Syntheses of Alkylphosphonic Esters by the Reactions of Aliphatic Thiones with Trialkyl Phosphites

Tokuzo KAWASE, Shigeo YONEDA, and Zen-ichi YOSHIDA*

Department of Synthetic Chemistry, Kyoto University, Yoshida, Kyoto 606

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Aliphatic thiones were found to react with trialkyl phosphites to give (alkylthio)- and/or mercapto-alkylphosphonic esters. The reaction is interpreted in terms of the carbophilic attack with trialkyl phosphites at the carbon atom of the thiocarbonyl group, and the subsequent migration mechanism *via* the betaine intermediate.

Reactions of thiocarbonyl compounds with nucleophiles are different from those of carbonyl compounds.[1] For example, though Grignard reagents normally attack at the carbon atom of a carbonyl group (carbophilic attack), they may attack at the sulfur atom of a thiocarbonyl group (thiophilic attack) rather than at the carbon atom.[2] The reactions of thiocarbonyl compounds with phosphites have been the focus of interest in the past several years, because phosphites have both "carbophilicity" and "thiophilicity"[3] toward organosulfur compounds. When trivalent phosphorus compounds such as phosphines and phosphites are employed as nucleophiles, they have generally been regarded as thiophiles, not as carbophiles, in the previously reported works.[4] However, in our preceding papers,[5] it was elucidated that cycloalkanethiones react with trialkyl phosphites at the carbon atom of the thiocarbonyl group to give phosphonic esters.

In this work, we have carried out the reactions of aliphatic thiones with trialkyl phosphites and succeeded in the syntheses of sulfur-containing phosphonic esters. This reaction is also explained by the initial carbophilic attack of phosphites at the thiocarbonyl carbon atom to form the betaine intermediate.

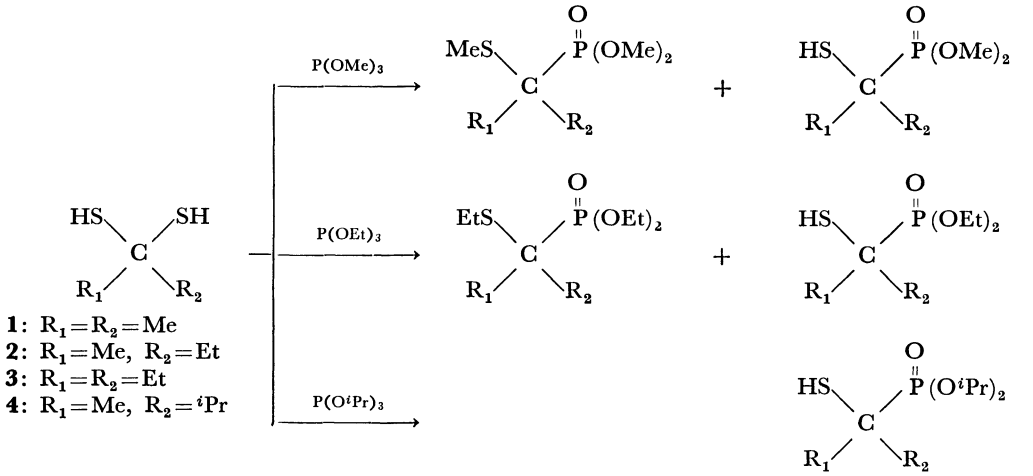
Results and Discussion

The syntheses of 1-(alkylthio)- and 1-mercaptocycloalkylphosphonic esters by the reactions of cycloalkanethiones with trialkyl phosphites were reported in our previous papers.[5] Similar reactions of aliphatic thioketones with trialkyl phosphites successfully yielded new sulfur containing alkylphosphonates.

In our preceding papers,[5] cycloalkanedithiols were utilized as precursors of cycloalkanethiones because of the instability of the latter. Cycloalkanethiones were easily generated from the corresponding dithiols at elevated temperatures. Similarly, the *gem*-dithiols[6] (**1**—**4**), as precursors of thioacetone, methyl ethyl thioketone, diethyl thioketone, and methyl isopropyl thioketone, were also employed in this study.

