Thionophosphine Sulfides. I. Preparation and Use in the Friedel–Crafts Reaction[1]

PETER E. NEWALLIS,[2a,b] JOHN P. CHUPP,[2a] AND LEO C. D. GROENWEGHE[2c]

Research Departments of the Agricultural Chemicals Division and the Inorganic Chemicals Division, Monsanto Chemical Company, St. Louis, Missouri

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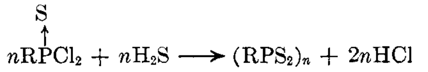
A convenient new method for the preparation of thionophosphine sulfides is described. These compounds undergo a modified Friedel–Crafts reaction with benzene and provide a route for the synthesis of unsymmetrical phosphinodithioic acids, unobtainable from reactions employing phosphorus pentasulfide (P_4S_{10}).

Only a few reports in the literature have appeared describing the synthesis of thionophosphine sulfides (II). The reaction of aromatic compounds with phosphorus pentasulfide, has been reported by Lecher, *et al.*,[3] to give aryl thionophosphine sulfides. Fay and Lankelma[4] obtained Δ^2-cyclohexenylthionophosphine sulfide from the reaction of phosphorus pentasulfide and a large excess of cyclohexene. To our knowledge, the only other reported case of the preparation of a thionophosphine sulfide (II) was that by Kinnear and Perren,[5] who obtained ethylthionophosphine sulfide by partial hydrolysis of the reaction product obtained from hydrogen sulfide and the ethyl chloride–phosphorus trichloride–aluminum chloride complex. They were not successful, however, in obtaining methylthionophosphine sulfide by this procedure.

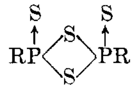
We have found that thionophosphine sulfides (II) can be prepared in excellent yields from alkyl or aryl phosphonothionic dichlorides (I) and hydrogen sulfide at elevated temperatures. The temperature at which reaction occurred was dependent upon the dichloride used. Excess hydrogen sulfide and prolonged heating had no detectable effect on the yield or quality of the product. The crude products generally had wide melting ranges and higher molecular weight values (see Table I) than calculated for dimer[6] (II, $n = 2$), suggesting the presence of trimer (II. $n = 3$) or higher polymers. Purification could be accomplished to a limited degree by recrystallization from chlorobenzene. These compounds were generally high melting solids (see Table I) which were insoluble in most aprotic solvents and which reacted with protonic solvents.[7]



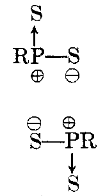
$$n\mathrm{R}\overset{\overset{\displaystyle S}{\uparrow}}{\mathrm{P}}\mathrm{Cl}_2 + n\mathrm{H}_2\mathrm{S} \longrightarrow (\mathrm{RPS}_2)_n + 2n\mathrm{HCl}$$

I II

Two plausible structures have been proposed for the dimeric form of II; a cyclic covalent form[4] III and a bimolecular associated dipolar form[3] IV. A three dimensional X-ray diffraction analysis[8] of methylthionophosphine sulfide (Va) confirmed our finding that it was predominantly dimeric and the bond distances are in good agreement with those reported in the literature[9] for the corresponding covalent bonds (see Fig. 1). No evidence was obtained for the existence of any appreciable amount of *cis* isomer from the x-ray or the hydrogen n.m.r. data[10] of methylthionophosphine sulfide. The infrared spectra of these compounds showed the characteristic absorption bands for the various R groups.



III



IV

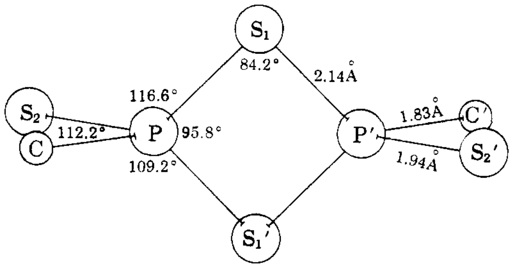


Fig. 1.—X-Ray data for methylthionophosphine sulfide $(CH_3PS_2)_2$.

