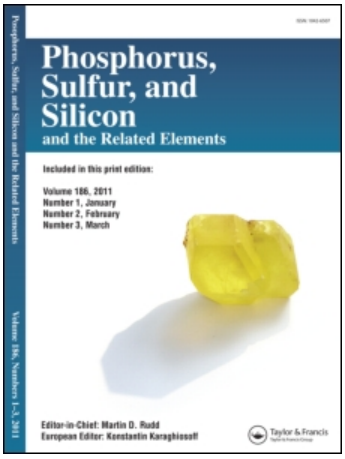

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SYNTHESIS AND CHARACTERIZATION OF 2-MERCAPTO-2-THIONO-1,3,2-DIOXAPHOSPHOLANES AND DIOXAPHOSPHORINANES

H. P. S. Chauhan[a]; C. P. Bhasin[a]; G. Srivastava[a]; R. C. Mehrotra[a]
[a] The Chemical Laboratories, University of Rajasthan, Jaipur, India

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SYNTHESIS AND CHARACTERIZATION OF 2-MERCAPTO-2-THIONO-1,3,2-DIOXAPHOSPHOLANES AND DIOXAPHOSPHORINANES

H. P. S. CHAUHAN, C. P. BHASIN, G. SRIVASTAVA and R. C. MEHROTRA*

The Chemical Laboratories, University of Rajasthan, Jaipur-302004, India

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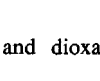
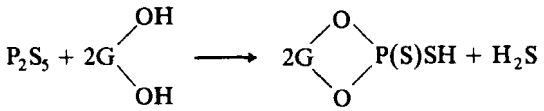
2-Mercapto-2-thiono-1,3,2-dioxaphospholanes and dioxaphosphorinanes,  have been synthesized by the reactions of phosphorus pentasulphide with some 1,2-diols (*viz.*, butane-2,3-diol and 2,3-dimethylbutane-2,3-diol) and 1,3-diols (*viz.*, 2-methylpentane-2,4-diol, 2,2-dimethylpropane-1,3-diol and 2,2-diethylpropane-1,3-diol) in 1 : 2 molar ratio in dry benzene. These volatile compounds have been purified by distillation under reduced pressure. The 2-methylpentane-2,4-diol derivative, however, decomposed during attempted distillations. These new compounds have been characterized by elemental analysis, molecular weight determinations, measurement of pK_a values and IR as well as NMR spectroscopic studies. The ammonium and sodium salts of some of these acids have also been characterized.

INTRODUCTION

Amongst the ligands containing both phosphorus and sulphur atoms, the coordination chemistry of which has been extensively studied, the dialkyldithiophosphoric acids,[1] $(RO)_2PSSH$, occupy a prominent place. These find numerous agricultural and industrial applications (e.g., as pesticides, antioxidants, oil additives, coloring agent for plastics and analytical reagents). In recent years more emphasis has been given to the study of bonding modes of these versatile ligands towards transition as well as main group metals. Surprisingly, the chemistry of corresponding cyclic dithiophosphates derived from glycols has been little explored although some of these have been described in patent literature.[2-9] Pudovik *et al.*[10] have reported a systematic study of the polytransesterification of diethyldithiophosphoric acid with 1,2- and 1,3-diols. Pudovik *et al.*[11] have also made a systematic study of the reactions of a few glycols with phosphorus pentasulphide and found that ethylene and trimethylene glycols gave oily linear polymers while propane-1,2-diol, butane-2,3-diol and butane-1,3-diol gave mixtures of polymeric derivatives and the cyclic 2-mercapto-2-thiono-1,3,2-dioxaphospholane and dioxaphosphorinane. Thus, the cyclisation appears to be governed by the nature of the alkylene chain of the glycol. The present study is concerned with the corresponding cyclic derivatives of glycols (*viz.*, butane-2,3-diol, 2,3-dimethylbutane-2,3-diol, 2-methylpentane-2,4-diol, 2,2-dimethylpropane-1,3-diol and 2,2-diethylpropane-1,3-diol) containing branched alkylene chains.