When a solution of propane-2,2-dithiol (**1**) and 4 equiv of trimethyl phosphite in toluene was heated under refluxing, hydrogen sulfide evolved vigorously and the reaction mixture became pink. The evolution of hydrogen sulfide and the pink coloration indicate the formation of thioacetone. After the complete decoloration, distillation gave a mixture of *O*,*O*-dimethyl 1-methyl-1-(methylthio)ethylphosphonate (**5a**) and *O*,*O*-dimethyl 1-mercapto-1-methylethylphosphonate (**6a**), which were separated by gas chromatography. The structures were determined by the elemental analyses and spectral data.

The reaction of **1** with triethyl phosphite also gave a mixture of *O*,*O*-diethyl 1-(ethylthio)-1-methylethylphosphonate (**5b**) and *O*,*O*-diethyl 1-mercapto-1-methylethylphosphonate (**6b**). The reaction of **1** with triisopropyl phosphite gave only *O*,*O*-diisopropyl 1-mercapto-1-methylethylphosphonate (**6c**), but no esters



1: $R_1=R_2=Me$
2: $R_1=Me$, $R_2=Et$
3: $R_1=R_2=Et$
4: $R_1=Me$, $R_2={}^iPr$

5: $R_1=R_2=Me$
7: $R_1=Me$, $R_2=Et$
9: $R_1=R_2=Et$
11: $R_1=Me$, $R_2={}^iPr$

6: $R_1=R_2=Me$
8: $R_1=Me$, $R_2=Et$
10: $R_1=R_2=Et$
12: $R_1=Me$, $R_2={}^iPr$

Scheme 1.

Table 1. Reaction conditions and yields of products in the reactions of aliphatic alkanedithiols with trialkyl phosphites

Substrates (Dithiols)	Reactants (Phosphites)	Reaction time/h	Products (Yield/%)	
			Alkylthio	Mercapto
Propane-2,2-dithiol (**1**)[a]	$P(OMe)_3$	20	23	23
	$P(OEt)_3$	20	25	17
	$P(O^iPr)_3$	20	0	62
Butane-2,2-dithiol (**2**)	$P(OMe)_3$	20	35	18
	$P(OEt)_3$	25	17	24
	$P(O^iPr)_3$	20	0	76
Pentane-3,3-dithiol (**3**)	$P(OMe)_3$	30	43	11
	$P(OEt)_3$	30	24	29
	$P(O^iPr)_3$	20	0	80
2-Methylbutane-3,3-dithiol (**4**)	$P(OMe)_3$	30	22	10
	$P(OEt)_3$	35	18	10
	$P(O^iPr)_3$	25	0	46

a) Hexamethyltrithiane was obtained in 30—40% yields.

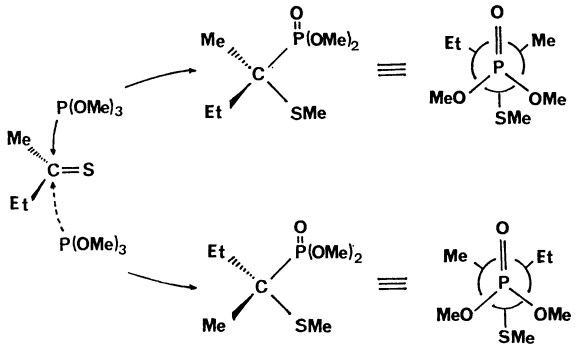


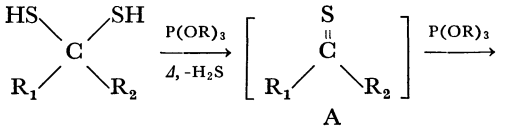
Fig. 1. Projection formulas of **7a** with respect to the C–P bond (staggered conformers).

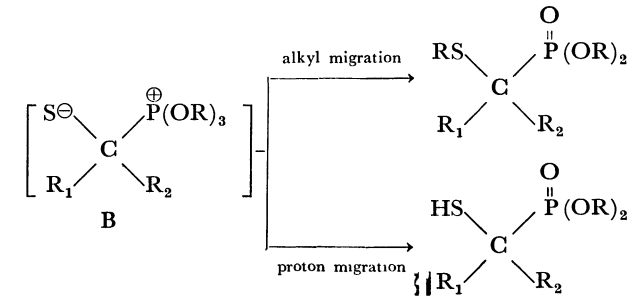
having an alkylthio group were obtained.

In these reactions, a side reaction (trimerization) also occurred to afford hexamethyltrithiane in 30—40% yield.