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(2) (a) Agricultural Chemicals Division; (b) Present address: General Chemicals Division, Allied Chemicals Corp., Morristown, N. J.; (c) Inorganic Chemicals Division.

(3) H. Z. Lecher, R. A. Greenwood, K. C. Whitehouse, and T. H. Chao, *J. Am. Chem. Soc.*, **78**, 5018 (1956).

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

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

(6) Excellent agreement for phenylthionophosphine sulfide was obtained by us and by Lecher *et al.* (ref. 3).

(7) Some of these reactions are the subject of a forthcoming publication.

(8) We are indebted to Dr. P. J. Wheatley of our Zurich Research Laboratories for making these data available prior to publication, see *J. Chem. Soc.*, 300 (1962).

(9) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, 1948, p. 167; P. J. Wheatley, *J. Chem. Soc.*, 523 (1960).

(10) Only two distinct peaks were observed downfield from tetramethylsilane. We would anticipate four peaks if any appreciable amount of *cis* isomer were present, since the hydrogens of the two isomers are in different environments. Because of its low solubility, the sample in carbon tetrachloride was heated to *ca.* 80° in a sealed tube and the NMR spectrum was rapidly taken. We are grateful to Dr. W. H. Urry for performing this experiment.

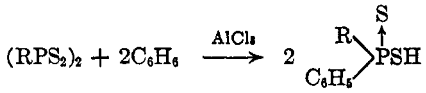
TABLE I

PHYSICAL AND ANALYTICAL DATA OF THIONOPHOSPHINE SULFIDES $(RPS_2)_2$

R	Reaction temp.	Yield, %	M.p. °C.	Phosphorus, % Calcd.	Phosphorus, % Found	Sulfur, % Calcd.	Sulfur, % Found	Mol. wt. Calcd.	Mol. wt. Found
CH_3	160–215	99	200–208					220	235 (220.3)[b]
			206–211[a]	28.2	27.9	58.4	58.4		
C_2H_5	165–205	98	142–147					248	249
			146–148[a]	25.0	24.2				
C_3H_7	170–205	80	86–96					276	301
			97–99[a]	22.5	21.9				
i-C_3H_7	170–205	92	160–175					276	298
			180–181.5[a]	22.4	21.8	46.4	46.5		
n-C_4H_9	180–205	94	105–110	20.4	20.2			304	314
C_6H_5	215–240	96	215–232					344	342
			233–243[a]	18.0	17.4	37.2	37.4		
C_6H_{11}	200–215	86	138–155					356	419
			189–192[a]	17.5	17.2	36.6	36.8		

[a] Recrystallized from chlorobenzene. [b] Obtained by Dr. P. J. Wheatley by X-ray.

Thionophosphine sulfides (V) were found to undergo the Friedel–Crafts reaction with benzene in a facile manner. This reaction appears to be general for the preparation of phosphinodithioic acids (VI) with one aromatic group and was found to proceed according to the following equation:



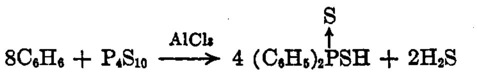
$$(RPS_2)_2 + 2C_6H_6 \xrightarrow{AlCl_3} 2\ (R)(C_6H_5)P(\rightarrow S)SH$$

Va. R = CH_3 VIa. R = CH_3
b. R = C_2H_5 b. R = C_2H_5
c. R = n-C_3H_7 c. R = n-C_3H_7
d. R = i-C_3H_7 d. R = i-C_4H_7
e. R = n-C_4H_9 e. R = n-C_4H_9
f. R = C_6H_5 f. R = C_6H_5

The synthesis of phosphinodithioic acids has been accomplished by the Grignard reaction with phosphorus pentasulfide,[11,12] by the addition of sulfur to secondary phosphines,[13] from phosphinothionic chlorides and sodium sulfhydrate[14] and by the Friedel-Crafts reaction of benzene with phosphorus pentasulfide.[15]

While the Grignard and Friede–Crafts procedures can be employed only for making symmetrical phosphinodithioic acids, the other methods suffer from the disadvantage of affording low yields of product or from difficulty in obtaining the requisite starting materials.

