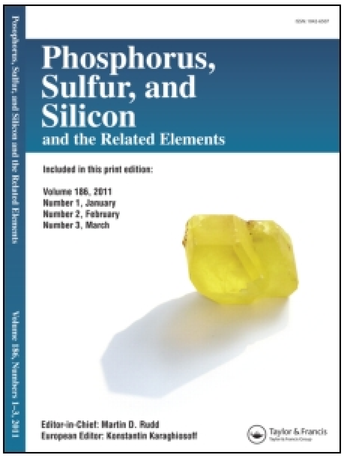

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Synthesis and Properties of Sulfuryl Chloride Derivatives of Ammonium Dialkyl/Alkylene Dithiophosphates in Different Molar Ratios

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The reaction of sulfuryl chloride with ammonium salts of alkylene (dialkyl)dithiophosphate, $\overline{OGOP}S_2NH_4$*;G=*$—CH_2CH_2CHMe$*,* $—CH_2C(Me)_2CH_2$*-,* $(RO)_2PS_2NH_4$*, and R =* $i\text{-}C_3H_7$*; in 1:1 and 1:2 molar ratios in refluxing benzene solution yields orange-yellow semisolids of the type* $(RO)_2PS_2R$*,* $OGOPS_2R'$*,* $\{(RO)_2PS_2\}R''$*, and* $\{OGOPS_2\}_2R''$*, where* $R' = SO_2Cl$ *and* $R'' = SO_2$*], which are hygroscopic in nature. These newly synthesized complexes have been characterized by physico-chemical and spectroscopic techniques (MW, IR,* ^1H*, and* ^{31}P *NMR). On the basis of the above studies, the formation of (S)-P-S-S chemical linkage has been established.*

Keywords 2-[(Chlorosulfonyl)thio]-4-methyl-1,3,2dioxaphosp- hinanesulfide; IR; NMR spectra; *O*,O′,O′tetraethyl[sulfonylbis(thio)]bis(phosphonothioate)

INTRODUCTION

A lot of work has been reported on metal and organometal derivatives of O,O′-alkylene dithiophosphates from our laboratories,[1–9] among them, the organic derivatives have a wide range of utility as contact insecticides,[10] acaricides[11] and ovicides.[12,13] In continuation of our earlier investigation,[14–20] it was considered of interest to extend the research work on the synthesis and properties of dialkyl/alkylene dithiophosphates derivatives of sulfuryl chloride in 1:1 and 1:2 ratios. N $\overset{+}{N}$

RESULTS AND DISSCUSION

Reactions of sulfuryl chloride with ammonium dialkyl (alkylene) dithiophosphate in a 1:1 molar ratio in refluxing benzene yielded the product

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of following type:

$$(\mathrm{RO})_2\mathrm{P(S)}\bar{\mathrm{S}}\overset{+}{\mathrm{N}}\mathrm{H}_4 + \mathrm{SO_2Cl_2} \rightarrow (\mathrm{RO})_2\mathrm{P(S)SS(O)_2Cl} + \mathrm{NH_4Cl}\downarrow \qquad (1)$$

$$\overline{\mathrm{OGOP}}\mathrm{(S)}\bar{\mathrm{S}}\overset{+}{\mathrm{N}}\mathrm{H}_4 + \mathrm{SO_2Cl_2} \rightarrow \overline{\mathrm{OGOP}}\mathrm{(S)SS(O)_2Cl} + \mathrm{NH_4Cl}\downarrow \qquad (2)$$

Similarly, reactions of sulfuryl chloride with ammonium dialkyl (alkylene) dithiophosphate in a 1:2 molar ratio in refluxing benzene yielded the product of following type:

$$2(\mathrm{RO})_2\mathrm{P(S)}\bar{\mathrm{S}}\overset{+}{\mathrm{N}}\mathrm{H}_4 + \mathrm{SO_2Cl_2} \rightarrow (\mathrm{RO})_2\mathrm{P(S)SS(O)_2S(S)P(OR)_2} + 2\mathrm{NH_4Cl}\downarrow \qquad (3)$$

$$2\overline{\mathrm{OGOP}}\mathrm{(S)}\bar{\mathrm{S}}\overset{+}{\mathrm{N}}\mathrm{H}_4 + \mathrm{SO_2Cl_2} \rightarrow \overline{\mathrm{OGOP}}\mathrm{(S)SS(O)_2S(S)POGO} + 2\mathrm{NH_4Cl}\downarrow \qquad (4)$$

It is interesting to note here that the sulfur atom of sulfuryl chloride has been retained in the products, which is also revealed by sulfur analysis. The products thus obtained are orange-yellow semisolids with a foul-smelling odor and are found to be soluble in common organic solvents. On heating above $\sim$120°C, these compounds neither evolve SO_2 gas nor H_2S gas (tested by acidic $K_2Cr_2O_7$ paper and lead acetate paper), but they convert into a blackish mass.

