TERVALENT PHOSPHORUS THIO ESTERS

COMMUNICATION 1. ETHYLPHOSPHONODITHIOUS, ETHYLPHENYLPHOSPHINOTHIOUS, AND DIETHYLPHOSPHINOTHIOUS ESTERS*

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Apart from diethyl ethylphosphonodithioite [1], alkylphosphonodithious esters have not been described in the literature. The chemical and physical properties of this class of organophosphorus compounds have been little studied, and it was therefore of some considerable interest to continue the investigation of alkylphosphonodithious esters started by one of us and, in particular, to study the reaction of chloral with these esters (Perkow reaction), all the more in that this reaction with alkylphosphonous esters has been studied in our laboratory [2].

The first alkylphosphonodithious ester — diethyl ethylphosphonodithioite — was prepared by the reaction of ethylphosphonous dichloride with ethanethiol in an ether medium in presence of triethylamine [1]:

$$C_2H_5PCl_2 + 2C_2H_5SH + 2(C_2H_5)_3N \rightarrow C_2H_5P(SC_2H_5)_2 + 2(C_2H_5)_3N \cdot HCl.$$

By the use of this method we prepared a number of dialkyl ethylphosphonodithioites. The constants and analyses of these esters are given in Table 1.

They are all mobile liquids with a specific unpleasant smell, and they are readily soluble in organic solvents (diethyl ether, benzene, petroleum ether, etc.). It is noteworthy that ethylphosphonodithious esters are much less active in oxidation by atmospheric oxygen than ethylphosphonous esters.

As they contain a tervalent phosphorus atom, ethylphosphonodithious esters combine with sulfur with formation of ethylphosphonotrithioic esters:

$$C_2H_5P(SR)_2 + S \rightarrow C_2H_5P(S)(SR)_2.$$

However, in this reaction also (as would be expected from the behavior in oxidation), the addition of sulfur goes less vigorously than in the case of the oxygen analogs. To initiate the addition of sulfur to alkyl-phosphonodithious esters the reaction mixture must be heated to 50-80°C, after which reaction goes with liberation of heat. The constants and analyses of the ethylphosphonotrithioic esters prepared in this way are given in Table 2.

Taking diethyl ethylphosphonodithioite as our example, we studied the reactions of acid halides with ethylphosphonodithious esters. By the reaction of diethyl ethylphosphonodithioite (I) with benzoyl or acetyl chloride (II) we obtained ethyl ethylphosphonochloridothioite (III) and S-ethyl thiobenzoate or thioacetate (IV). In these reactions no Arbuzov-rearrangement products were isolated. It was thus shown that the reaction of diethyl ethylphosphonodithioite with acid halides goes in accordance with the rearrangement scheme proposed by Kabachnik and co-workers [3] for phosphorotrithious esters.

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TABLE 1

%
76 73
76 62
03 84
03 57
P,

TABLE 2

		20	- 20	Found			Calculated			
$C_2H_5P(SR)_2$	B.p., °C (p, mm)	$^{n}D^{20}$	d4 ²⁰	Р,%	s, %	MR	Р, %	s,%	MR	Yield %
RS										
n∽C ₃ H ₇	94-96(0.05)	1.5689	1.0856	12.50	39.84	73.08	12.81	39.67	71.98	87.0
$i-C_{3}H_{7}$	76-78(0.05)	1.5616	1.0704	12.61	-	73.27	12.81	-	71.98	77.0
$n-C_4H_9$	109-110(0.05)	1.5528	1.0481	11.55	-	82.41	11.48	-	81.13	81.0
i-C ₄ H ₉	103-105 (0.05)	1.5516	1.0453	11.40	-	82.41	11.48	-	81.13	84.0
- SCalla - SCalla										
	$C_2H_5P(SC_2H_5)_2 + RCOCI \rightarrow$	C ₂ H ₅ P	C_2H_5	$\rightarrow C_2H_5$		$+ C_2 H_5 S$	COR			
	(1) (11)	CI S	COR -		`Cl (III)	(IV	.)			