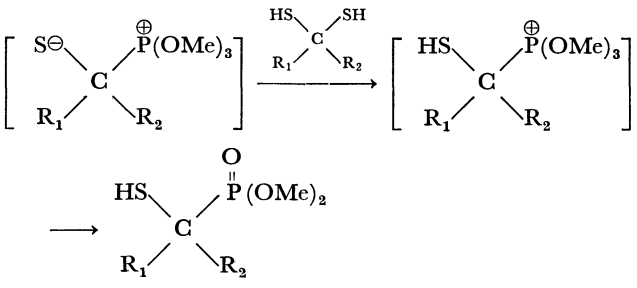
The reactions of butane-2,2-dithiol (**2**) with trialkyl phosphites were carried out under similar conditions. The reaction with trimethyl phosphite gave a mixture of *O,O*-dimethyl 1-methyl-1-(methylthio)propylphosphonate (**7a**) and *O,O*-dimethyl 1-mercapto-1-methylpropylphosphonate (**8a**). In the NMR spectrum of **7a**, the protons of the methyl group attached to the oxygen atom appeared as two doublets at δ 3.73 and 3.79 in the ratio 1 : 1 with $J_{P-H}=10.0$ Hz. As seen in Fig. 1, in the staggered conformer of the projection formulas of **7a** with respect to the C–P bond, the two methyl groups attached to the oxygen atoms are situated in different environments, which accounts for the appearance of two doublets in the NMR spectrum. In addition, the attacks of trimethyl phosphite at the thiocarbonyl group of methyl ethyl thioketone from the different sides of the molecular plane should also yield two isomers possessing different configurations (*R*- and *S*-) in the ratio 1 : 1. Such an indication could be obtained with the aid of chiral shift reagent [europium(III)-tris(3-trifluoroacetyl-1*R*-camphorate)], that is, the methyl protons attached to the oxygen atom appeared as two kinds of two doublets.[7]

The reactions of pentane-3,3-dithiol (**3**) and 2-methylbutane-3,3-dithiol (**4**) with trialkyl phosphites





Scheme 2.



Scheme 3.

were carried out under similar conditions.[8] The results are summarized in Scheme 1 and Table 1.

The mechanistic interpretation of the reactions of aliphatic thioketones with trialkyl phosphites is outlined in Scheme 2. The reaction is initiated by the removal of hydrogen sulfide from *gem*-dithiols to form the corresponding thioketones (A). The resulting thioketones might immediately react with excess trialkyl phosphites. The phosphites should attack at the carbon atom of thiocarbonyl group and from the betaine intermediate (B). From the intermediate B the migration of an alkyl group or proton would afford the phosphonic esters containing a sulfur atom in alkylthio and/or mercapto groups. When the phosphites are trimethyl and/or triethyl phosphites, the negatively charged sulfur

atom would intramolecularly attack the alkyl group attached to the oxygen atom; this would result in the formation of alkylthio phosphonic esters. When triisopropyl phosphite was used, this nucleophilic attack should be hindered, and so the proton migration would occur to afford the mercapto phosphonic esters.

However, even when the trimethyl phosphite was used, the mercapto phosphonic esters were obtained in fair yields; their formation can be explained by Scheme 3.

Experimental

The infrared spectra were recorded on a Hitachi EPI-G3 grating infrared spectrophotometer; the ^1H NMR spectra were recorded on a Varian Associates AH-100 spectrometer with TMS as an internal standard. Mass spectra were taken on a Hitachi RMU-6C mass spectrometer. Gas-liquid chromatography was carried out with a Shimadzu gas chromatograph Model GC-6A, using a stainless steel column packed with 20% silicon DC-550 on Celite 545, and the preparative VPC was carried out with a Varian Aerograph Model 920 using 20% Silicon DC-550. Elemental analyses were carried out at the Elemental Analytical Center of Kyoto University.

