with the chemical shifts of **3** (δ_P 82.7 ppm of **3b** in CCl_4 and 85 ppm of **3a**), it can be observed that the presence of S—S bond in molecules of **3** displaces the chemical shifts to a lower field.

According to the data in Reference 7 the aldehyde fragment, R—$\underset{|}{\overset{|}{C}}$—H, was not included in the composition of organothiophosphorus compounds in the reaction of **LR** with thioacetals. In this connection it should be noted that we had previously carried out the interaction of thioacetals with tetraphosphorus trisulfide as thiophosphorylating agent and obtained the products with the 1-(alkylthio)alkylphosphonotrithioate structure which included the aldehyde fragments, R—$\underset{|}{\overset{|}{C}}$—H.[10,11] We assumed that dialkyl 4-methoxyphenylphosphonotrithioates[7] might be secondary products of decomposition under severe reaction conditions of some intermediates with an aldehyde fragment, R—$\underset{|}{\overset{|}{C}}$—H.

We decided to verify this idea and reinvestigated the reaction of **LR** with thioacetals. Indeed the reaction of **LR 1** and 2,4-bis-(4-ethoxyphenyl)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetane **4** with bis(ethylthio)methane **5a**, 1-phenyl-1,1-bis(ethylthio)methane **5b**, and 1-phenyl-1,1-bis(i-propylthio)methane **5c** at 90–140°C

TABLE I

Experimental, physical and analytical data of the products obtained

Initial cpd.	Prod.	Reaction conditions		Yield[a](%)	B.p.[b]	d_4^{20}	n_D^{20}	^{31}P NMR	Molecular	Analytical data Found/Calc. (%)				$M^{+\cdot}$ or $[M+H]^+$
		time (h)	temp.(°C)	crude/isolated	°C (mm Hg)			δ, ppm	Formula	C	H	P	S	Found/Calc.
1, 2a[f]	3a	1	120–130	56/40	150–160 (0.02)	1.2738	1.6659	85[g]	$C_{11}H_{17}OPS_4$	40.52	5.58	9.75	39.96	325
										40.74	5.30	9.56	39.47	325
1, 2b[f]	3b	2/3	120	46/30	170 (0.02)	1.1223	1.6209	82.7[h]	$C_{15}H_{25}OPS_4$	47.09	6.72	7.98	33.34	381
										47.36	6.64	8.15	33.44	381
1, 5a	6a[c]	3	140	66/58	175–200 (0.02)	1.2384	1.6441	76.4[h]	$C_{12}H_{19}OPS_4$	42.64	5.82	9.35	37.66	338
										42.60	5.68	9.16	37.83	338
1, 5b	6b[d]	4	70–80	91/66	150–175 (0.02)	1.1752	1.6207	75.6[h]	$C_{18}H_{23}OPS_4$	52.34	5.74	7.13	30.69	
								76.5[h]		52.17	5.61	7.48	30.88	
4, 5c	6c[d]	1	90–100	81/14[e]			1.6280	73.8[h]	$C_{21}H_{29}OPS_4$	55.88	6.77	7.03	27.47	
								74.6[h]		55.25	6.42	6.79	28.03	
1, 7	8a[d]	1	110	77/63	200 (0.02)	1.1577	1.5895	92.3[h]	$C_{18}H_{23}O_3PS_2$	57.21	6.31	8.58	16.62	
								94.5[h]		56.52	6.08	8.10	16.73	
4, 7	8b[d]	1	110	83/77	240–250 (0.02)	1.1571	1.5895	93[g]	$C_{19}H_{25}O_3PS_2$	57.82	6.35	7.38	15.69	
								95[g]		57.35	6.37	7.82	16.14	

[a]Yield of crude/isolated product (by distillation).
[b]Temperature of the spiral of the termal element of the thin layer distillation apparatus.
[c]According to our procedure.
[d]The mixture of diastereosiomers.
[e]Yield of chromatographed product, R_f 0.90.
[f]Solvent: toluene.
[g]Neat.
[h]In CCl_4.

