ESTERS OF TERVALENT PHOSPHORUS THIO ACIDS COMMUNICATION 8. 0,0-DIALKYL S-PHENYL PHOSPHOROTHIOITES

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This paper is concerned with the synthesis of O,O-dialkyl S-phenyl phosphorothioites and a study of some of their properties. Michaelis [1] first attempted to prepare compounds of this type [1]. With this object he studied the reactions of phenyl phosphorodichloridothioite with alcohols in absence of a base and in presence of sodium alkoxides, but in neither way was he able to prepare O,O-dialkyl S-phenyl phosphorothioites.

We have found that O,O-dialkyl S-phenyl phosphorothioites can be prepared by the reactions of phenyl phosphorodichloridothioite with alcohols in presence of triethylamine (method A):

 $C_6H_5SPCl_2 + 2ROH + 2(C_2H_5)_3N \rightarrow C_6H_5SP(OR)_2 + 2(C_2H_5)_3N \cdot HCl$

These phosphorothious esters can also be prepared by the reactions of dialkyl phosphorochloridites with benzenethicl in presence of triethylamine (method B) or by their reactions with sodium benzenethiolate (method C):

 $(\text{RO})_2\text{PCl} + \text{C}_6\text{H}_5\text{SH} + (\text{C}_2\text{H}_5)_3\text{N} \rightarrow (\text{RO})_2\text{PSC}_6\text{H}_5 + (\text{C}_2\text{H}_5)_3\text{N} \cdot \text{HCl}$ $(\text{RO})_2\text{PCl} + \text{C}_6\text{H}_5\text{SNa} \rightarrow (\text{RO})_2\text{PSC}_6\text{H}_5 + \text{NaCl}$

The constants of the O,O-dialkyl S-phenyl phosphorothioites synthesized are given in Table 1. The compounds obtained are colorless liquids with a characteristic unpleasant smell, oxidized relatively slowly by atmospheric oxygen. The structure which we propose for the compounds synthesized is in accord with their vibrational spectra (Fig. 1). Absorption associated with the vibrations of the P-S bond is usually found in the region 510-575 cm⁻¹ [2]. However, these data refer to quinquevalent phosphorus compounds. A detailed investigation of the IR spectra of phosphorus dithio acids has shown that P-S vibrations are responsible for the appearance of two absorption bands in the ranges 478-523 and 510-540 cm⁻¹ [3]. Two absorption bands in the ranges 472-489 and 553-564 cm⁻¹ observed in the IR spectra of trialkyl phosphorotrithioites have also been assigned to P-S vibrations [4]. The IR spectra of the O,O-dialkyl S-phenyl phosphorothioites studied by us also contain analogous absorption in this region. With the object of clarifying the assignment of the vibrations we determined the Raman spectrum of O.O-dimethyl S-phenyl phosphorothioite. We supposed that ν_{P-S} vibrations would show up more distinctly in the Raman spectrum because of the considerable change in polarizability in the vibration of the atoms forming this bond. In the spectrum we did in fact observe a line at 520 cm⁻¹, coincident in frequency with a band in the IR spectrum. As a result of the interaction of the benzene ring with the sulfur atom the $\nu_{C=C}$ band of phenyl is observed at 1580 cm⁻¹, which is in accord with data in [5]. The monosubstituted benzene ring leads to the appearance of bands at 700 and 750 cm^{-1} in the spectrum (out-of-plane deformation vibrations). Very strong absorption at 1030 cm⁻¹ may be

	q	20				Found, %			Calculated		
R	Metho	Yield,	bp, °C (p, mm)	$n^{20}D$	d_4^{20}	MR.	P, %	s, %	МВ	P, %	s, %
CH ₃ C ₂ H ₅ <i>n</i> -C ₃ H ₇ <i>i</i> -C ₃ H ₇ <i>n</i> -C ₄ H ₉	A B C A A A	68,7 73,5 70,5 57,2 58,1 78,0	$ \begin{vmatrix} 76-77 & (0,04) \\ 84-84,5 & (0,04) \\ 83-84 & (0,04) \\ 91-92 & (0,04) \\ 81-82 & (0,04) \\ 103-104 & (0,04) \end{vmatrix} $	1,5723 1,5498 1,5490 1,5370 1,5292 1,5289	1,1654 1,1027 1,0986 1,0633 1,0517 1,0349	57,12 36,50 36,67 75,87 75,78 35,33	15,33 13,39 11,89 11,90 10,97	16,08 13,65 12,40 12,10 11,20	55,86 65,10 65,10 74,33 74,33 83,57	15,32 13,45 11,99 11,99 10,75	15,86 13,92 12,41 12,41 11,20