Materials. Propane-2,2-dithiol (**1**), butane-2,2-dithiol (**2**), pentane-3,3-dithiol (**3**), and 2-methylbutane-3,3-dithiol (**4**) were prepared from the ketimines and hydrogen sulfide according to the literature procedure by Magnusson,[6] and distilled under reduced pressure at temperatures below 70 °C. Trimethyl and triethyl phosphites were commercial matrials and were used after distillation. Triisopropyl phosphite was prepared utilizing the procedure of Ford-Moore.[9]

*General Procedure for the Reactions of Alkanedithiols (**1**—**4**) with Trialkyl Phosphites.* A mixture of 0.01 mol of alkanedithiol (**1**—**4**) and 0.04 mol of trialkyl phosphite in 30 ml of toluene was heated at reflux temperature under nitrogen for 20—30 h. When the temperature of the mixture exceeded 80 °C, gas evolution and pink coloration were observed. After removal of toluene and excess phosphite, the residue was distilled under reduced pressure to give a colorless viscous liquid. In the reactions with trimethyl and triethyl phosphites, the distillates were mixtures of the (alkylthio)- and mercapto-alkylphosphonates. They were separated by gas chromatography to determine the yields.

The boiling points, IR, ^1H NMR, and mass spectral data, and the results of elemental analyses are as follows.

O,O-*Dimethyl 1-Methyl-1-(methylthio)ethylphosphonate (**5a**)*: Bp 78—80 °C (14 Torr) as a mixture of **5a** and **6a**; 23% yield; IR (Neat) 1255 (P=O), 1180, 1060, 1030, 830, and 800 cm^{-1}. NMR (CCl_4) δ=1.49 (d, 6H, J_{P-H}=15.5 Hz, CH_3), 2.28 (s, 3H, SCH_3) and 3.80 (d, 6H, J_{P-H}=10.0 Hz, $POCH_3$); MS *m/e* 198 (M^+). Found: C, 36.53; H, 7.86; P, 15.66%. Calcd for $C_6H_{15}O_3PS$: C, 36.36; H, 7.63; P, 15.63%.

O,O-*Dimethyl 1-Mercapto-1-methylethylphosphonate (**6a**)*: 23% yield; IR (Neat) 2500 (SH), 1250 (P=O), 1180, 1060, 1025, 830, and 790 cm^{-1}. NMR (CCl_4) δ=1.59 (d, 6H, J_{P-H}=15.5 Hz, CH_3), 2.16 (d, 1H, J_{P-H}=4 Hz, SH) and 3.78 (d, 6H, J_{P-H}=10.0 Hz, $POCH_3$); MS *m/e* 184 (M^+). Found: C, 32.43; H, 7.07; P, 16.85%. Calcd for $C_5H_{13}O_3PS$: C, 32.60; H, 7.11; P, 16.82%.

O,O-*Diethyl 1-(Ethylthio)-1-methylethylphosphonate (**5b**)*: Bp 82—83 °C (9 Torr) as a mixture of **5b** and **6b**; 25% yield; IR (Neat) 1250 (P=O), 1060, 1030, and 963 cm^{-1}. NMR (CCl_4) δ=1.13 (t, 3H, J=7.5 Hz, $SCH_2C\underline{H}_3$), 1.25 (t, 6H, J_{H-H}=7.0 Hz, $POCH_2C\underline{H}_3$), 1.30 (d, 6H, J_{P-H}=15 Hz, CH_3), 2.78 (q, 2H, J=7.5 Hz, $SC\underline{H}_2CH_3$), and 4.03 (dq, 4H, J_{H-H}=7.0 Hz, J_{P-H}=8.0 Hz, $POC\underline{H}_2CH_3$); MS *m/e* 240 (M^+). Found: C, 44.65; H, 9.08; P, 12.69%. Calcd for $C_9H_{21}O_3PS$: C, 44.98; H, 8.81; P, 12.89%.

O,O-*Diethyl 1-Mercapto-1-methylethylphosphonate (**6b**)*: 17% yield; IR (Neat) 2503 (SH), 1245 (P=O), 1050, 1023, and 955 cm^{-1}. NMR (CCl_4) δ=1.26 (t, 6H, J_{H-H}=7.0 Hz, $POCH_2C\underline{H}_3$), 1.40 (d, 6H, J_{P-H}=15 Hz, CH_3), 2.16 (d, 1H, J_{P-H}=4 Hz, SH), and 4.05 (dq, 4H, J_{H-H}=7.0 Hz, J_{P-H}=8.5 Hz, $POC\underline{H}_2CH_3$); MS *m/e* 212 (M^+). Found: C, 39.67; H, 8.11; P, 14.41%. Calcd for $C_7H_{17}O_3PS$: C, 39.61; H, 8.07; P, 14.59%.