A study of the reaction variables for the synthesis of VIf from Vf was undertaken to obtain a comparison with the phosphorus pentasulfide method. Higgins *et al.*[15] reported a crude yield of 80% using an 8:1 molar ratio of aluminum chloride to phosphorus pentasulfide and a reflux period of eight hours. Decreased yields were obtained when the amount of aluminum chloride was reduced. With Vf, we obtained a crude yield of 95% using a 2:1 molar ratio of aluminum chloride to Vf (as monomer) and an eight-hour reflux period.[16]



$$8C_6H_6 + P_4S_{10} \xrightarrow{AlCl_3} 4\ (C_6H_5)_2P(\rightarrow S)SH + 2H_2S$$

No decrease in yield was encountered with molar excesses of aluminum chloride above the 2:1 ratio. However, decreased yields were obtained with lower ratios (see Table II).

TABLE II

EFFECT OF CATALYST CONCENTRATION ON YIELD OF $(C_6H_5)_2$-PSSH[c]

Ratio, $AlCl_3$–$C_6H_5PS_2$	Yield, %
4.0	89[a]
3.0	89[a]
2.0	89[a]
1.5	71
1.0	76[b]

[a] Crude yield was 95%. [b] Crude yield. [c] Reaction time was eight hours.

The physical and chemical properties of VIf prepared by this method were in agreement in every detail with an authentic sample.[15] No depression in the melting point of an admixture of both samples was observed. Both samples exhibited the characteristic SH absorption band[17] at 2300 cm.$^{-1}$ and the phosphorus n.m.r. spectra of these materials showed a chemical shift of −52.3 p.p.m. (relative to 85% phosphoric acid).

The phosphinodithioic acids (VI) (see Table III) were light green liquids[18] which slowly decomposed on standing at room temperature. Conversion to the corresponding white crystalline ammonium salts was accomplished by passing ammonia into a benzene solution of VI (see Table IV). Nickel salts of VI were prepared from aqueous solutions of the appropriate ammonium salts and nickel chloride.

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[11] L. Malatesta and R. Pizzotti, *Gazz. Chim. ital.*, **76**, 167 (1946).

[12] L. Malatesta, *Gazz. chim. ital.*, **77**, 509 (1947).

[13] W. Hofman and F. Mahla, *Ber.*, **25**, 2436 (1892); L. Malatesta, *Gazz. chim. ital.*, **77**, 518 (1947).

[14] T. A. Mastryukova, A. E. Shipov, and M. I. Kabachnik, *J. Gen. Chem. USSR*, **31**, 507 (1961).

[15] W. A. Higgins, P. W. Vogel, and W. G. Craig, *J. Am. Chem. Soc.*, **77**, 1864 (1955).

[16] An eight-hour reflux period was maintained in this study for purposes of comparison. Observations indicated a much shorter period might be used without affecting the yield.

[17] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, New York, 2nd ed., 1958, p. 350.

[18] Except for VIb and VIf, which were white solids.

TABLE III

PHOSPHINODITHIOIC ACIDS[a]

$R(C_6H_5)PSSH$

R	Reflux period, hr.	Yield, %	n^{22}_{D}	M.p. b.p.(mm.)	N.m.r.[f] (p.p.m.)	Phosphorus, %		Sulfur, %	
						Calcd.	Found	Calcd.	Found
CH_3	4[b]	72	1.6787	[c]	−52.4	16.5	16.4	34.0	33.8
C_2H_5	8	79		64.5[d]	−62.8	15.3	15.1	31.6	31.6
i-C_3H_7	8	81	1.6354	92/0.001 mm.	−74.6	14.4	14.6	29.8	29.7
n-C_4H_9	4	92	1.6222	[c]	−60.5	13.5	12.9	27.8	27.7
C_6H_5	8	89		54–55[e]	−52.3	12.4	12.2	25.6	25.6

[a] $AlCl_3/RPS_2$ ratios were 2:1. [b] Using an 8-hr. reflux period gave 75% yield. [c] Decomposed on attempted distillation. [d] Recrystallized from ethanol. [e] Recrystallized from isopropyl alcohol. [f] Relative to 85% phosphoric acid.