TABLE 1. $(RO)_2 PSC_6 H_5$

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Fig. 2. IR spectra: 1) O, O-dimethyl S-phenyl phosphorothioate; 2) O,O-dimethyl S-phenyl phosphorodithioate; 3) O-methyl S-phenyl methylphosphonothioate.

associated with the P-O-C group [6]. The IR spectra of O,O-dialkyl S-phenyl phosphorothioites also contain bands characteristic for the stretching and deformation vibrations of AlkO-groups. Confirmation of the purity of the O,O-dialkyl S-phenyl phosphorothioites is provided by the absence of appreciable IR absorption at about 1250 cm⁻¹, characteristic for P = O. O,O-Dialkyl S-phenyl phosphorothioites are oxidized by nitrogen dioxide into the corresponding phosphorothioates.

Comparison of the IR spectra of O,O-dialkyl S-phenyl phosphorothioates and the corresponding phosphorothioites (Figs. 1 and 2, curve 1) shows that the spectra of the former contain additional strong absorption in the range 1255-1265 cm⁻¹ belonging to P = O. Also, in these spectra both P-S bands suffer appreciable shifts toward higher frequencies (565-573 and 600-605 cm⁻¹).

The addition of sulfur to O,O-dialkyl S-phenyl phosphorothioites goes exothermically, but it is necessary to heat the reaction mixture to 40-50° to initiate reaction. In the IR spectra of O,O-dialkyl S-phenyl phosphorodithioates (Fig. 2, curve 2) absorption at about 650 cm⁻¹ can be definitely associated with the P = S group [4]. The constants of the O,O-dialkyl S-phenyl phosphorothioates and phosphorodithioates obtained are given in Table 2.

In view of the fact that the reactivities of esters of tervalent phosphorus thio acids depend both on the structure of the ester and on the nature of the electrophilic reagent [7-10], we studied the reactions of the O,O-dialkyl S-phenyl phosphorothioites synthesized with alkyl and acyl halides. The reactions with alkyl halides go mainly in accordance with the Arbuzov-rearrangement scheme with formation of O-alkyl S-phenyl alkylphosphonothioates:

$$C_{6}H_{5}SP(OR)_{2} + R'X \rightarrow \begin{bmatrix} R' \\ \downarrow \\ C_{6}H_{5}S - P & (OR)_{2} \end{bmatrix}^{+} X^{-} \rightarrow R' - P + RX$$

The IR spectra of the compounds obtained contain the following characteristic absorption bands (cm⁻¹): 1230-1240 (P = O); 1030-1040 (P-O-C); 482-487 and 530-535 (P-S-C), 1580-1585 (Ph) (Fig. 2, curve 3).

TABLE 2. $(RO)_2 PSC_6 H_5$

		А							
R		Yield, %	bp, °C (p, mm)		d,20	Found		Calculated	
	x			$n^{20}D$		MR	P, %	MR	P, %
$\begin{array}{c} CH_{3} \\ i - C_{3}H_{7} * \\ n - C_{4}H_{9} \dagger \\ CH_{3} \ddagger \\ n - C_{3}H_{7} \\ i - C_{3}H_{7} \end{array}$	0 0 0 5 5 5	80,4 83,8 81,1 83,5 84,0 85,0	93-94 (0,046) 94-95 (0,04) 127-128 (0,04) 93-94 (0,04) 115-116 (0,04) 106-107 (0,04)	1,5450 1,5098 1,5106 1,5911 1,5532 1,5440	1,2586 1,1144 1,0925 1,2529 1,1330 1,1188	54,82 73,60 82,86 63,20 82,04 81,94	14,27 11,15 10,67 12,97 10,48 10,75	54,73 73,20 82,44 62,22 80,69 80,69	14,19 11,29 10,24 13,22 10,66 10,66

* Found: S 11.68%. Calculated: S 11.69%.

[†]Found: C 55.76; H 7.40%. Calculated: C 55.61; H 7.67%.

‡Found: C 41.07; H 4.90%. Calculated: C 41.01; H 4.73%.

O,O-Dialkyl S-phenyl phosphorothioites react with acyl halides without change in the valence of the phosphorus atom with formation of dialkyl phosphorohalidites and S-phenyl carbothioates. This reaction can be represented by the scheme proposed for the reactions of triethyl phosphorotrithioites with acyl halides [8]:

 $C_{6}H_{5}SP(OR)_{2}+R'COX \rightarrow \begin{bmatrix} COR^{\dagger} \\ (RO)_{2}P \stackrel{\frown}{\longrightarrow} S^{\dagger} \\ \swarrow \\ \swarrow \\ \swarrow \\ \swarrow \\ \swarrow \\ \swarrow \\ \blacksquare \end{bmatrix} \xrightarrow{(RO)_{2}PX + R'CSC_{6}H_{5}} (RO)_{2}PX + R'CSC_{6}H_{5}$

It must be stated that in none of the experiments on the action of acyl halides on O,O-dialkyl S-phenyl phosphorothioites were Arbuzov-rearrangement products isolated.

