Thionophosphine Sulfides. II. Preparation and Chlorination of Phosphonodithioic Acids[1a]

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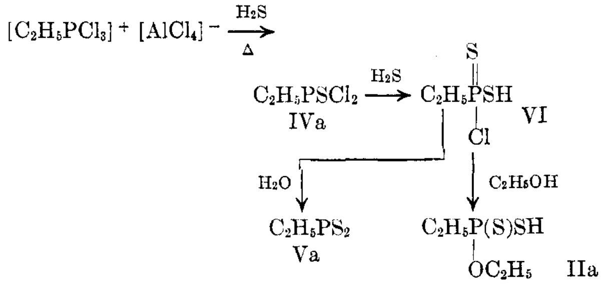
The reaction of thionophosphine sulfides $(RPS_2)_n$, with alcohols and phenols has been found to give excellent yields of the corresponding *O*-alkyl and *O*-aryl phosphonodithioic acids. A number of halo-alkanols, alkenols, and dihydric alcohols, as well as simple primary and secondary alcohols have been smoothly converted to phosphonodithioic acids. Chlorination of these *O*-alkyl and *O*-aryl phosphonodithioic acids has been found to yield the corresponding phosphonochloridothioates. The reaction conditions are discussed and some properties of the products are given.

The facile preparation of phosphorodithioic acids (I) from phosphorus pentasulfide is well known.[2]

$$4ROH + P_2S_5 \longrightarrow \underset{(I)}{2(RO)_2P(S)SH} + H_2S$$

Several phosphonodithioic acids (II) have been made by reaction of metal hydrosulfides with phosphonochloridothioates (III), or by reaction of phosphonothioic dichlorides (IV) in anhydrous alcohol with dry alkali metal hydrosulfide, followed by neutralization of the phosphonodithioate salt.[3]

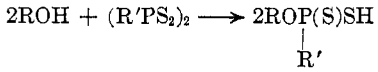
It would be desirable if II could be made conveniently as the free acid directly, in a fashion analogous to the excellent preparation of I from phosphorus pentasulfide. In this connection, the thionophosphine sulfides (V)[4] appeared to be promising intermediates for conversion to II. Kinnear and Perren[5] reported the formation of *O*-ethyl ethylphosphonodithioic acid (IIa) in 40% yield by reaction of ethanol with an intermediate VI resulting from treatment of ethyl chloride, phosphorus trichloride, and aluminum chloride with hydrogen sulfide at elevated temperature.



The postulated intermediate VI, complexed with aluminum chloride, could be treated with water to obtain Va.

Fay and Lankelma[6] described a thionophosphine sulfide derived from cyclohexene and phosphorus pentasulfide, which upon refluxing with excess methanol for twenty-four hours, gave a 62% yield of a neutral ester, *O*-methyl-*S*-methyl cyclohexenylphosphonodithioate, with evolution of methyl mercaptan and hydrogen sulfide.

We have now demonstrated that II can be prepared directly from V by reaction with alcohols and phenols.



$$2ROH + \underset{V}{(R'PS_2)_2} \longrightarrow \underset{II}{2RO\underset{R'}{P}(S)SH}$$

A large number of alcohols and phenols reacted smoothly with V. Nearly quantitative yields of the corresponding acids (85–98% assay) were isolated. Primary and secondary aliphatic alcohols reacted with equivalent amounts of V at 40–70° in the presence or absence of inert solvents. There was no evidence of appreciable neutral ester formation or gas evolution, even when an excess of alcohol was employed, providing the reaction was carried out at moderate temperatures and terminated with complete dissolution of V. Olefinic and halogen-containing alcohols also reacted successfully. Ethylene cyanohydrin and 2-nitrobutanol gave viscous oils with poorly defined acid numbers, and could not be successfully converted to the ammonium salts. While propargyl alcohol reacted to form the acid, it was slowly transformed to a viscous oil of low neutralization equivalent, probably by addition of the thiol group to the acetylenic bond. *O*-Propargyl isopropylphosphonodithioic acid was converted, however, to the more stable ammonium and nickel salts. Tertiary alcohols, as represented by *t*-butyl alcohol, reacted easily, but almost simultaneously evolved gas to form a viscous oil.