RESULTS AND DISCUSSION

Alkylene dithiophosphoric acids (2-mercapto-2-thiono-1,3,2-dioxaphospholanes and dioxaphosphorinanes) have been prepared by the reactions of phosphorus pentasulphide with corresponding glycols in 1 : 2 molar ratio:

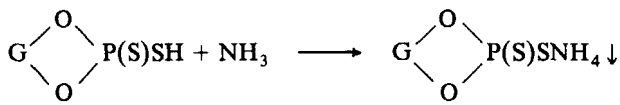


$$P_2S_5 + 2G(OH)_2 \longrightarrow 2G(O_2)P(S)SH + H_2S$$

[G = $(CH_3)CHCH(CH_3)$—, —$(CH_3)_2CC(CH_3)_2$—, —$(CH_3)_2CCH_2CH(CH_3)$—, —$CH_2C(CH_3)_2CH_2$— and —$CH_2C(C_2H_5)_2CH_2$—]

These reactions have been carried out by stirring the reagents in dry benzene at ~ 50° for 8–12 hours. The completion of the reaction is indicated by almost complete dissolution of phosphorus pentasulphide. The products obtained have been purified by distillation under reduced pressure. The 2-methylpentane-2,4-diol (hexylene glycol) derivative, however, decomposed during attempted distillation. These white crystalline solids or colourless viscous liquids are soluble in common organic solvents. Molecular weight determinations in freezing benzene exhibit their monomeric nature. pK_a values under identical conditions for the dialkyldithiophosphoric acids and alkylene dithiophosphoric acids are quite similar (2.65–2.67) which indicate that these are strong acids and pK_a values are not affected by changing alkylene or alkyl groups by each other (Table I).

Ammonium salts of these alkylene dithiophosphoric acids have been prepared by passing dry ammonia through their benzene solutions:



$$G(O_2)P(S)SH + NH_3 \longrightarrow G(O_2)P(S)SNH_4\downarrow$$

TABLE I

pK_a values for some dialkyldithiophosphoric acids and alkylene dithiophosphoric acids

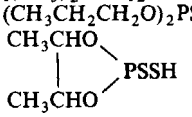
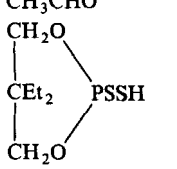
S. No.	Compound	pK_a
1	$[(CH_3)_2CHO]_2PSSH$	2.67
2	$(CH_3CH_2CH_2O)_2PSSH$	2.66
3		2.65
4		2.65

TABLE II

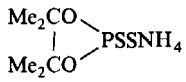
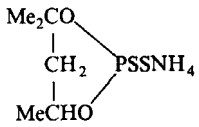
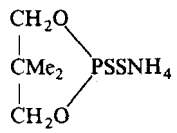
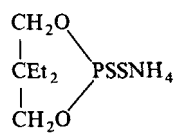
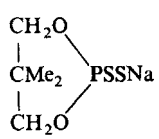
Synthesis and properties of alkylene dithiophosphoric acids