EXPERIMENTAL

Synthesis of Phenyl Phosphorodichloridothioite. A four-necked flask fitted with stirrer, dropping funnel, tube for the passage of carbon dioxide, and reflux condenser was charged with 120 g of PCl₃, which was heated to the boil while 27.5 g of benzenethiol was added dropwise. The contents of the flask were refluxed until no more HCl came off. Excess of PCl₃ was driven off in vacuum fractionation. We obtained 46.3 g (78%) of phenyl phosphorodichloridothioite, bp 62.5-63° (0.04 mm); n_D^{20} 1.6370; d_4^{20} 1.3797. Found: P 14.34%; MR 54.91. C₆H₅Cl₂PS. Calculated: P 14.67%; MR 53.81. [1] gives: bp 125° (10 mm); d_{15}^{15} 1.2560.

Synthesis of O,O-Dialkyl S-Phenyl Phosphorothioites. Method A. A solution of 0.5 mole of an alcohol and 0.5 mole of triethylamine in 50 ml of petroleum ether was added dropwise with vigorous stirring to 0.25 mole phenyl phosphorodichloridothioate in 1200 ml of petroleum ether with maintenance of the temperature in the flask between -10 and -15° . Triethylamine hydrochloride was filtered off under suction. Solvent was driven off, and by the vacuum fractionation of the crude product we obtained the corrresponding O,O-dialkyl S-phenyl phosphorothioite. The constants of the products are given in Table 1. All operations in the synthesis were conducted in an atmosphere of carbon dioxide.

<u>Method B.</u> With stirring at a temperature in the flask of -10 to -15° 14 g of diethyl phosphorochloridite was added dropwise to a solution of 10 g of benzenethiol and 9.1 g of triethylamine in 500 ml of petroleum ether. Triethylamine hydrochloride was filtered off and petroleum ether was driven off. In the vacuum distillation of the crude product from a Favorskii flask we obtained 15.3 g (73.5%) of O,O-diethyl Sphenyl phosphorothioite.

<u>Method C</u>. With vigorous stirring 15.6 g of diethyl phosphorochloridite was added dropwise to 0.1 mole of sodium benzenethiolate prepared from 11 g of benzenethiol and 2.3 g of sodium in 500 ml of benzene. The reaction mixture was heated for 5 h at 40-45°, sodium chloride was filtered off, and benzene was removed in a vacuum. By vacuum fractionation from a Favorskii flask we obtained 16.4 g (70.5%) of O,O-diethyl S-phenyl phosphorothioite.

Addition of Sulfur to 0,0-Dialkyl S-Phenyl Phosphorothioites. A flask fitted with reflux condenser, thermometer, and tube for the passage of carbon dioxide was charged with 0.04 mole of an 0,0-dialkyl S-phenyl phosphorothioite and 0.04 mole of sulfur powder. The reaction mixture was heated to 40-50°, when an exothermic reaction set in and the temperature rose to 100-140°. Vacuum distillation from a Favorskii

flask gave the corresponding O,O-dialkyl S-phenyl phosphorodithioate. The constants of these products are given in Table 2.

Oxidation of O,O-Dialkyl S-phenyl Phosphorothioites. This was conducted with nitrogen dioxide by the procedure described in [10]. For the oxidation we took 0.04 mole of the phosphorothious ester in 10-15 ml of CH_2Cl_2 . The constants of the O,O-dialkyl S-phenyl phosphorothioates obtained are given in Table 2.

<u>Action of CH₃I on O,O-Dimethyl S-Phenyl Phosphorothioite</u>. A mixture of 10.1 g of the phosphorothious ester and 7.1 g of CH₃I was heated in a sealed tube for 16 h at 80-85°. By fractional distillation we obtained: 1) O-methyl S-phenyl methylphosphonothioate, 8.2 g (81%); bp 101-102° (0.04 mm); nD^{20} 1.5632; d_4^{20} 1.2177. Found: C 47.45; 47.75: H 5.42; 5.72; P 14.90%; MR 53.95. C₈H₁₁O₂PS. Calculated: C 47.51; H 5.48; P 15.32%; MR 53.61; 2) CH₃I, 5.9 g (84%); bp 42.5°; nD^{20} 1.5290; d_4^{20} 2.2673. Found: MR 19.31. CH₃I. Calculated: MR 19.62.