O,O-*Diisopropyl 1-Mercapto-1-methylethylphosphonate (**6c**)*: Bp 92—93 °C (11 Torr); 62% yield; IR (Neat) 2500 (SH), 1250 (P=O), 1005, and 985 cm^{-1}. NMR (CCl_4) δ=1.33 [d, 12H, J_{H-H}=6.5 Hz, $POCH(C\underline{H}_3)_2$], 1.45 (d, 6H, J_{P-H}=15 Hz, CH_3), 2.24 (d, 1H, J_{P-H}=4 Hz, SH), and 4.64 [dsep, 2H, J_{H-H}=6.5 Hz, J_{P-H}=8.5 Hz, $POC\underline{H}(CH_3)_2$]; MS *m/e* 240 (M^+). Found: C, 44.65; H, 9.13; P, 12.51%. Calcd for $C_9H_{21}O_3PS$: C, 44.98; H, 8.81; P, 12.89%.

O,O-*Dimethyl 1-Methyl-1-(methylthio)propylphosphonate (**7a**)*: Bp 98—99 °C (13 Torr) as a mixture of **7a** and **8a**; 35% yield; IR (Neat) 1249 (P=O), 1185, 1060, 1031, 823, and 780 cm^{-1}. NMR (CCl_4) δ=0.97 (t, 3H, J=7.1 Hz, $CH_2C\underline{H}_3$), 1.27 (d, 3H, J_{P-H}=15.5 Hz, CH_3), 1.58—1.97 (m, 2H, $C\underline{H}_2CH_3$), 2.19 (s, 3H, SCH_3), and 3.73 and 3.79 (two d, 6H, J_{P-H}=10.0 Hz, $POCH_3$); MS *m/e* 212 (M^+). Found: C, 39.58; H, 8.14; P, 14.49%. Calcd for $C_7H_{17}O_3PS$: C, 39.61; H, 8.07; P, 14.59%.

O,O-*Dimethyl 1-Mercapto-1-methylpropylphosphonate (**8a**)*: 18% yield; IR (Neat) 2520 (SH), 1252 (P=O), 1186, 1060, 1034, 830, and 782 cm^{-1}. NMR (CCl_4) δ=1.04 (t, 3H, J=7.5 Hz, $CH_2C\underline{H}_3$), 1.40 (d, 3H, J_{P-H}=15.0 Hz, CH_3), 1.61—2.01 (m, 2H, $C\underline{H}_2CH_3$), 2.07 (d, 1H, J_{P-H}=5 Hz, SH), and 3.76 and 3.80 (two d, 6H, J_{P-H}=10.5 Hz, $POCH_3$); MS *m/e* 198 (M^+). Found: C, 36.52; H, 7.42; P, 15.28%. Calcd for $C_6H_{15}O_3PS$: C, 36.36; H, 7.63; P, 15.63%.

O,O-*Diethyl 1-(Ethylthio)-1-methylpropylphosphonate (**7b**)*: Bp 98—103 °C (5.5 Torr) as a mixture of **7b** and **8b**; 17% yield; IR (Neat) 1245 (P=O), 1058, 1030, and 960 cm^{-1}. NMR (CCl_4) δ=0.98 (t, 3H, J=7.0 Hz, $CH_2C\underline{H}_3$), 1.20 (t, 3H, J=7.5 Hz, $SCH_2C\underline{H}_3$), 1.28 (d, 3H, J_{P-H}=15 Hz, CH_3), 1.32 and 1.33 (two t, 6H, J_{H-H}=7.0 Hz, $POCH_2C\underline{H}_3$), 1.61—1.97 (m, 2H, $C\underline{H}_2CH_3$), 2.73 and 2.83 (two q, 2H, J=7.5 Hz, $SC\underline{H}_2CH_3$), and 4.08 and 4.13 (two dq, 4H, J_{H-H}=7.0 Hz, J_{P-H}=8.0 Hz, $POC\underline{H}_2CH_3$); MS *m/e* 254 (M^+). Found: C, 47.10; H, 9.23; P, 12.25%. Calcd for $C_{10}H_{23}O_3PS$: C, 47.23; H, 9.12; P, 12.18%.