TABLE IV

SALTS OF PHOSPINODITHIOIC ACIDS

$R(C_6H_5)PSSM$

R	M	Yield	M.p., °C	Phosphorus, %		Sulfur, %		Nitrogen, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
CH_3	NH_4	95	160–161	15.2	15.2	31.2	31.6	6.8	6.2
	Ni	96	203–206	14.3	14.6	29.6	29.7		
C_2H_5	NH_4	95	166–170	14.2	14.3	29.2	29.3	6.4	6.4
	Ni	90	164–165	13.4	13.9	27.8	27.3		
i-C_3H_7	NH_4	89	148–158	13.3	13.2	27.5	27.6	6.0	6.2
	Ni	100	206–207	12.7	12.9	26.2	26.1		
n-C_4H_9	NH_4	100	120–122	12.6	12.3	25.9	25.3	5.7	5.4
	Ni	99	154–156	11.8	12.2	25.3	25.8		

Experimental

Preparation of Thionophosphine Sulfides.—The reaction vessel consisted of a 1-l. resin flask equipped with a stirrer, water cooled reflux condenser,[19] gas inlet tube, and thermometer. A weighed hydrogen sulfide cylinder was connected in turn to a flowmeter and a trap and thence to an open 7-mm. o.d. gas inlet tube. The condenser outlet was connected to a safety trap and thence to a hydrogen chloride scrubber. Unchanged hydrogen sulfide was burned in a gas flame.

The appropriate alkyl or aryl phosphonothionic dichloride (I) (500–700 g.) was charged into the reaction flask[20] and was heated to near the reflux temperature with stirring (see Table I). Hydrogen sulfide was introduced subsurface at a rate of *ca.* 0.2 g. per min. The reflux temperature slowly increased as the reaction progressed and the rate of hydrogen sulfide addition was increased to *ca.* 0.5–1.0 g. per min. The reaction temperature was finally adjusted above the melting point of the thionophosphine sulfide (see Table I). The heating was terminated after hydrogen chloride evolution had nearly ceased. The reaction was complete in about 16–24 hr. after a 2–4 *M* excess of hydrogen sulfide had been introduced. The yellow melt was allowed to cool, broken out of the reaction flask, and pulverized under hexane. The solid was then quickly filtered and placed in a vacuum desiccator. The crude materials were of adequate purity for further synthesis. Smaller amounts were conveniently made in small wide-necked, round-bottomed flasks.

Purification was accomplished by recrystallization from chlorobenzene.

Phosphinodithioic Acids.—A suspension of 0.1 mole of thionophosphine sulfide in 178 ml. of benzene at 50° was treated with 0.4 mole of aluminum chloride added in three portions. The reaction mixture was heated at incipient reflux for 8 hr., cooled, and poured into an ice water-hydrochloric acid mixture. Extraction with benzene and subsequent removal of solvent gave the crude phosphinodithioic acid. The purified product was obtained by treating the benzene extracts with dilute potassium hydroxide solution, acidification of the aqueous solution, extraction with benzene, and subsequent removal of solvent under reduced pressure.

Ammonium Phosphinodithioates.—An excess of ammonia was introduced subsurface into a solution of 0.03 mole of phosphinodithioic acid in 100 ml. of benzene. A white precipitate formed which was filtered, washed with fresh benzene, and air dried.

Nickel Phosphinodithioates.—A solution of 0.01 mole of nickel chloride in 50 ml. of water was added dropwise with vigorous stirring to a solution of 0.02 mole of ammonium phosphinodithioate in 100 ml. of water. A purple precipitate was formed which was filtered, washed with water, and air dried.

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(19) When a Dry Ice–acetone cooled condenser was employed, the reaction proceeded somewhat faster and only a slight excess over stoichiometric amounts of hydrogen sulfide was necessary. Care was taken, however, to avoid a decrease in temperature due to excessive build-up of refluxing hydrogen sulfide in the reaction vessel.

(20) It was found advantageous when preparing Va to charge in about 10% by weight of the methylthionophosphine sulfide in order to hasten initial reaction by increasing the temperature of the reaction mixture.