Action of CH₃I on O,O-Diethyl S-Phenyl Phosphorothioite. A mixture of 11.6 g of the phosphorothious ester and 7.1 g of CH₃I was heated in a tube for 11 h at 100-105°. By fractionation we obtained: 1) O-ethyl S-phenyl methylphosphonothioate, 9.75 g (90.2%); bp 96-97° (0.03 mm); nD^{20} 1.5508; d_4^{20} 1.1764. Found: P 14.52; S 14.67; 14.92%; MR 58.63. $C_{10}H_{15}O_2PS$. Calculated: P 14.32; S 14.87%; MR 58.23; 2) C_2H_5I , 7.0 g (89.9%); bp 71-72°; nD^{20} 1.5121; d_4^{20} 1.9394. Found: MR 24.14. C_2H_5I . Calculated: MR 24.24.

Action of CH₃I on O,O-Dipropyl S-Phenyl Phosphorothioite. A mixture of 10 g of the phosphorothious ester and 5.5 g of CH₃I was heated in a tube for 11 h at 100-105°. By fractional distillation we obtained: 1) O-propyl S-phenyl methylphosphonothioate, 7.5 g (84%); bp 113-114° (0.04 mm); nD²⁰ 1.5417; d₄²⁰ 1.1405. Found: P 13.28; S 13.90%; MR 63.51. C₁₂H₁₉O₂PS. Calculated: P 13.45; S 13.92%; MR 62.84; 2) propyl iodide, 5.6 g (83.8%); bp 101-102; nD²⁰ 1.5051; d₄²⁰ 1.7523. Found: MR 28.78. C₃H₇I. Calculated: MR 18.85.

Action of Acetyl Chloride on O,O-Diethyl S-Phenyl Phosphorothioite. In an atmosphere of carbon dioxide 4.1 g of acetyl chloride was added dropwise to 12.2 g of the phosphorothious ester in a flask fitted with reflux condenser. The temperature of the reaction mixture rose from 25 to 42°. The mixture was then heated for 3 h at 90°. By fractional distillation we obtained 1) diethyl phosphorochloridite, 6 g (74%) bp 55-56° (30 mm); nD^{20} 1.4373; d_4^{20} 1.0893. Found: MR 37.67. $C_4H_{10}C1O_2P$. Calculated: MR 37.33. [11] gives: nD^{20} 1.4370; d_4^{20} 1.0876; 2) S-phenyl thioacetate, 7.3 g (91.5%); bp 101-102° (9 mm); nD^{20} 1.5692; d_4^{20} 1.1252. Found: C 62.91; 62.94; H 5.16; 5.27%; MR 44.33. C_8H_9OS . Calculated: C 63.12; H 5.30%; MR 44.39. [12] gives nD^{25} 1.5681.

Action of Benzoyl Chloride on O,O-Dipropyl S-Phenyl Phosphorothioite. A mixture of 10 g of the phosphorothious ester and 5.44 g of benzoyl chloride was heated for 11 h in a sealed tube at 100-105°. By fractional distillation we isolated 5.3 g (74.2%) of dipropyl phosphorochloridite, bp 69-70° (11 mm); nD^{20} 1.4440; d_4^{20} 1.0410. Found: MR 47.10. $C_6H_{14}C1O_2P$. Calculated: MR 46.62. [11] gives: nD^{20} 1.0420.

The substance remaining in the flask when dipropyl phosphorochloridite had been distilled off crystallized and had mp 51-53°; yield 6.1 g (74.2%). After being recrystallized from a mixture of petroleum ether and benzene it had mp 55.5-56°. For S-phenyl thiobenzoate [13] gives mp 56°.

IR spectra were determined with a UR-10 spectrophotometer, slit program 4, rate $150 \text{ cm}^{-1}/\text{min}$ (with retarder). A drop of the substance was pressed between KBr plates; the layer thickness was not checked. The Raman spectrum of O,O-dimethyl S-phenyl phosphorothioite was determined with an ISP-51 spectrometer. To obtain accurate frequencies the spectra of standard substances (polystyrene for IR spectra) were determined.

CONCLUSIONS

1. Three methods for the preparation of O,O-dialkyl S-phenyl phosphorothioites are proposed.

2. O,O-Dialkyl S-phenyl phosphorothioites are oxidized by nitrogen oxide and combine with sulfur with formation of the corresponding phosphorothioates and phosphorodithioates.

3. O,O-Dialkyl S-phenyl phosphorothioites show dual reactivity in their reactions with alkyl and acyl halides.

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