S. No.	Reactants (g)	(g)	Molar ratio	Reaction condition	Product (g,/ yield of distilled product)	m.p. (°C)	b.p. (°C/mm)	Acidity[a] (%)	Physical State	Anals. % sulphur Found (Calcd)	Mol. Wt. Found (Calcd)
1	P_2S_5 (24.40)	+ MeCHOH | MeCHOH (19.78)	1 : 2	stirred at ~ 50° for 8 h. in benzene	MeCHO | PSSH | MeCHO (24.50, 60.6)	—	100/0.3	97.5	colourless liquid	34.56 (34.78)	186 (184)
2	P_2S_5 (8.32)	+ Me_2COH | Me_2COH (8.71)	1 : 2	stirred at ~ 40° for 10 h. in benzene	Me_2CO | PSSH | Me_2CO (8.72, 54.8)	60	95/0.2	97.7	white crystalline solid	29.72 (30.19)	202 (212)
3	P_2S_5 (8.63)	+ Me_2COH | CH_2 | MeCHOH (9.17)	1 : 2	stirred at ~ 50° for 8 h. in benzene	Me_2CO | CH_2 PSSH | MeCHO (14.25, 86.5) undistilled	—	decomposed	87.7	colourless viscous liquid	29.90 (30.19)	—
4	P_2S_5 (17.48)	+ CH_2OH | CMe_2 | CH_2OH (16.38)	1 : 2	stirred at ~ 50° for 12 h. in benzene	CH_2O | CMe_2 PSSH | CH_2O (22.52, 72.4)	78	120/1.0	98.9	white crystalline solid	31.62 (32.32)	201 (198)
5	P_2S_5 (11.17)	+ CH_2OH | CEt_2 | CH_2OH (13.12)	1 : 2	stirred at ~ 50° for 12 h. in benzene	CH_2O | CEt_2 PSSH | CH_2O (15.60, 68.6)	86	130/0.3	99.0	white crystalline solid	28.50 (28.32)	238 (226)

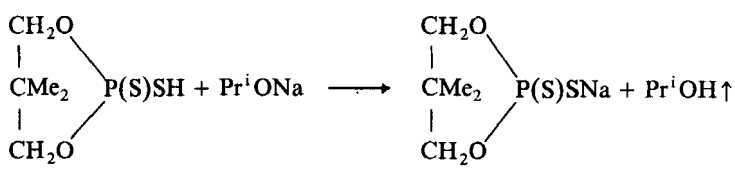
[a] Determined by titrating the product with standard alkali solution.

TABLE III

Synthesis and properties of a few ammonium and sodium salts of alkylene dithiophosphoric acids.

S. No.	Compound	Yield (%)	m.p. (°C)	Analyses Found (Calcd.) S	C	H
1		70.4	215–25 (dec.)	26.79 (27.95)	29.74 (31.44)	5.24 (5.07)
2		72.3	210–16 (dec.)	27.85 (27.95)	30.22 (31.44)	5.32 (5.07)
3		84.4	230–40 (dec.)	28.42 (29.77)	—	—
4		82.6	257–63 (dec.)	26.74 (26.34)	—	—
5		88.6	262–75 (dec.)	28.64 (29.01)	—	—

Sodium salt of neopentylene dithiophosphoric acid has been prepared by the reaction of acid with sodium isopropoxide in 1 : 1 molar ratio:



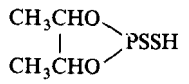
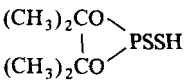
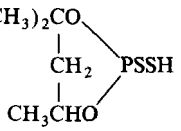
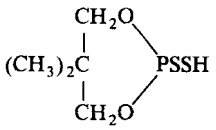
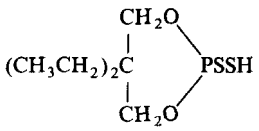
These ammonium and sodium salts are white powders insoluble in benzene, diethylether, chloroform, carbon tetrachloride, hexane and light petroleum, but they dissolve in alcohols and are sparingly soluble in water.

IR Spectra

The ir spectra have been recorded in the range 4000–200 cm^{-1} and assignments made on the basis of earlier investigations.[1,11,12] The band in the region 2530–2430 cm^{-1} observed in the ir spectra of alkylene dithiophosphoric acids due to ν(S—H) stretching vibrations, is absent in the spectra of their ammonium and sodium salts. The bands present in the regions 1090–990 cm^{-1} and 880–780 cm^{-1} have been