IR Spectra

The IR spectra of these derivatives show the following characteristic changes (Table I):

1) The νSO_2 absorption band present in the region 1180–1170 cm^{-1} and 1410–1380 cm^{-1} for ν_{sym} and ν_{asym}, respectively, which shows a slight shift (10–20 cm^{-1}) toward a lower wave number, for (1:1) derivatives and an absorption band present in the region 1180–1170 cm^{-1} and 1410–1380 $cm^{-1}$for $\nu_{sym}$and ν_{asym} vibrations show a strong shift toward a lower wave number (30–55 cm^{-1}), due to the absence of the electrical effect of chlorine atom for (1:2) derivatives.
2) The absorption band present in the region 1015–975 cm^{-1} and 870–850 cm^{-1} has been observed for ν(P)—O—C and νP—O(C) vibrations, respectively, for (1:1) derivatives, and the absorption band present in the region 1045—990 cm^{-1} and 890–865 cm^{-1} has been observed for ν(P)—O—C and νP—O(C) vibrations , respectively, for (1:2) derivatives.

TABLE I IR Spectral Data of Sulfuryl Chloride Derivatives of Ammonium Dialkyl/Alkylene Dithiophosphate

S. no.	Compounds	P)O—C	P—O(C)	Ring vibration	P═S	P—S	SO_2as (sym.)	**S—Cl (S—S)**
1	$\overline{OCH_2CH_2CHMeOP}(S)SS(O)_2Cl$	1010	875	990	680	615	1410 (1180)	765 (440)
2	$\overline{OCH_2C(Me)_2CH_2OP}(S)SS(O)_2Cl$	1015	870	965	700	615	1409 (1175)	760 (435)
3	$(iC_3H_7O)_2P(S)SS(O)_2Cl$	980	855	—	660	598	1405 (1176)	755 (432)
4	$\{\overline{OCH_2CH_2CHMeOP}(S)S\}_2SO_2$	1040	889	970	680	610	1330 (1140)	(412)
5	$\{\overline{OCH_2C(Me)_2CH_2OP}(S)S\}_2SO_2$	1040	880	955	679	610	1330 (1133)	(408)
6	$\{i{-}C_3H_7O)_2P(S)S\}_2SO_2$	990	865	—	665	575	1325 (1135)	(375)

3) Ring vibrations for 1:1 molar ratio type derivatives have been observed in the ranges 990–965 cm^{-1} and 970–940 cm^{-1} for (1:2) derivatives.
4) The νO=S—Cl absorption band present in the region 790–750 cm^{-1}, which shifted toward lower wave numbers (20–30 cm^{-1}) for (1:1) derivatives and $\nu S(O)_2Cl$ absorption band, disappeared in the region 790–750 cm^{-1} for (1:2) derivatives.
5) A νP=S absorption band present in the region 700–645 cm^{-1} and 615–598 cm^{-1} for νP—S vibrations for (1:1) derivatives, and an absorption band present in the region 685–660 cm^{-1} for νP=S vibrations, and 610–575 cm^{-1} for the νP=S absorption band have been observed for (1:2) derivatives.
6) A new νP—S—S(O) absorption band has been observed in the region 440–430 cm^{-1} for (1:1) derivatives, and a new absorption band has been observed in the region 362–412 cm^{-1} for νP—S—S(O) vibrations, which support the formation of (S)—P—S—S chemical linkage for (1:2) derivatives.

NMR (^{1}H and ^{31}P) Spectra

The ^{1}H NMR spectra of previously discussed derivatives have been recorded in Benzene/$CDCl_3$ and are tabulated in Table II. In ^{1}H NMR spectra, an usual (n + 1) splitting pattern has been observed for all the

TABLE II NMR ^{1}H and^{31}P Spectral Data of Sulfuryl Chloride Derivatives of Ammonium Dialkyl/Alkylene Dithiophosphate