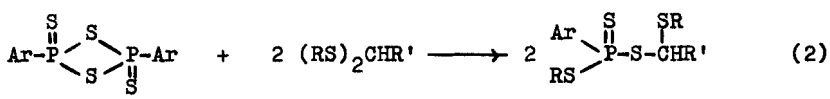
TABLE II

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	P=S[a]	PS_2[a]
3a	3070, 3010	2970, 2930, 2875, 2840	1590, 1497	696	535, 515
3b[b]	3075, 3010	2967, 2935, 2910, 2810, 2847	1594, 1500	698	540, 510
6a	3070, 3010	2972, 2930, 2875, 2842	1593, 1499	696	541, 512
6b	3090, 3067, 3030, 3010	2970, 2930, 2075, 2842	1590, 1498	699	539, 510
6c[b]	3068, 3035	2980, 2968, 2930, 2870	1596, 1498	705	540, 510
8a[a,c]	3090, 3070, 3038	2985, 2945, 2905, 2850	1598, 1502	710	535, 517
8b[a,c]	3090, 3070, 3040	2987, 2940, 2905, 2825	1598, 1505	710	540, 520

[a]Valence vibrations.
[b]Deformation vibrations δ 1388, 1370 cm^{-1} $(CH_3)_2C$ gem.
[c]γ 1030–1035 (PO-C), 959–960 cm^{-1} (OC-C).

during 1–3 h proceeds with the formation of alkyl(1-alkylthioalkyl) 4-alkoxyphenylphosphonotrithioates **6a–c** (Equation 2) (Tables I–III).



(2)

1, Ar=4-$MeOC_6H_4$ 5a, R=Et, R'=H 6a, Ar=4-$MeOC_6H_4$, R=Et R'=H

4, Ar=4-$EtOC_6H_4$ b, R=Et, R'=Ph b, Ar=4-$MeOC_6H_4$, R=Et R'=Ph

c, R=Pr-i, R'=Ph c, Ar=4-$EtOC_6H_4$, R=Pr-i R'=Ph

The ^1H NMR spectrum of **6a** contains a triplet at 1.23 ppm (3H, $\underline{CH_3}CSC$, $^3J_{H-H}$ 7.2 Hz), a triplet at 1.29 ppm (3H, $\underline{CH_3}CSP$, $^3J_{H-H}$ 7.2 Hz), a quartet at 2.58 ppm (2H, $C\underline{CH_2}SC$, $^3J_{H-H}$ 7.2 Hz), double quartets at 2.83 ppm (2H, $C\underline{CH_2}SP$, $^3J_{H-H}$ 7.2 Hz, $^3J_{P-H}$ 23.0 Hz), a singlet at 3.80 ppm (3H, $\underline{CH_3}OAr$), a doublet at 3.97 ppm (2H, $S\underline{CH_2}SP$, $^3J_{P-H}$ 10.0 Hz), double doublets at 6.85 ppm (2H, 3,5-$\underline{H_2}C_6H_2$, $^3J_{H-H}$ 9.0 Hz, $^4J_{P-H}$ 4.0 Hz), and double doublets at 7.87 ppm (2H, 2,6-$\underline{H_2}C_6\underline{H_2}$, $^3J_{H-H}$ 9.0 Hz, $^3J_{P-H}$ 15.0 Hz). There is one singlet at 76.4 ppm in the ^{31}P NMR spectrum of **6a** (in CCl_4). Electron impact mass spectrum of **6a** reveals a mass peak of molecular ion ($M^{+\cdot}$) m/e 338. As there are two asymmetrical centres (phosphorus atom and 1-carbon atom of the aldehyde fragment, R—C(H)—, in the molecules of **6b,c** the latters exist as a mixture of diastereosiomers (Table I and III).

TABLE III

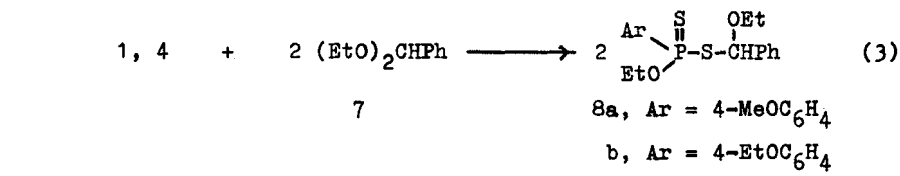
^{1}H NMR spectral data of the products obtained