O,O-*Diethyl 1-Mercapto-1-methylpropylphosphonate (**8b**)*: 24% yield; IR (Neat) 2510 (SH), 1250 (P=O), 1055, 1030, and 963 cm^{-1}. NMR (CCl_4) δ=1.06 (t, 3H, J=7.0 Hz, $CH_2C\underline{H}_3$), 1.34 (t, 6H, J_{H-H}=7.0 Hz, $POCH_2C\underline{H}_3$), 1.40 (d, 3H, J_{P-H}=15.5 Hz, CH_3), 1.60—1.93 (m, 2H, $C\underline{H}_2CH_3$), 2.04 (d, 1H, J_{P-H}=6 Hz, SH), 4.12 and 4.15 (two dq, 4H, J_{H-H}=7.0 Hz, J_{P-H}=8.0 Hz, $POC\underline{H}_2CH_3$); MS *m/e* 226 (M^+). Found: C, 42.62; H, 8.64; P, 13.47%. Calcd for $C_8H_{19}O_3PS$: C, 42.46; H, 8.46; P, 13.69%.

O,O-*Diisopropyl 1-Mercapto-1-methylpropylphosphonate (**8c**)*: Bp 100—101 °C (6.7 Torr); 76% yield; IR (Neat) 2505 (SH), 1246 (P=O), 1108, 1005, and 980 cm^{-1}. NMR (CCl_4) δ=1.04 (t, 3H, J=7.0 Hz, $CH_2C\underline{H}_3$), 1.32 [d, 12H, J_{H-H}=6 Hz, $POCH(C\underline{H}_3)_2$], 1.40 (d, 3H, J_{P-H}=13.0 Hz, CH_3), 1.54—1.97 (m, 2H, $C\underline{H}_2CH_3$), 2.07 (d, 1H, J_{P-H}=6 Hz, SH), and 4.35—4.96 [m, 2H, $POCH(CH_3)_2$]; MS *m/e* 254 (M^+). Found: C, 47.31; H, 9.36; P, 11.92%. Calcd for $C_{10}H_{23}O_3PS$: C, 47.23; H, 9.12; P, 12.18%.

O,O-*Dimethyl 1-Ethyl-1-(methylthio)propylphosphonate (**9a**)*;

Bp 111—112 °C (6.5 Torr) as a mixture of **9a** and **10a**; 43% yield; IR (Neat) 1246 (P=O), 1182, 1060, 1031, 824, and 770 cm^{-1}. NMR (CCl_4) δ=0.95 (t, 6H, J=7.1 Hz, $CH_2C\underline{H}_3$), 1.54—1.97 (m, 4H, $C\underline{H}_2CH_3$), 2.18 (s, 3H, SCH_3), and 3.76 (d, 6H, J_{P-H}=10.2 Hz, $POCH_3$); MS *m/e* 226 (M^+). Found: C, 42.37; H, 8.62; P, 13.90%. Calcd for $C_8H_{19}O_3PS$: C, 42.46; H, 8.46; P, 13.69%.

O,O-*Dimethyl 1-Ethyl-1-mercaptopropylphosphonate (**10a**)*: 11% yield; IR (Neat) 2500 (SH), 1245 (P=O), 1060, 1030, 820, and 770 cm^{-1}. NMR (CCl_4) δ=1.00 (t, 6H, J=6.5 Hz, $CH_2C\underline{H}_3$), 1.73 and 1.87 (dq, 4H, J_{H-H}=6.5 Hz, J_{P-H}=13.5 Hz, $C\underline{H}_2CH_3$), 2.03 (d, 1H, J_{P-H}=6 Hz, SH), and 3.77 (d, 6H, J_{P-H}=10.1 Hz, $POCH_3$); MS *m/e* 212 (M^+). Found: C, 39.51; H, 8.00; P, 14.79%. Calcd for $C_7H_{17}O_3PS$: C, 39.61; H, 8.07; P, 14.59%.

O,O-*Diethyl 1-Ethyl-1-(ethylthio)propylphosphonate (**9b**)*: Bp 123—124 °C (6.7 Torr) as a mixture of **9b** and **10b**; 24% yield; IR (Neat) 1250 (P=O), 1060, 1032, and 960 cm^{-1}. NMR (CCl_4) δ 0.98 (t, 6H, J=7.0 Hz, $CH_2C\underline{H}_3$), 1.21 (t, 3H, J=7.5 Hz, $SCH_2C\underline{H}_3$), 1.33 (t, 6H, J_{H-H}=7.0 Hz, $POCH_2C\underline{H}_3$), 1.73 and 1.88 (dq, 4H, J_{H-H}=7.0 Hz, J_{P-H}=14 Hz, $C\underline{H}_2CH_3$), 2.78 (q, 2H, J=7.0 Hz, $SC\underline{H}_2CH_3$), 4.05 (dq, 4H, J_{H-H}=7.0 Hz, J_{P-H}=8.1 Hz, $POC\underline{H}_2CH_3$); MS *m/e* 268 (M^+). Found: C, 46.24; H, 8.97; P, 10.71%. Calcd for $C_{11}H_{25}O_3PS$: C, 46.16; H, 8.80; P, 10.82%.