TABLE IV

PMR spectral data for alkylene dithiophosphoric acids

S. No.	Compound	Chemical shift (δ) ppm
1		1.48, d, 6H(CH_3) 3.68, s, 1H(SH) 4.35, m, 2H(CHO)
2		1.50, s, 6H(CH_3) 3.26, s, 1H(SH)
3		1.50, m, 11H(CH_3, CH_2) 3.55, s, 1H(SH) 4.85, s, 1H(CHO)
4		1.04, s, 6H(CH_3) 3.39, s, 1H(SH) 4.07, d, 4H(CH_2O)
5		0.89, t, 6H(CH_3) 1.53, q, 4H(CH_2) 3.13, s, 1H(SH) 4.10, d, 4H(CH_2O)

d = doublet, m = multiplet, q = quartet, s = singlet, t = triplet.

assigned to (P)—O—C and P—O—(C) stretching vibrations respectively. A strong band between 950–925 cm^{-1} may be attributed to the vibrations of the dioxaphospholanes and dioxaphosphorinanes.[13] A sharp intense peak in the region 720–590 cm^{-1} has been assigned to ν(P=S) vibrations. The bands present in the region 540–470 cm^{-1} are attributed to P—S symmetric and asymmetric vibrations.

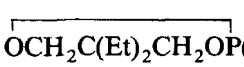
^{1}H NMR Spectra

Due to insolubility of ammonium and sodium salts in suitable organic solvents such as CCl_4 and $CDCl_3$ etc., the PMR spectra of only cyclic dithiophosphoric acids could be recorded and data are summarized in Table IV.

In addition to a sharp singlet at σ3.13–3.68 ppm due to S—H protons the spectra show the characteristic proton resonances of the corresponding glycoxy groups. The peaks due to the protons on carbon atom nearest to phosphorus atom are doubled due to their coupling with phosphorus.

^{31}P NMR Spectra

The ^{31}P NMR spectrum of only one representative compound



has been recorded. Only one sharp peak at 75.8 ppm was obtained which is almost equal to the ^{31}P NMR chemical shift for the corresponding dialkyldithiophosphoric acids.[14]

EXPERIMENTAL

Benzene was dried by standard methods and glycols were distilled before use. Phosphorus pentasulphide (Sisco) was used as received. Molecular weights were determined cryoscopically in benzene. pK_a values of the acids in N/100 (50% alcoholic) solutions were measured at 30°C on Elico LI 120 digital pH meter using the method of Albert and Sergent.[15] Ir spectra of the neat liquids or Nujol mulls were recorded on a Perkin-Elmer 557 spectrometer. NMR spectra in carbon tetrachloride solutions were recorded on a Varian XL 100A spectrophotometer using TMS as external standard. Sulphur was estimated gravimetrically as barium sulphate.

Typical methods used for the preparation of 2-mercapto-2-thiono-1,3,2-dioxaphospholanes and dioxaphosphorinanes and their ammonium or sodium salts are described below in brief:

(i) To P_2S_5 (17.48 g) in benzene (100 ml) was added 2,2-dimethylpropane-1,3-diol (16.38 g) and the contents were stirred for about 12 hours at ~ 50°C till there was no further evolution of H_2S gas and almost all the P_2S_5 was dissolved. Now the contents were filtered to remove the trace amounts of unreacted P_2S_5. Solvent was removed from the filtrate under reduced pressure and the white sticky solid (28.88 g, 95.7% yield) so obtained was distilled at 120°C/1 mm to give a white crystalline solid.
(ii) To the benzene solution of 2-mercapto-2-thiono-1,3,2-dioxaphospholane or dioxaphosphorinane, dry ammonia gas was passed for half an hour. An exothermic reaction occurred with the precipitation of ammonium salt. Now contents were allowed to settle overnight and filtered to get white powder which was washed twice with benzene.
(iii) To sodium isopropoxide (prepared by dissolution of 0.58 g sodium in ~ 15 ml of isopropanol) was added neopentylene dithiophosphoric acid, $\overline{OCH_2C(CH_3)_2CH_2OP(S)SH}$ (5.27 g) in benzene (~ 25 ml) drop by drop. After heating the contents for about one hour, solvent was removed under reduced pressure; white solid thus obtained was washed twice with benzene and dried to give white powder (4.90 g, 88.6% yield).

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