Ethylene glycol reacted smoothly with two equivalents of methylthionophosphine sulfide to form *O,O* - (1,2 - ethylene)bis(methylphosphonodithioic acid). This represents a departure from the reaction of phosphorus pentasulfide with dihydric alcohols, where polymeric or cyclic phosphorodithioic acids are formed.

In contrast to the reaction of phenols with phosphorus pentasulfide, where reaction temperatures of 120–150° are generally required, thionophosphine sulfides reacted readily with a wide variety of phenols at 60–90°. The crude thio acids were

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[1] (a) Presented before the Division of Organic Chemistry at the Southwide Regional Meeting of the American Chemical Society, New Orleans, December, 1961; (b) Present address: General Chemicals Division, Allied Chemicals Corp., Morristown, N. J.

[2] Pischtschinuka, *J. Russ. Phys. Chem. Soc.*, **44**, 1406 (1912).

[3] L. Malatesta and R. Pizzotti, *Chim. e ind.* (Milan), **27**, 6 (1945).

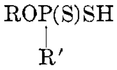
[4] P. E. Newallis, J. P. Chupp, and L. C. D. Groenweghe, *J. Org. Chem.*, **27**, 3829 (1962).

[5] A. M. Kinnear and E. A. Perren, *J. Chem. Soc.*, 3437 (1952).

[6] P. Fay and H. P. Lankelma, *J. Am. Chem. Soc.*, **74**, 4933 (1952).

TABLE I

PHYSICAL AND ANALYTICAL DATA OF PHOSPHONODITHIOIC ACIDS[a]



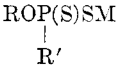
$\underset{R'}{ROP(S)SH}$

R	R′	B.p. (mm.)	$n^{22.5}_D$	Neut. equiv.[b] Crude	Neut. equiv.[b] Dist.	Neut. equiv.[b] Calcd.	P[c] Calcd.	P[c] Obsd.	S Calcd.	S Obsd.	Cl Calcd.	Cl Obsd.
CH_3	CH_3	28 (0.01)	1.5659	146	147	142	21.8	21.4	45.1	44.9		
C_2H_5	CH_3	45–48 (0.2)	1.5440	160	159	156	19.8	19.7	41.0	40.9		
n-C_3H_7	CH_3	50 (0.02)	1.5356	176	179	170	18.2	17.8	37.7	37.5		
n-C_4H_9	CH_3	47 (0.005)	1.5280	187	186	184	16.8	16.6	34.8	34.1		
$(CH_3)_2CHCH_2$	CH_3	37 (0.003)	1.5232	188		184	16.8	16.8	34.8	34.8		
n-C_5H_{11}	CH_3	61–64 (0.04)	1.5230	214	198	198	15.6	15.4	32.3	32.5		
$CH_3O(CH_2)_3$	CH_3	57 (0.002)	1.5325	202		200	15.5	15.4	32.0	32.1		
$CH_3O(CH_2)_2$	CH_3	58–60 (0.01)	1.5421	189	182	186	16.6	16.3	34.4	34.3		
$C_2H_5O(CH_2)_2$	CH_3	92 (0.005)	1.5308	200	201	200	15.5	15.4	32.0	32.0		
ClC_2H_4	CH_3	58 (0.007)		192	190	191	16.2	16.1	33.6	33.3	18.6	18.5
Cl_2CHCH_2	CH_3	66.5 (0.006)	1.5722	232	225	225	13.8	13.4	28.5	29.2		
Cl_3CCH_2	CH_3	[d]		264	263	260	11.9	11.9			41.0	41.0
$CH_2{=}CClCH_2$	CH_3	58 (0.02)	1.5689	210	205	203	15.3	15.1	31.6	31.6	17.5	17.6
C_2H_5	C_2H_5	56 (0.4)	1.5389	170	171	170	18.2	17.9	37.7	37.6		
n-C_4H_9	C_2H_5	50 (0.006)	1.5237	200	199	198	15.6	15.5	32.3	31.6		
n-C_3H_7	n-C_4H_9	60 (0.003)	1.5189	218	215	212	14.6	14.4	30.2	30.0		
$Cl(CH_2)_2$	i-C_3H_7	57 (0.002)	1.5499	221	218	219	14.2	14.1	29.3	30.1		
$Cl(CH_2)_2$	n-C_4H_9	89 (0.024)	1.5438	233	230	233	13.3	13.1	27.6	28.3	15.2	15.9

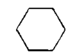
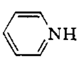
[a] All yields of crude phosphonodithioic acids based on thionophosphine sulfide were essentially quantitative. [b] Titrated to a Methyl Red end point. [c] Analysis of distilled material. [d] M.p. 42–43°, recrystallized from hexane.