We supposed that, if the reaction of (I) with (II) were carried out at a reactant ratio of 1: 2, both sulfur atoms of the ester would enter the reaction:

$$C_{2}II_{5}P (SC_{2}II_{5})_{2} + 2RCQCl \rightarrow \begin{bmatrix} Cl \\ S - C_{2}H_{5} \\ C_{2}H_{5}P & COR \\ S - C_{2}H_{5} \\ Cl \\ S - C_{2}H_{5} \end{bmatrix} \rightarrow C_{2}H_{5}PCl_{2} + 2C_{2}H_{5}SCOR$$

This reaction was carried out, and our supposition proved correct. On fractionation of the reaction products we isolated ethylphosphonous dichloride and S-ethyl thiobenzoate. The reaction of diethylphosphonodithioite with ethyl bromide went as follows:

 $C_{2}H_{5}P(SC_{2}H_{5})_{2} + C_{2}H_{5}Br \rightarrow (C_{2}H_{5})_{2}P(S)SC_{2}H_{5} + (C_{2}H_{5})_{3}PS$

Such a course of reaction was observed earlier by Arbuzov, Rizpolozhenskii, and Zvereva [1].

It was stated above that one of our objects in this work was the study of the reactions of ethylphosphonodithious esters with chloral. These reactions were conducted under various conditions: with cooling (from -10 to -15°), at higher temperatures (15-30°), in solvents, and without solvent; in all cases, however, we obtained a mixture of several products whose composition we have not been able to establish. However, a test with bromine water and spectral analysis indicate the presence of a double bond. It was suggested that, if the reactions with chloral were conducted with diethylphosphinothious or ethylphenylphosphinothious esters, the resolution of this question would be simplified, for these esters contain only one SR group which can react with chloral. These phosphinothious esters were prepared by the same method as the ethylphosphonodithious esters, and their constants and analyses are given in Table 3.

However, this view proved to be incorrect. In the reactions of these esters with chloral we again obtained a mixture of reaction products, from which we have not been able to isolate any pure substances.

TABLE 3

	B.p., °C (p, mm)		d4 ²⁰	MR				Calcu		
R		${^{n}D}^{20}$		Found	Calcu- lated	Ele- ment	Found %	lated %	Yield %	
$(C_2H_5)_2PSR$										
$C_{2}H_{5}$	50-52(7.0)	1.5047	0.9172	48.94	48.29	s	21.29	21.23	70.0	
$n - C_3 H_7$	65-67(7.0)	1.5010	0.9121	52.98	52.91	s	19.62	19.51	61.0	
	$C_2H_5 \sim C_6H_5 \sim$	> psr								
C_2H_5	73-75(0.05)	1.5832	1.0362	63.90	63.17	Р	15.57	15.66	45.0	
$n-C_3H_7$	78-79(0.04)	1.5738	1.0192	68.64	67.78	Р	14.50	14.62	63.0	
$i-C_3H_7$	71-73(0.07)	1.5680	1.0131	68.46	67.78	Р	14.74	14.62	55.0	
$n-C_4H_9$	86-88(0.05)	1.5665	1.0094	73.09	72.39	Р	13.86	13.72	59.0	
$i-C_4H_9$	79-81(0.05)	1.5624	1.0042	73.04	72.39	S	13.98	14.16	52.0	

TABLE 4

an a				Found	Calcu	lated		
R	B.p., °C (p, mm)	n_D^{20}	d4 ²⁰	MR	Ρ,	% Yiel	Yield %	
nge of the second s		$(C_2H_5)_2P(S)SR$						
C_2H_5	61-62(0.05)	1.5532	1.0557	55.18 16.9	96 54.33	17.03 75.0		
$n - C_3 H_7$	74-76(0.05)	1.5442	1.0363	59.73 15.	81 58.95	15.81 87.0		
	4	$\mathcal{D}_{2}H_{5} \longrightarrow \mathcal{P}(S)$	SR					
$C_{2}H_{5}$	112-115 (0.1)	1.6140	1.1392	70.36 13.3	30 69.20	13.48 80.0	,	
$n - C_3 H_7$	104-105 (0.05)	1.6032	1.1142	75.24 12.0	61 73.82	12.70 67.0		
$i - C_3 H_7$	97-98 (0.05)	1.5993	1.1061	75.39 12.0	30 73.82	12.70 81.0		
$n-C_4H_9$	121-123 (0.06)	1.5925	1.0941	79.85 11.	76 78.43	12.01 83.0		
$i - C_4 H_9$	124-125(0.1)	1.5916	1.0913	79.95 11.	38 78.43	12.01 82.0		