S. No.	Compounds	^{1}H (ppm)	^{31}P (ppm)
1	$\overline{OCH_2CH_2CHMeOP}(S)SS(O)_2Cl$	1.45, d, 3H (CH_3); 2.4–2.8, m, 2H (CH_2); 4.3–5.1, m, 3H(OCH, OCH_2)	83.51
2	$\overline{OCH_2C(Me)_2CH_2OP}(S)SS(O)_2Cl$	1.67, s, 6H(CH_3); 5.01, d, 4H (CH_2O)	83.67
3	$(iC_3H_7O)_2P(S)SS(O)_2Cl$	1.45–1.61, d, 12H(CH_3)	76.31
4	$\{\overline{OCH_2CH_2CHMeOP}(S)S\}_2SO_2$	1.36, d, 6H (CH_3); 1.49–1.55, m, 4H (CH_2); 4.37–4.55, m, 6H (OCH_2)	62.21
5	$\{\overline{OCH_2C(Me)_2CH_2OP}(S)S\}_2SO_2$	1.25, s, 12H (CH_3); 4.01–4.21, d, 8H (OCH_2)	59.23
6	$\{i\text{-}C_3H_7O)_2P(S)S\}_2SO_2$	4.09–4.3, m, 4H (OCH); 1.89, d, 24H (CH_3)	58.8

resonance signals for protons. The resonance signals for the CH_3 proton have been observed in the range 1.25–1.67 ppm. The protons, which are not directly attached to oxygen and phosphorus, do not show significant deshielding of resonance signals (1.4–2.8 ppm). A multiplet has been observed for the glycoxy proton (CHOP and CH_2OP) in the range 4.0–5.1 ppm due to coupling with the magnetically active phosphorus atom.

^{31}P NMR resonance signals have been observed in the range 83.5–78.3 ppm for 1:1 derivatives and 58.8–62.2 ppm in 1:2 derivatives. Only one sharp resonance signal has been observed, which indicates the presence of one type of chemically/magnetically equivalent phosphorus atom. The phosphorus atom of the dithiophosphate moiety that appears in the range δ 83–77 ppm is variably deshielded in comparison to its position in parent dialkyl (alkylene) dithiophosphate (15–20 ppm) in 1:1 derivatives. A slightly higher upfield shifting of ^{31}P resonance signal (15–25 ppm) has also been observed for 1:2 derivatives. It appears that due to the replacement of chlorine by the dithiophosphato moiety, which led to the formation of a polysulphide-type linkage (>P(S)SPS(S)<) on one hand and on the other hand sulfur being more electronegative than chlorine, which causes further deshielding of phosphorus atom.

On the basis of the previously discussed spectroscopic (IR, NMR [^1H, ^{31}P]) data, elemental analysis, and molecular weight measurement, the poly sulphide (S)P-S(O)S(O)SP(S)-type structure has been tentatively proposed for these derivatives (Figures 1 and 2).

EXPERIMENTAL

Solvents were dried by standard methods. Ammonium salt of dialkyl/alkylene dithiophosphates have been prepared by the method

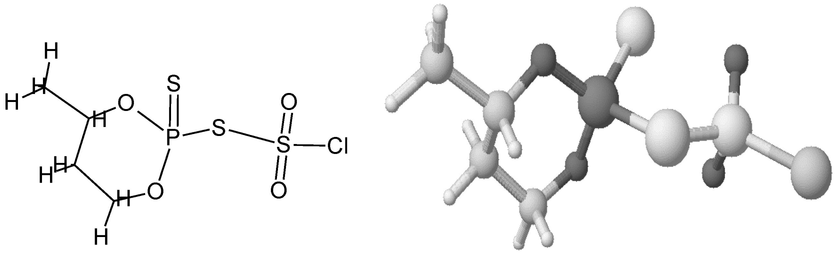

FIGURE 1 2-[(chlorosulfonyl)thio]-4-methyl-1,3,2-dioxaphosphinane 2-sulfide.

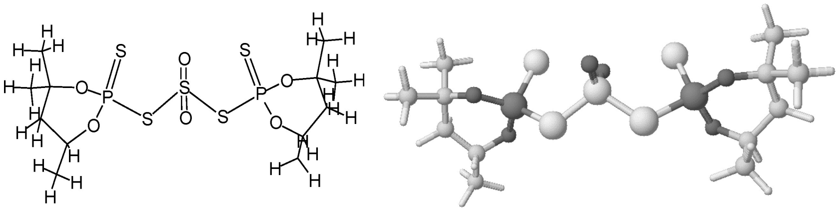

FIGURE 2 2,2′-[sulfonylbis(thio)]bis(4,4,6-trimethyl-1,3,2 -dioxaphosphinane) 2,2′-disulfide.