TABLE II

SALTS OF SOME PHOSPHONODITHIOIC ACIDS



$\underset{R'}{ROP(S)SM}$

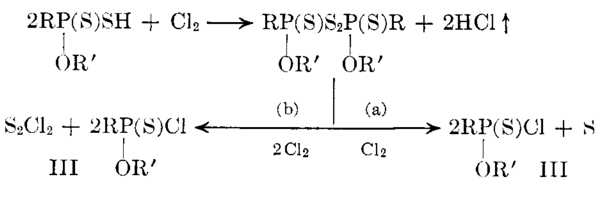
R	R′	M	Neut. equiv. Calcd.	Neut. equiv. Obsd.[b]	Yield,[a] %	M.p.	P Calcd.	P Obsd.	S Calcd.	S Obsd.	N Calcd.	N Obsd.
C_2H_5	CH_3	H	156	160	99.8							
		NH_4			98		17.9	17.6	34.0	33.5	8.1	7.8
		Ni				134–135	16.8	16.6	34.7	35.0		
$C_6H_5CH_2$	CH_3	H	218	223	97							
		NH_4			87	132–134	12.9	13.2			5.7	5.9
C_6H_5	CH_3	H	204	231	100							
		NH_4			93		14.0	14.4	29.0	28.1	6.3	6.1
		Ni				200–202	13.3	13.0	27.5	27.3		
C_2H_5		H	224	232	99							
		NH_4			95		12.8	12.4	26.5	26.2	5.8	6.0
		Ni				167–169	12.3	12.1	25.3	25.1		
C_2H_5	C_6H_5	H	218	225	99							
		NH_4			90		13.2	13.2	27.3	27.2	5.9	5.9
		Ni				184–185[c]	12.6	12.3	26.0	25.7		
p-$(O_2N)C_6H_4$	CH_3	H	251	270	99	45–50						
		NH_4					11.6	11.0			10.5	10.6
		Ni				190–193	11.3	11.0	23.4	22.9		
$HC{\equiv}CCH_2$	$(CH_3)_2CH$	H	194	219[d]	100							
		NH_4			75		14.7	14.7	30.4	29.8	6.6	6.8
		Ni				84–86	13.9	13.2	28.8	28.6		
$-CH_2CH_2$	CH_3	H	141	147	100							
		 NH			82	118–121	14.1	14.0	29.1	28.8	6.4	6.2

[a] Yield of acid based on thionophosphine sulfide; yield salt based on crude acid. [b] Crude phosphonodithioic acid. [c] Lit.,[3] gives m.p. 180°. [d] After 17 days neut. equiv. had increased to 282.

formed in high yield (85–90% assay as determined by neutralization number and conversion to ammonium salt).

A number of thio acids successfully prepared from the appropriate thionophosphine sulfide and alcohol are listed in Tables I and II. In some instances no attempt was made to obtain physical constants of the thio acids. They were directly chlorinated to III as listed in Table III.

The preparation of III by direct chlorination of II apparently proceeds as follows.

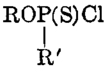


$$2\underset{OR'}{RP(S)SH} + Cl_2 \longrightarrow \underset{OR'\quad OR'}{RP(S)S_2P(S)R} + 2HCl\uparrow$$

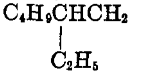
$$\underset{III}{S_2Cl_2} + 2\underset{OR'}{RP(S)Cl} \xleftarrow[2Cl_2]{(b)} \quad \xrightarrow[Cl_2]{(a)} 2\underset{OR'}{RP(S)Cl} + \underset{III}{S}$$