O,O-*Diethyl 1-Ethyl-1-mercaptopropylphosphonate (**10b**)*: 29% yield; IR (Neat) 2500 (SH), 1245 (P=O), 1060, 1025, and 965 cm^{-1}. NMR (CCl_4) δ=1.01 (t, 6H, J=7.0 Hz, $CH_2C\underline{H}_3$), 1.32 (t, 6H, J_{H-H}=7.0 Hz, $POCH_2C\underline{H}_3$), 1.74 and 1.87 (dq, 4H, J_{H-H}=7.0 Hz, J_{P-H}=13.5 Hz, $C\underline{H}_2CH_3$), 2.10 (d, 1H, J_{P-H}=5.5 Hz, SH), and 4.03 (dq, 4H, J_{H-H}=7.0 Hz, J_{P-H}=8.0 Hz, $POC\underline{H}_2CH_3$); MS *m/e* 240 (M^+). Found: C, 45.11; H, 8.90; P, 12.67%. Calcd for $C_9H_{21}O_3PS$: C, 44.98; H, 8.81; P, 12.89%.

O,O-*Diisopropyl 1-Ethyl-1-mercaptopropylphosphonate (**10c**)*: Bp 120—121 °C (5.5 Torr); 80% yield; IR (Neat) 2502 (SH), 1243 (P=O), 1108, 1004, and 980 cm^{-1}. NMR (CCl_4) δ=1.00 (t, 6H, J=7.0 Hz, $CH_2C\underline{H}_3$), 1.32 [d, 12H, J_{H-H}=6.1 Hz, $POCH(C\underline{H}_3)_2$], 1.71 and 1.84 (dq, 4H, J_{H-H}=7 Hz, J_{P-H}=13.4 Hz, $C\underline{H}_2CH_3$), 2.05 (d, 1H, J_{P-H}=6 Hz, SH), and 4.63 [dsep, 2H, J_{H-H}=6.1 Hz, J_{P-H}=7.2 Hz, $POC\underline{H}(CH_3)_2$]; MS *m/e* 268 (M^+). Found: C, 46.29; H, 9.01; P, 10.57%. Calcd for $C_{11}H_{25}O_3PS$: C, 46.14; H, 8.80; P, 10.82%.

O,O-*Dimethyl 1,2-Dimethyl-1-(methylthio)propylphosphonate (**11a**)*: Bp 101—104 °C (7.8 Torr) as a mixture of **11a** and **12a**; 22% yield; IR (Neat) 1250 (P=O), 1178, 1060, and 1030 cm^{-1}. NMR (CCl_4) δ=1.04 [d, 6H, J=6.5 Hz, $(C\underline{H}_3)_2CH$], 1.23 (d, 3H, J_{P-H}=15.5 Hz, CH_3), 1.75—2.45 [m, 1H, $(CH_3)_2C\underline{H}$], 2.19 and 2.20 (two s, 3H, SCH_3), 3.73 and 3.79 (two d, 6H, J_{P-H}=10.0 Hz, $POCH_3$); MS *m/e* 226 (M^+). Found: C, 42.26; H, 8.66; P, 13.58%. Calcd for $C_8H_{19}O_3PS$: C, 42.46; H, 8.46; P, 13.69%.

O,O-*Dimethyl 1-Mercapto-1,2-dimethylpropylphosphonate (**12a**)*: 10% yield; IR (Neat) 2500 (SH), 1248 (P=O), 1180, 1060, and 1028 cm^{-1}. NMR (CCl_4) δ=1.03 and 1.13 [two d, 6H, J=6.5 Hz, $(C\underline{H}_3)_2CH$], 1.41 and 1.43 (two d, 3H, J_{P-H}=15.5 Hz, CH_3), 1.7—2.4 [m, 1H, $(CH_3)_2C\underline{H}$], 2.04 (d, 1H, J_{P-H}=7 Hz, SH), 3.77 and 3.85 (two d, 6H, J_{P-H}=10.1 Hz, $POCH_3$); MS *m/e* 212 (M^+). Found: C, 39.45; H, 8.17; P, 14.55%. Calcd for $C_7H_{17}O_3PS$: C, 39.61; H, 8.07; P, 14.59%.