Diethylphosphinothious and ethylphosphinothious readily combine with sulfur with formation of diethylphosphinodithioic and ethylphosphinodithioic esters respectively. The constants of these esters are given in Table 4.

EXPERIMENTAL

Synthesis of Dipropyl Ethylphosphonodithioite. A mixture of 38.0 g of 1-propanethiol, 52.0 g of triethylamine, and 350 ml of ether was prepared in a four-necked flask fitted with stirrer, dropping funnel, and reflux condenser. With vigorous stirring and external cooling of the flask with snow and salt 32.7 g of ethylphosphonous dichloride was added in the course of two hours. The reaction and all subsequent operations were conducted in an atmosphere of nitrogen. Triethylamine hydrochloride was filtered off and washed with ether. By vacuum fractionation from a Favorskii flask we isolated 38.2 g (73%) of dipropyl ethylphosphonodithioite, b.p. 86-88° (0.1 mm); n_D^{20} 1.5362; d_4^{20} 0.9901. Found %: P 14,69; 14.88. MR 66.13. $C_8H_{19}PS_2$. Calculated %: P 14.76. MR 65.66. By this method we prepared all the ethylphosphonodithious, diethylphosphinothious, and ethylphenylphosphinothious esters listed in the tables.

<u>Addition of Sulfur to Dipropyl Ethylphosphonodithioite</u>. A mixture of 5.4 g of dipropyl ethylphosphonodithioite and 0.82 g of sulfur powder was prepared in a flask fitted with thermometer, calcium chloride tube, and tube for the passage of nitrogen. No reaction went in the cold. The mixture was heated, and the sulfur-addition reaction started at 50°. The application of heat was stopped, but the temperature in the flask rose to 155°. The whole of the sulfur taken for reaction reacted. By vacuum distillation from an Arbuzov flask we isolated dipropyl ethylphosphonotrithioate; yield 5.4 g (87.0%); b.p. 94-96° (0.05 mm); n_D^{20} 1.5689; d_4^{20} 1.0856. Found %: P 12.50; 12.47; S 39.84; 39.99. MR 73.03. $C_8H_{19}PS_3$. Calculated %: P 12.81; S 39.67. MR 71.98.

All the other ethylphosphonotrithioic, diethylphosphinodithioic, and ethylphenylphosphinodithioic esters listed in the tables were prepared by the above-described method. It was not necessary to apply heat in the addition of sulfur to diethyl- and ethylphenyl-phosphinothious esters; the reaction went with liberation of heat.

Action of Acetyl Chloride on Diethyl Ethylphosphonodithioite (molar ratio 1:1). 10 g of diethyl ethylphosphonodithioite was introduced into a four-necked flask fitted with thermometer, reflux condenser protected by a calcium chloride tube, and dropping funnel, and 4.9 g of acetyl chloride was added dropwise. The reaction did not go at room temperature, and the mixture was therefore heated at 80° for 2 h. All operations were conducted in a stream of nitrogen.

By vacuum fractionation from a Favorskii flask we isolated: Fraction I – S-ethyl thioacetate – 2.3 g (40.2%); b.p. 71-72° (185 mm); n_D^{20} 1.4587; d_4^{20} 0.9811. The literature [4] gives: $n_D^{20^{\circ}6}$ 1.4583; d_4^{20} 0.9792. Found %: S 31.02%. MR 28.96. $C_4H_8O_5$. Calculated %: S 30.77. MR 29.52. Fraction II – ethyl ethylphosphonochloridothioite – 4.1 g (47.7%); b.p. 88.90° (36 mm); n_D^{20} 1.5307; d_4^{20} 1.1047. Found %: P 20.07; S 20.20; Cl 22.32. MR 43.80. C_4H_{10} PSCl. Calculated %: P 19.81; S 20.45; Cl 22.68. MR 43.22.