TABLE III

PHYSICAL AND ANALYTICAL DATA OF PHOSPHONOCHLORIDOTHIONATES



$$\mathrm{RO}\underset{\overset{|}{\mathrm{R'}}}{\mathrm{P}}\mathrm{(S)Cl}$$

R	R′	Yield,[a] %	B.p. (mm.)	$n^{25}D$	P		Cl		S	
					Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.
n-C_3H_7	CH_3	57	54–55 (2.0)	1.4886	17.9	17.9	20.5	20.4	18.6	18.6
n-C_4H_9	CH_3	64	58 (1.5)	1.4850	16.6	16.4	19.0	19.2	17.2	17.6
n-C_5H_{11}	CH_3	61	78–82 (1.8)	1.4850	15.4	15.3	17.7	17.7	16.0	15.7
n-$C_{10}H_{21}$	CH_3	62	133–135 (0.4)	1.4816	11.4	11.4	13.1	13.2		
$(CH_3)_2CHCH_2$	CH_3	66	68 (5)	1.4814	16.6	16.6	19.0	19.0	17.2	17.2
$C_6H_5CH_2CH_2$	CH_3	70	110 (0.1)	1.5597	13.2	12.7	15.1	14.7		
$(CH_3)_3CCH_2$	CH_3	77	[b]	...	15.4	14.9	17.7	17.8		
 $C_4H_9\underset{\overset{\vert}{C_2H_5}}{C}HCH_2$	CH_3	80	94–95 (0.4)	1.4817	12.8	12.6	14.6	14.6	13.2	13.6
$C_2H_5OC_2H_4$	CH_3	55	71–72 (0.2)	1.4890	15.3	15.1	17.5	17.6		
$CH_3OC_2H_4$	CH_3	68[c]	82–83 (2.8)	1.4990	16.4	16.2			17.0	17.5
$CH_3OC_3H_6$	CH_3	68	77–80 (0.4)	1.4915	15.3	14.9	17.5	17.8	15.8	16.3
$Cl(CH_2)_2$	CH_3	80[c]	72–73 (0.3)	1.5225	16.0	15.7	36.7	37.5		
$Cl(CH_2)_3$	CH_3	75	73–75 (0.4)	1.5138	15.0	14.9	34.3	35.0	15.5	15.5
$Cl(CH_2)_4$	CH_3	60	92–94 (0.4)	1.5153	14.0	13.8	32.1	32.1		
$Cl(CH_2)_6$	CH_3	42	96–100 (0.1)	1.5057	12.4	11.9	28.5	28.2		
$ClCH_2CHClCH_2$	CH_3	51	84–86 (0.2)	1.5346	12.8	12.7	44.0	44.0		
$(ClCH_2)_2CH$	CH_3	64	77–86 (0.3)	1.5305	12.8	12.8	44.0	44.7		
Cl_2CHCH_2	CH_3	72	66 (.10)	1.5282	13.6	13.4	46.8	46.1	14.1	14.5
$Cl_2CH(CH_2)_2$	CH_3	64	108–110 (1.2)	1.5275	12.8	12.7	44.0	44.0	13.3	13.6
Cl_3CCH_2	CH_3	64	69–72 (0.4)	1.5309	11.8	11.7	54.1	53.5	12.2	12.4
$Br(CH_2)_2$	CH_3	56	74–75 (0.3)	1.5480	13.0	12.8	14.9	15.0	33.6	33.5
$CH_2{=}CClCH_2$	CH_3	60	54–59 (0.2)	1.5234	15.1	14.8	34.6	34.9		
$ClCH{=}CHCH_2$	CH_3	48	69–79 (0.2)	1.5332	15.1	15.1	34.6	35.1		
$CH_3CCl{=}CHCH_2$	CH_3	28	76 (0.3)	1.5267	14.1	13.8	32.4	32.7	14.6	15.2
$CHCl{=}CClCH_2$	CH_3	63	87–90 (0.6)	1.5454	12.9	12.6	44.4	44.4	13.4	13.6
$CCl_2{=}CHCH_2$	CH_3	36	98–102 (2.0)	1.5465	12.9	13.0	44.4	44.3	13.4	13.4
$CCl_2{=}CClCH_2$	CH_3	57	85–88 (0.2)	1.5540	11.3	11.3	51.7	51.0	11.7	11.9
C_6H_5	CH_3	60	92 (0.3)	1.5700	15.0	14.6	17.2	17.4	15.5	15.9
p-$O_2NC_6H_4$	CH_3		[d]		12.3	11.9	14.0	13.9	12.7	12.6
p-$CH_3C_6H_4$	CH_3	58	111 (0.4)	1.5654	14.0	13.8	16.1	16.3	14.5	15.0
m-$CH_3C_6H_4$	CH_3	50	87 (0.1)	1.5650	14.0	13.7				
o-$CH_3C_6H_4$	CH_3	61	94 (0.2)	1.5661	14.0	13.8	16.1	16.1	14.5	14.9
p-$CH_3OC_6H_4$	CH_3	50	109 (0.1)	1.5737	13.1	12.8	15.0	15.1		
C_2H_5	C_2H_5	73	55–55.5 (2.8)	1.4900	17.9	17.8	20.5	20.2	18.6	18.8
n-C_4H_9	C_2H_5	60	67 (0.2)	1.4845	15.4	15.1			16.0	16.2
$Cl(CH_2)_2$	C_2H_5	66	68–72 (0.13)	1.5162	15.0	14.9	34.2	34.5		
$Cl(CH_2)_3$	C_2H_5	70	78 (0.15)	1.5111	14.0	13.6	32.1	31.9	14.5	14.8
$Br(CH_2)_2$	C_2H_5	59	79 (0.2)	1.5395	12.3	12.0	14.1	13.8		
C_6H_5	C_2H_5	54	99 (0.24)	1.5642	13.5	13.8	15.4	16.1		
n-C_3H_7	i-C_3H_7	70	58–59 (0.7)	1.4865	15.4	15.1	17.7	17.9	16.0	16.4
$Cl(CH_2)_2$	i-C_3H_7	66	78–82 (0.7)	1.5120	14.0	13.8	32.1	32.2	14.5	15.1
$Cl(CH_2)_2$	n-C_3H_7	65	78–80 (0.3)	1.5116	14.0	13.8	32.1	32.0	14.5	15.1
n-C_3H_7	n-C_4H_9	18.5[e]	70 (0.7)	1.4853	14.4	14.3	16.5	16.5	14.9	15.4
$Cl(CH_2)_2$	n-C_4H_9	66	87–90 (0.3)	1.5085	13.2	13.1	30.2	30.1	13.6	14.1