Prod.	δ, ppm, J, Hz
3a	δ_1 1.17, δ_2 1.32 (two t, 6H, $\underline{CH_3}CS$, $^3J_{H-H}$ 7.2); 2.45-2.85 (m, 2H, $C\underline{CH_2}SP$); 2.85 (q, 2H, $C\underline{CH_2}SS$, $^3J_{H-H}$ 7.2); 3.75 (s, 3H, $\underline{CH_3}O$); 6.83 (d.d, 2H, 3,5-$H_2C_6\underline{H}_2$, $^3J_{H-H}$ 9.0, $^4J_{P-H}$ 4.5); 7.85 (d.d, 2H, 2,6-$\underline{H}_2C_6H_2$, $^3J_{H-H}$ 9.0, $^3J_{P-H}$ 15.0).
3b	δ_1 0.98, δ_2 1.00 (two d, 12H, $\underline{CH_3}CC$, $^3J_{H-H}$ 6.5); 1.50-2.17 (m, 2H, $\underline{CH}CS$); 2.52 (d, 2H, $\underline{CH_2}SS$, $^3J_{H-H}$ 6.5); 2.86 (dd, 2H, $\underline{CH_2}SP$, $^3J_{H-H}$ 6.5, $^3J_{P-H}$ 14.0); 3.79 (s, 3H, $\underline{CH_3}O$); 6.84 (dd, 2H, 3,5-$H_2C_6\underline{H}_2$, $^3J_{H-H}$ 9.0, $^4J_{P-H}$ 3.0); 7.87 (dd, 2H, 2,6-$\underline{H}_2C_6H_2$, $^3J_{H-H}$ 9.0, $^3J_{P-H}$ 14.0).
6a	1.23 (t, 3H, $\underline{CH_3}CSC$, $^3J_{H-H}$ 7.2); 1.29 (t, 3H, $\underline{CH_3}CSP$, $^3J_{H-H}$ 7.2); 2.58 (q, 2H, $C\underline{CH_2}SC$, $^3J_{H-H}$ 7.2); 2.83 (dq, 2H, $C\underline{CH_2}SP$, $^3J_{H-H}$ 7.2, $^3J_{P-H}$ 23); 3.80 (s, 3H, $\underline{CH_3}OC_6H_4$); 3.97 (d, 2H, $S\underline{CH_2}SP$, $^3J_{P-H}$ 10.0); 6.85 (dd, 2H, 3,5-$H_2C_6\underline{H}_2$, $^3J_{H-H}$ 9.0, $^3J_{P-H}$ 15.0).
6b+	1.04-1.46 (m, 6H, $\underline{CH_3}CS$); 2.30-3.17 (m, 2H, $\underline{CH_2}SP$); 2.47 (q, 2H, $\underline{CH_2}SC$, $^3J_{H-H}$ 7.2); δ_1 3.65, δ_2 3.75 (two s, 3H, $\underline{CH_3}O$); δ_1 5.27, δ_2 5.48 (d, 1H, $\underline{CH}SP$, $^3J_{P-H}$ 10.0); 6.63-6.93 (m, 2H, 3,5-$H_2C_6\underline{H}_2$); 6.98-7.46 (m, 5H, $C_6\underline{H}_5$); 7.55 8.05 (m, 2H, 2,6-$\underline{H}_2C_6H_2$).
6c+	0.98-1.49 (m, 15H, $\underline{CH_3}C$); 2.55-3.31 (m, 2H, $C\underline{CH}SC$, $C\underline{CH}SP$); 3.65-4.08 (m, 2H, $\underline{CH_2}O$); δ_1 5.32 (d, 1H, $Ar\underline{CH}SP$, $^3J_{P-H}$ 10.0); δ_2 5.48 (d, 1H, $Ar\underline{CH}SP$, $^3J_{P-H}$ 11.0); 6.60-6.88 (m, 2H, 3,5-$H_2C_6\underline{H}_2$); 6.94-7.48 (m, 5H, $C_6\underline{H}_5$); 7.57-7.99 (m, 2H, 2,6-$\underline{H}_2C_6H_2$).
8a+	0.93-1.42 (m, 6H, $\underline{CH_3}CO$); 3.17-4.25 (m, 4H, $\underline{CH_2}OP$, $\underline{CH_2}OCS$); δ_1 3.66, δ_2 3.70 (two s, 3H, $\underline{CH_3}O$); δ_1 5.98, δ_2 6.06 (two d, 1H, $\underline{CH}SP$, $^3J_{P-H}$ 11.0); δ_1 6.73, δ_2 6.76 (two dd, 2H, 3,5-$H_2C_6\underline{H}_2$, $^3J_{H-H}$ 9.0, $^4J_{P-H}$ 4.0); 6.97-7.35 (m, 5H, $C_6\underline{H}_5$); δ_1 7.65, δ_2 7.77 (two dd, 2H, 2,6-$\underline{H}_2C_6H_2$, $^3J_{H-H}$ 9.0, $^3J_{P-H}$ 15.0).
8b+	1.05-1.43 (m, 9H, $\underline{CH_3}$); 3.27-4.19 (m, 6H, 2,6-$\underline{H_2}C_6\underset{\underline{H_2}}{}OCH_2$, $\underline{CH_2}OP$, $\underline{CH_2}OCS$); δ_1 6.05, δ_2 6.09 (two d, 1H, $\underline{CH}SP$, $^3J_{P-H}$ 11.0); δ_1 6.78, δ_2 6.83 (two dd, 2H, 3,5-$H_2C_6\underline{H}_2$, $^3J_{H-H}$ 9.0, $^4J_{P-H}$ 4.0); 7.15-7.43 (m, 5H, $C_6\underline{H}_5$); δ_1 7.78, δ_2 7.82 (two dd, 2H, 2,6-$\underline{H}_2C_6H_2$, $^3J_{H-H}$ 9.0, $^3J_{P-H}$ 15.0).