Action of Benzoyl Chloride on Diethyl Ethylphosphonodithioite (molar ratio 1:1). 7.7 g of benzoyl chloride was added dropwise to 10 g of the ester heated to 133° in a stream of nitrogen in a flask fitted with reflux condenser, thermometer, and dropping funnel. The reaction mixture was then kept at 130-140° for 8 h. By vacuum distillation from a Favorskii flask we isolated: Fraction I – ethyl ethylphosphonochloridothioite – 4.2 g (48.8%); b.p. 53-54° (7 mm); n_D^{20} 1.5309; d_4^{20} 1.1038. Fraction II – S-ethyl thiobenzoate – 5.7 g (62.5%); b.p. 104-106° (8 mm); n_D^{20} 1.5687; d_4^{20} 1.0967. Found %: S 19.4. MR 49.57. $C_9H_{10}OS$. Calculated %: S 19.28. MR 49.01.

Action of Benzoyl Chloride on Diethyl Ethylphosphonodithioite* (molar ratio 2:1). For reaction we took 6 g of the ester and 9.3 g of benzoyl chloride. The reaction was conducted in a sealed tube at 130-140° for 10 h. By vacuum fractionation from a Favorskii flask we isolated: Fraction I – ethylphosphonous dichloride – 1.5 g (35%); b.p. 111-113°; n_D^{20} 1.4948; d_4^{20} 1.2526. For ethylphosphonous dichloride the literature [5] gives n_D^{20} 1.4938; 1.4990; 1.4930; d_4^{20} 1.2562; 1.2384; 1.2485. Fraction II – S-ethyl thiobenzoate – 4.7 g (43.1%); b.p. 106-108° (9 mm); n_D^{20} 1.5695; d_4^{20} 1.1051. Found MR 49.23. $C_9H_{10}OS$. Calculated MR 49.01.

<u>Reaction of Ethyl Bromide with Diethyl Ethylphosphonodithioite</u>. For reaction we took 15 g of the ester and 9 g of ethyl bromide. The reaction was conducted in a sealed tube at 140-150° for 10 h. Ethyl bromide was distilled from the reaction products, and 1.1 g (8.9%) of crystals of triethylphosphine sulfide was precipitated. After recrystallization from isopropyl alcohol they melted at 94-95°. The literature [1] gives m.p. 94-95°. After the separation of the crystals, the filtrate was vacuum-distilled. We isolated 10.2 g (68%) of ethyl diethylphosphinodithioate; b.p. 78-80° (0.05 mm), n_D²⁰ 1.5559; d₄²⁰ 1.0594. Found %: P 17.25; S 35.42. MR 55.21. C₆H₁₅PS₂. Calculated %: P 17.03; S 35.16. MR 54.33.

<u>Reaction of Diethyl Ethylphosphonodithioite with Chloral.</u> 20 g of the ester was added dropwise to 18 g of chloral contained in a flask. The reaction was conducted in a stream of nitrogen. As the ester was added the temperature in the flask rose and a gelatinous precipitate was formed simultaneously. When about one-half of the ester had been added, the liquid in the flask was converted into a gelatinous mass, and the temperature rose to 50°. As further ester was added, the contents of the flask were again liquefied. When the whole of the ester had been added, the reaction products were heated to 110-120° and kept at this temperature for 30 minutes. Almost the whole of the gelatinous precipitate disappeared and was converted into a tea-colored liquid. The reaction was accompanied by the liberation of ethyl chloride, which was collected in a trap; we collected 4.1 g (57.7%). By vacuum fractionation of the reaction products we isolated a fraction of b.p. 99-100° (0.07 mm) (it must be mentioned that as the bath temperature was raised, the temperature in the vapor of the distilling liquid also rose); $d_4^{20} 1.2588$; $n_D^{20} 1.5627$. Found %: C 29.36; H 5.01; P 12.05; S 27.85; Cl 21.1. MR 68.38. $C_6H_{11}POS_2Cl_2$. Calculated %: C 27.16; H 4.18; P 11.70; S 24.15; Cl 26.4. MR 64.72.