O,O-*Diethyl 1,2-Dimethyl-1-(ethylthio)propylphosphonate (**11b**)*: Bp 98—101 °C (6.2 Torr) as a mixture of **11b** and **12b**; 18% yield; IR (Neat) 1250 (P=O), 1055, and 1030 cm^{-1}. NMR (CCl_4) δ=1.00 and 1.10 [two d, 6H, J=6.5 Hz, $(C\underline{H}_3)_2CH$], 1.21 (t, 3H, J=7.5 Hz, $SCH_2C\underline{H}_3$), 1.32 and 1.34 (two t, 6H, J_{H-H}=7.0 Hz, $POCH_2C\underline{H}_3$), 1.33 and 1.35 (two d, 3H, J_{P-H}=15.5 Hz, CH_3), 1.8—2.4 [m, 1H, $(CH_3)_2C\underline{H}$], 2.79 and 2.88 (two q, 2H, J=7.5 Hz, $SC\underline{H}_2CH_3$), 4.07 and 4.11 (two dq, 4H, J_{H-H}=7.0 Hz, J_{P-H}=8.1 Hz, $POC\underline{H}_2CH_3$); MS *m/e* 268 (M^+). Found: C, 46.22; H, 8.96; P, 10.67%. Calcd for $C_{11}H_{25}O_3PS$: C, 46.14; H, 8.80; P, 10.82%.

O,O-*Diethyl 1-Mercapto-1,2-dimethylpropylphosphonate (**12b**)*: 10% yield; IR (Neat) 2510 (SH), 1250 (P=O), 1058, and 1030 cm^{-1}. NMR (CCl_4) δ=1.04 and 1.15 [two d, 6H, J=6.5 Hz, $(C\underline{H}_3)_2CH$], 1.30 and 1.31 (two t, 6H, J_{H-H}=7.0 Hz, $POCH_2C\underline{H}_3$), 1.35 and 1.38 (two d, 3H, J_{P-H}=15.5 Hz, CH_3), 1.7—2.4 [m, 1H, $(CH_3)_2C\underline{H}$], 2.05 (two d, 1H, J_{P-H}=6.5 Hz, SH), 4.01 and 4.05 (two dq, 4H, J_{H-H}=7.0 Hz, J_{P-H}=8.0 Hz, $POC\underline{H}_2CH_3$); MS *m/e* 240 (M^+). Found: C, 44.73; H, 9.01; P, 12.79%. Calcd for $C_9H_{21}O_3PS$: C, 44.98; H, 8.81; P, 12.89%.

O,O-*Diisopropyl 1-Mercapto-1,2-dimethylpropylphosphonate (**12c**)*: Bp 105—106 °C (6 Torr); 46% yield; IR (Neat) 2505 (SH), 1243 (P=O), 1003, and 980 cm^{-1}. NMR (CCl_4) δ=0.99 and 1.08 [two d, 6H, J=6.5 Hz, $(C\underline{H}_3)_2CH$], 1.30 and 1.33 [two d, 12H, J_{H-H}=6.3 Hz, $POCH(C\underline{H}_3)_2$], 1.37 and 1.38 (two d, 3H, J_{P-H}=15.5 Hz, CH_3), 1.7—2.4 [m, 1H, $(CH_3)_2C\underline{H}$], 2.06 (two d, J_{P-H}=7 Hz, SH), and 4.44—5.04 [m, 2H, $POC\underline{H}(CH_3)_2$]; MS *m/e* 268 (M^+). Found: C, 45.98; H, 9.01; P, 10.88%. Calcd for $C_{11}H_{25}O_3PS$: C, 46.14; H, 8.80; P, 10.82%.

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7) A similar feature (appearance of two kinds of signals in the ratio 1:1) was also observed in the NMR spectra of reaction products of **2** with triethyl and triisopropyl phosphites.

8) In the NMR spectra of **11** and **12**, similar to **7** and/or **8**, two kinds of signals, assigned to the alkyl protons attached to the oxygen atom, were observed.

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