+The mixture of diastereoisomers.

Thus the products **6a–c** include the aldehyde fragments, R—C(H)—, in their composition. It should be noted that we had performed these reactions (Equation 2) in the absence of a solvent. In order to avoid the decomposition of products **6** we isolated **6a,b** by thin layer distillation, and **6c** by column chromatography. To corroborate our findings we repeated the reaction of **LR** with bis(ethylthio)methane **5a** under the same conditions as described in the literature[7] (anhydrous xylene, 140°C, 3 h, column chromatography, see Experimental). Nevertheless the removal of the precipitate, the solvent, and the volatile materials resulted in the crude product **6a**, which in all respects (spectral and physical data) was identical to the product **6a** obtained according to our procedure. It should also be noted that the product **6a** was purified by column chromatography as well. Its physical constants were also identical to those of the **6a** isolated in accordance with our procedure.

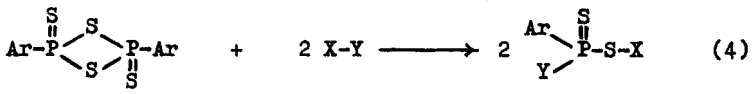
The reaction of equimolar amounts of **LR** with 1,1-diethoxymethylbenzene in anhydrous xylene at 140°C for 10 h was reported[7] to result in diethyl 4-methoxyphenylphosphonodithioate, O-ethyl S-ethyl di(4-methoxyphenyl)thiodiphosphonate, benzoic acid, ethyl thionobenzoate, and diethyl 4-methoxyphenylphosphonotrithioate. However there is no organothiophosphorus compound including the benzyl fragment, Ph—C(H)—, in its composition among these products. Obviously, these compounds are the products of decomposition of some initial products. In order to avoid the decomposition of initial organothiophosphorus products we decided to carry out the reaction of **LR 1** and dithiadiphosphetane **4** with 1,1-diethoxymethylbenzene **7** in accordance with our procedure (molar ratio 1: 2, absence of a solvent, a thin layer distillation apparatus). As expected this reaction resulted in the formation of O-ethyl S-(1-ethoxybenzyl) 4-alkoxyphenylphosphonodithioates **8a,b** (Equation 3, Tables I–III) under milder conditions (110°C, 0.5–1 h).



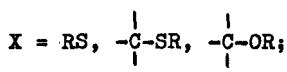
(3)

Similarly to the phosphonotrithioates **6b,c** the molecules of **8a,b** are also the mixtures of diastereosiomers. In the ^{1}H NMR spectrum of **8a** there are a multiplet at 3.17–4.25 ppm (4H, $\underline{CH_2}OP$, $\underline{CH_2}OCS$), two singlets at δ_1 3.66 ppm and δ_2 3.70 ppm (3H, $\underline{CH_3}O$), two doublets at δ_1 5.98 ppm (1H, $\underline{CH}SP$, $^3J_{P\text{-}H}$ 11.0 Hz) and δ_2 6.06 ppm (1H, $\underline{CH}SP$, $^3J_{P\text{-}H}$ 11.0 Hz), two double doublets at δ_1 6.73 ppm and δ_2 6.76 ppm (2H, 3,5-$H_2C_6\underline{H}_2$, $^3J_{H\text{-}H}$ 9.0 Hz, $^4J_{P\text{-}H}$ 4.0 Hz), a multiplet at 6.97–7.35 ppm (5H, $C_6\underline{H}_5$), two double doublets at δ_1 7.65 ppm and δ_2 7.77 ppm (2H, 2,6-$H_2C_6H_2$, $^3J_{H\text{-}H}$ 9.0 Hz, $^3J_{P\text{-}H}$ 15.0 Hz).