Separate fractions of identical boiling point were taken, and the n_D^{20} values of these fractions were determined and the fractions were analyzed. Fractionation was conducted with a Widmer column. Fraction I - b.p. 99.5° (0.07 mm); n_D^{20} 1.5641. Found %: P 12.18; S 27.5 Cl 21.72. Fraction II - b.p. 99.5°

* The ester was prepared by the method given in [1].

(0.07 mm); n_{D}^{20} 1.5635. Found %: P 12.22; S 27.75; Cl 21.21. Fraction III – b.p. 100° (0.07 mm); n_{D}^{20} 1.5620. Found %: P 11.95; S 27.85; Cl 21.37.

A mixture of 10.3 g of chloral and 20 ml of benzene was prepared in the flask, which was cooled with snow and salt. 12.7 g of diethyl ethylphosphonodithioite was added with stirring at a temperature of 0 to -3° in flask. The reaction was conducted in a stream of nitrogen. The mixture was kept for 24 h at room temperature, and the reaction products were then fractionated in a vacuum from a flask with a Widmer column. We isolated a fraction in 75% yield; b.p. 92-93° (0.03 mm); d_4^{20} 1.2571; n_D^{20} 1.5642. Found %: C 29.84; H 5.1; P 12.61; S 27.28; Cl 19.91.

<u>Reaction of Ethyl Diethylphosphinothioite with Chloral.</u> 7.6 g of chloral was added dropwise to 7.5 g of ethyl diethylphosphinothioite dissolved in 20 ml of ether with cooling of the flask with water so that the temperature in the flask was 19-20°. The reaction was conducted in a stream of nitrogen. With the addition of the first few drops of chloral a slimy precipitate formed in the flask, and it increased in amount as more chloral was added. The mixture was set aside for 10 h, but part of the precipitate had not dissolved. After filtration and vacuum-fractionation of the reaction products we obtained a fraction having: b.p. 66-68° (0.06 mm); n_D^{20} 1.5245; d_4^{20} 1.2223. Found %: C 34.49; H 5.31; P 13.18. MR 58.37. $C_6H_{11}POSCl_2$. Calculated %: C 30.9; H 4.7; P 13.13. MR 56.40.

<u>Reaction of Ethyl Ethylphenylphosphinothioite with Chloral</u>. For reaction we took 5.7 g of the ester and 4.8 g of chloral. The solvent was benzene, and the temperature during the reaction was 45-50°. In other respects the procedure was similar to that described above. We isolated a fraction having: b.p. 106-108° (0.05 mm); n_D^{20} 1.5850; d_4^{20} 1.2690. Found %: C 44.6; H 4.3; P 10.9; S 12.51; Cl 21.9. MR 74.15. $C_{10}H_{11}POSCl_2$. Calculated %: C 42.71; H 3.91; P 11.03; Cl 25.27. MR 71.27.

<u>Reaction of Chloral with Butyl Ethylphenylphosphinothioite</u>. For reaction we took 10.5 g of the ester and 8 g of chloral. The reaction was conducted without solvent at 20-22°. By fractionation we isolated a fraction having: b.p. 118-120° (0.06 mm); n_D^{20} 1.5810; d_4^{20} 1.2651. Found %: C 44.62; H 4.6; P 11.15; Cl 22.05. MR 74.03. $C_{10}H_{11}POSCl_2$. Calculated %: C 42.71; H 3.91; P 11.03; Cl 25.27. MR 71.27.

CONCLUSIONS

1. By the reaction of alkanethiols with ethylphosphonous dichloride, ethylphosphinous chloride and diethylphosphinous chloride the corresponding ethylphosphonodithious, ethylphosphinothious, and diethylphosphinothious esters were obtained.

2. By the addition of sulfur to these esters ethylphosphonotrithioic, ethylphenylphosphinodithioic, and diethylphosphinodithioic esters were obtained.

3. The reactions of acyl chlorides with diethyl ethylphosphonodithioite were studied.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-tocover English translations appears at the back of this issue.