reported in the literature.[21] Sulphur was estimated gravimetrically as barium sulphate (messenger method)[21] and was purified by vacuum distillation. Molecular weights were determined by the Knaur vapor pressure osmometer using a chloroform solution at 45°C. IR spectra were recorded in Nujol mull (4000–200 cm^{-1}) on an FT IR spectrophotometer model Megna-IR-550 Micolac-Usa. Carbon and hydrogen analyses were performed on a Perkin Elemer CHN/O analyzer. ^{1}H NMR spectra were recorded in CDCl$_3$ solution on a 90 MHz JEOL FX 300Mhz FT NMR spectrometer using TMS as an internal reference. ^{31}P NMR were recorded in C$_6$H$_6$using H$_3$PO$_4$ as an external reference. The experimental details of the representative compounds follow. Analytical results are summarized in Table III.

Prepration of 2-[(Chlorosulfonyl)thio]-4-methyl-1,3,2-dioxaphosphinane 2-sulfide (1:1 Molar Ratio)

The mixture of sulfuryl chloride (1.22 g) and ammonium salt of 1,3-butylene dithiophosphate (1.81 g) in benzene (50–60 mL) was refluxed with constant stirring of the reaction mixture for 8–9 h. The precipitated ammonium chloride was filtered off. The solvent was removed from the filtrate in vacuo, and a orange–yellow semisolid (1.96 g, 77.02%) was obtained.

Prepration of 2,2′-[Sulfonylbis(thio)]bis(4,4,6-trimethyl-1,3,2-dioxaphosphin-ane) 2,2′-disulfide (1:2 Molar Ratio)

Ammonium salt of Neopentyldithiophosphate (3.85 g) was taken in 60–50 mL benzene, and it was refluxed with sulfuryl chloride (1.21 g) for 10–12 h. After removing the precipitate ammonium chloride by filtration, the solvent was removed under reduced pressure. A yellow semisolid was obtained as the desired product (3.136 g, 76.51%).

TABLE III Synthetic and Analytical Data of Sulfuryl Chloride Derivatives of Ammonium Dialkyl/Alkylene Dithiophosphate

S. no.	Reactant g I:1(1:2) m moles 1:1 (1:2)	SO_2Cl_2 in g 1:1(1:2) m moles 1:1 (1:2)	Product g (%)	C in (%) found (calcd)	H in (%) found (calcd)	S in (%) found (calcd)	M. wt found (calcd)
1	$\overline{\mathrm{OCH_2CH_2CHMeO}}\mathrm{P(S)SNH_4}$	1.22	$\overline{\mathrm{OCH_2CH_2CHMeO}}\mathrm{P(S)SS(O)_2Cl}$	17.61	2.79	35.51	279
	1.81 (3.42)	9.01	1.96 (77.02)	(18.01)	(3.00)	(36.02)	(282.5)
	9.01 (17.01)	(1.15)	$\{\overline{\mathrm{OCH_2CH_2CHMeO}}\mathrm{P(S)S}\}_2\mathrm{SO_2}$	—	—	45.34	—
		(8.51)	2.89 (79.11)			(44.65)	(430)
2	$\overline{\mathrm{OCH_2C(Me)_2CH_2O}}\mathrm{P(S)SNH_4}$	1.09	$\overline{\mathrm{OCH_2C(Me)_2CH_2O}}\mathrm{P(S)SS(O)_2Cl}$	20.80	2.71	33.66	289.12
	1.73 (3.85)	8.01	1.87 (78.60)	(21.39)	(3.56)	(34.22)	(296.5)
	8.51 (18.92)	(1.21)	$\{\overline{\mathrm{OCH_2C(Me)_2CH_2O}}\mathrm{P(S)S}\}_2\mathrm{SO_2}$	—	—	40.82	449
		(8.91)	3.13 (76.51)			(41.92)	(458)
3	$(\mathrm{i\text{-}C_3H_7O})_2\mathrm{PS_2NH_4}$	1.23	$(i\text{-}\mathrm{C_3H_7O})_2\mathrm{P\ (S)SS(O)_2Cl}$	23.91	3.62	31.14	—
	2.10 (3.86)	9.01	1.53 (73.10)	(24.28)	(4.72)	(32.37)	(312.5)
	9.01 (16.72)	(1.13)	$\{i\text{-}\mathrm{C_3H_7O})_2\mathrm{P(S)S}\}_2\mathrm{SO_2}$	—	—	40.01	481
		(8.31)	3.41 (83.31)			(39.18)	(490)

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