[a] Yields calculated on the basis of thio acid charged. [b] M.p. 45.5–46°. [c] Thio acids chlorinated with chlorine, remainder chlorinated with sulfuryl chloride. [d] M.p. 64–66°. [e] Only 0.62 equivalent of sulfuryl chloride charged.

Malatesta[7] and Hechenbleikner[8] showed that phosphorodithioic acids could be chlorinated to give the phosphorochloridothioates.

The formation of the intermediate disulfide is substantiated by the observance of appreciable weight gain in the reaction mixture only after approximately one-half equivalent of chlorine is added. As the reaction progresses, the amount of liberated hydrogen chloride diminishes. Moreover, during the chlorination of O-(p-nitrophenyl)-methylphosphonodithioic acid in benzene, a white insoluble solid precipitated after the addition of one-half equivalent of chlorine. This material showed an elemental analysis very close to the disulfide. On further chlorination the white solid dissolved and the desired O-(p-nitrophenyl)methylphosphonochloridothionate was obtained. There are two paths (a and b) which may be followed in the chlorination of III. Although yields might be expected to be greater when path b is employed, the concomitant sulfur chlorides are difficult to separate from the desired product by simple distillation, and aqueous quenching of the chlorination mixture is necessary. Path a allows the chlorination mixture to be distilled directly. In this case the desired product was obtained in 55–70% yield.

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(7) L. Malatesta, *Gazz. chim. ital.*, **81**, 596 (1951).

(8) I. Hechenbleikner, U. S. Patent 2,482,063 (September 13, 1949).