Thus a general scheme can be conceived on the basis of the results of the following reactions of 2,4-bis(4-alkoxyphenyl)-2,4-dithioxo-1,3,2λ^5, 4λ^5-dithiadiphosphetanes with disulfides, RS—SR, thioacetals, RS—C(H)—SR, acetals, RO—C(H)—OR (Equation 4).



(4)



It should be emphasized that formally organothiophosphorus compounds **3**, **6** and **8** are the products of the insertion of monomeric units of 1,3,2,4-dithiadiphosphetane 2,4-disulfides **1**, **4** into the X—Y bond.

EXPERIMENTAL

^{31}P NMR spectra were recorded with a Bruker WM 250 (101.3 MHz) in CCl_4, a Bruker MSL-400 (162 MHz) in CCl_4, and a non-serial NMR KGU-4 (10.2 MHz) spectrometers relative to external H_3PO_4 (85%). ^1H NMR spectra were run on a Varian T-60 (60 MHz) spectrometer in CCl_4 with Me_4Si as internal reference and on a Bruker WM 250 (250 MHz) spectrometer in CCL_4. 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-Ethyl-S'-ethyl (4-methoxyphenyl) phosphonotrithiolothionoate **3a**; *Typical Procedure.* The mixture of **1** (10.4 g, 25.7 mmol) and **2a** (6.3 g, 51.6 mmol) in 20 mL of anhydrous toluene was stirred at 120–130°C for 1 h. The mixture was filtered. The solvent was removed from the filtrate at reduced pressure (1 and 0.02 mm Hg) at 40–50°C for 2 h. Removal of the volatile materials from the residue gave crude **3a**. Thin layer distillation resulted in pure **3a** (physical, analytical and spectral data are listed in Tables I–III).

The product **3b** is obtained similarly.

Ethyl (1-ethylthiomethyl) 4-methoxyphenylphosphonotrithioate **6a**; *Typical Procedure.* The mixture of 1 (15.0 g, 37.1 mmol) and **5a** (10.2 g, 74.0 mmol) was stirred at 140°C for 3 h. The mixture was evaporated under vacuum (1 and 0.02 mm Hg) at 40–50°C for 2 h and gave crude **6a**. Pure **6a** was isolated from the residue by means of thin layer distillation (see Tables I–III).

The products **6b**, **8a** and **8b** are obtained similarly.

Preparation of **6a** *according to the literature.*[7] The mixture of **1** (7.5 g, 18.6 mmol) and **5a** (5.1 g, 37.0 mmol) in 10 mL anhydrous xylene was stirred at 140°C for 3 h. The precipitate was filtered. The solvent and the volatile materials were removed from the filtrate at reduced pressure (1 and 0.02 mm Hg) at 40°C for 2 h. The spectral and physical data of the residue were identical with **6a** obtained in accordance with our procedure. Part of the residue (3.0 g) was chromatographed on a silica gel column with 1:1 ether-petrol ether as an eluant and yielded pure **6a** (0.2 g), R_f 0.75, ^{31}P NMR spectrum δ 76.4 ppm. Mass spectrum (70 eV): m/e 338 ($M^{+\bullet}$), (100 eV) m/e 339 $[M + H]^+$. ^1H NMR and IR spectra are identical with those of **6a** obtained in accordance with our procedure.

i-Propyl (1-i-propylthiobenzyl) 4-methoxyphenyl phosphonotrithioate **6c.** The mixture of **4** (2.0 g, 8.3 mmol) and **5c** (2.2 g, 4.5 mmol) was stirred at 90–100°C for 1 h. The mixture was evaporated at reduced pressure (0.01 mm Hg) at 50–60°C for 1 h. The residue was refluxed twice in 25 mL anhydrous benzene for 1 h over absorbent carbon (1 g). The mixture was filtered. The solvent was removed under vacuum (0.02 mm Hg) at 40–50°C for 2.5 h and crude **6c** (3.4 g, 81%) was obtained. It was applied to silica gel column chromatography using 1:1 benzene-ether as an eluant and yielded **6c** (0.6 g, 14%) (see Tables I–III).

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