Experimental

General Preparation of Phosphonodithioic Acids and Salts.—The appropriate thionophosphine sulfide was weighed into a suitable flask with minimum exposure to atmospheric moisture. An equivalent amount of the appropriate alcohol or phenol was then added to the flask dropwise (an excess of low-boiling alcohol may be used to increase the rate of reaction), the temperature maintained at 55–65° (70–80° with phenols). Solid alcohols or phenols were dissolved or slurried in an inert solvent, such as benzene, and added to the thionophosphine sulfide. The temperature was maintained between 50–80° until complete dissolution of all solids. At the end of this time solvent, and excess alcohol, if present, were removed under vacuum, and the resulting residue obtained in 98–100% yield as crude thio acid.

The crude thio acids were generally of adequate purity for further synthesis, as shown by neutralization equivalents and formation in high yield of ammonium salts. Care was taken in distilling the crude thio acids, as considerable decomposition occurred when the still pot was heated too rapidly. In some cases, the thio acids could not be distilled.

The thio acids were converted to the ammonium salts by dissolving the acid in a twenty-fold excess by volume of benzene. Excess anhydrous ammonia was then sparged in, with stirring, keeping the temperature below 30°. The precipitated salt was filtered off, washed with fresh benzene, and air-dried. The nickel salts were obtained by preparing a 5% solution of ammonium salt in water and adding slowly with constant stirring, an equivalent amount of a 5% nickel chloride solution.

Chlorination of Phosphonodithioic Acid, Path a.—This procedure was used in all preparations listed in Table III, with the exception given below for path b. The procedure is illustrated by the preparation of *O*-propyl methylphosphonochloridothioate. To a well stirred solution of 52.6 g. (0.31 mole) of crude *O*-propyl methylphosphonodithioic acid (neut. equiv. 176) contained in 100 ml. of benzene, was added dropwise 37.8 g. (0.279 mole) of sulfuryl chloride. The temperature was maintained at 40–50° during the addition and for 30 min. thereafter. The chlorinated crude material was treated *in vacuo* to remove solvent and hydrogen chloride, and then distilled to give 30 g. (57%) of *O*-propyl methylphosphonochloridothioate, b.p. 54–55°/2.0 mm).

Anal. Calcd. for $C_4H_{10}ClOPS$: P, 17.9; S, 18.6; Cl, 20.5. Found: P, 17.9; S, 18.6; Cl, 20.4; $n^{25}D$ 1.4886, lit.[9] $n^{20}D$ 1.4890.

Chlorination of Phosphonodithioic Acid, Path b.—This procedure is illustrated by the preparation of *O*-(4-nitrophenyl) methylphosphonochloridothionate. To a slurry of 222 g. (1.6 moles) *p*-nitrophenol in 1 l. of benzene was added, with stirring, 176 g. (1.6 equiv.) of methyl thionophosphine sulfide. The mixture was heated at 60–70° until complete dissolution of solids. To this solution was added dropwise with agitation at 50–60°, 298 g. (2.21 moles) of sulfuryl chloride. The clear solution began to precipitate a white solid after about half the sulfuryl chloride had been added. Upon addition of two thirds of the chlorinating agent, copious amounts of white solid were obtained in the benzene solution. A sample was withdrawn from the reaction mixture and attempts made to recrystallize the material. Although the solid dissolved in boiling xylene, the crystals formed on cooling were principally *p*-nitrophenol. The crude solid (m.p. 118–140°) was finally titurated with ether and analyzed.

Anal. Calcd. for *O*-(4-nitrophenyl) methylphosphonodithioic disulfide, $C_{14}H_{14}N_2O_6P_2S_4$: P, 12.5; S, 25.8; N, 5.6. Found: P, 12.3; S, 24.9; N, 5.4; Cl, 0.2.

On completion of the sulfuryl chloride addition, a clear solution was again obtained. The mixture was stirred for an additional 30 min. at 50–60°, then cooled and added over 20 min. to 800 ml. of a well stirred, cold saturated solution of sodium sulfite. The benzene layer was separated and the solvent removed under vacuum to give 371 g. (93%) of solid crude *O*-(4-nitrophenyl) methylphosphonochloridothionate. The material was recrystallized from methylcyclohexane to give 270 g. (68%) of product, m.p. 64–66°.

Anal. Calcd. for $C_7H_7ClNO_3PS$: P, 12.3; S, 12.7; Cl, 14.0. Found: P, 11.9; S, 12.6; Cl, 13.9.

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