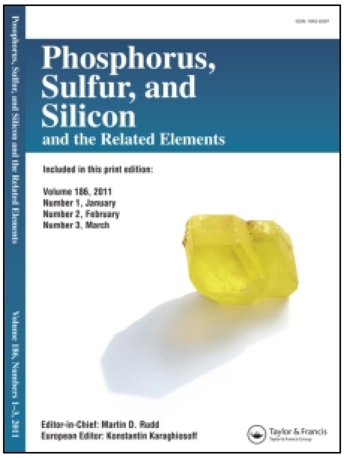

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Synthesis and Properties of 2-Alkylene/Dialkyl Dithiophosphato-2-oxo-1,3,2-dioxaphosphorinanes

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Synthesis and Properties of 2-Alkylene/Dialkyl Dithiophosphato-2-oxo-1,3,2-dioxaphosphorinanes

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Reactions of 2-chloro-2-oxo-1,3,2-dioxaphosphorinanes with ammonium alkylene/dialkyl dithiophosphates in a 1:1 molar ratio in refluxing benzene solution yields nonvolatile, yellow viscous liquids of the type $\overline{\text{OGOP}}\text{(S)S(O)}\overline{\text{POGO}}$ *and* $\text{(RO)}_2\text{P(S)S(O)}\overline{\text{POGO}}$*, respectively. [G =* $-CH_2CH_2CHCH_3-$*,* $-C(CH_3)_2CH_2CHCH_3-$*,* $-CH_2C(CH_3)_2CH_2$*; R = i-*C_3H_7*,* C_2H_5*].*

These compounds are hygroscopic and monomeric in nature. The newly synthesized derivatives have been characterized by physicochemical and spectroscopic techniques (IR, NMR [^{1}*H&*^{31}*P], and M.W).*

Keywords 2-Chloro-2-oxo-1,3,2-dioxaphosphorinanes; ammonium O; O^1-alkylene/dialkyl dithiophosphate

INTRODUCTION

The work carried out in the last two decades on the derivatives of organophosphorus ligands (cyclic phosphites,[1] dialkylphosphonates,[1] thiophosphites,[1,2] dialkyl [alkylene] dithiophosphates,[3–7] monoalkylmonosodiophosphonates,[8] and trithiophosphate were mainly centered on their metal and organometal derivatives.

In view of this, as well as the recent investigations carried out on dialkyl (aryl) phosphoryl derivatives of alkylene dithiophosphates[9] and o-alkyl and S-alkyl trithiophosphates derivatives[10] of organotin (IV), it was considered of interest to extend the present course of investigations on the synthesis and characterization of the 2-alkylene/dialkyl dithiophosphato-2-oxo-1,3,2-dioxa phosphorinanes.

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This article, is dedicated to the late Prof. Ram Charan Mehrotra, Professor Emeritus, U.O.R. Jaipur, India.

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Zwrierzak in 1967 had reported the synthesis and IR studies of cyclic hydrogen phosphates, thiophosphites,[11] and some sterically hindered cyclic hyphophosphate systems and related compounds.[12,13] The derivatives of type $\overline{\text{OGOP}}$(X) YP (Z) $\overline{\text{OGOP}}$, where X,Y,Z = O,S and Se[12,13] as well as phosphorus-containing polysulphides[14] [$R_2P(X)S_nP(X)R_2$, $R_2P(X)S_nR$] had also been reported with very little structural information.

RESULTS AND DISCUSSION

Reactions of ammonium alkylene/dialkyl dithiophosphates with 2-chloro-2-oxo-1,3,2-dioxaphosphorinanes $\overline{\text{OGOP}}$(O)Cl in a 1:1 molar ratio in anhydrous benzene yield the derivatives of the type 2-dialkyl dithiophosphato-2-oxo-1,3,2-dioxaphosphorinanes $(RO)_2P(S)S(O)\overline{\text{POGO}}$ and bis-(2-thiono-1,3,2-dioxaphosphorianyl sulphide) $\overline{\text{OGOP}}(S)S(O)\overline{\text{POGO}}$.

1. $(RO)_2P(S)SNH_4 + \overline{\text{OGOP}}(O)Cl \xrightarrow{C_6H_6} (RO)_2P(S)S(O)\overline{\text{POGO}} + NH_4Cl \downarrow$
2. $\overline{\text{OGOP}}\ (S)SNH_4 + \overline{\text{OGOP}}\ (O)Cl \xrightarrow{C_6H_6} \overline{\text{OGOP}}\ (S)S(O)\ \overline{\text{POGO}} + NH_4Cl \downarrow$ (where R = i-C_3H_7, C_2H_5 and G = $-CH_2CH_2CHCH_3-$, $-C(CH_3)_2CH_2CHCH_3-$, and $-CH_2C(CH_3)_2CH_2-$)

The reaction mixture has been refluxed for 5–6 h to reaction was complete. The above derivatives are light yellow viscous liquids and are soluble in common organic solvents.

IR SPECTRA

The characteristic IR spectral data of the above derivatives with tentative assignments of the absorption bands have been discussed (on the basis of published literature)[15–16] below (Table I).

1. The absorption bands present in the region of 1025–820 and 870–800 cm^{-1} have been assigned to ν(P)—OC and νP—O(C) vibrations.
2. A sharp absorption band present in the region of 710–600 cm^{-1} has been assigned to thiophosphoryl (νP=S) vibrations).[13]
3. The phosphoryl (νP=O) absorption band is observed in the region of 1300–1159 cm^{-1}, which shows a slight shift ($\sim$30 cm^{-1}) towards higher wave numbers in comparison to its position in 2-chloro-2-oxo-1,3,2-dioxo phosphorinanes. $\overline{\text{OGOP}}$ (O)Cl.

TABLE I IR Spectral Data of 2-Alkylene/Dialkyl Dithiophosphoato-2-Oxo-1,3,2-dioxaphosphorinanes

S. no.	Compounds	ν(P)OC	νP—O—(C)	Ring vibrations	νP═S	νP═O	νP—S
1.	$OCH_2CH_2CH(CH_3)OP(S)S(O)PO(CH_3)CHCH_2CH_2O$	989	865	979	654	1280	589
2.	$OCH_2CH_2CH(CH_3)OP\ (S)S(O)POCH(CH_3)CH_2(CH_3)_2CO$	1020	849	960	669	1270	552
3.	$OC(CH_3)_2(CH_2(CH_3)CHOP\ (S)S(O)POCH(CH_3)CH_2(CH_3)_2CO$	1024	867	963	647	1300	563
4.	$OCH_2C(CH_3)_2CH_2OP\ (S)S(O)POCH(CH_3)CH_2(CH_3)_2CO$	1025	870	965	650	1250	565
5.	$OCH_2C(CH_3)_2CH_2OP\ (S)S(O)POCH(CH_3)CH_2(CH_3)_2CO$	1020	862	960	645	1280	572
6.	$(C_2H_5O)_2P(S)S(O)PO(CH_3)CHCH_2CH_2O$	989	802	945	600	1270	589
7.	$(C_2H_5O)_2P(S)S(O)POCH(CH_3)CH_2(CH_3)_2CO$	820	840	950	635	1275	610
8.	$(i\text{—}C_3H_7O)_2P(S)S(O)PO(CH_3)CHCH_2CH_2O$	978	800	965	709	1159	532
9.	$(i\text{—}C_3H_7O)_2P(S)S(O)POCH(CH_3)CH_2(CH_3)_2CO$	980	860	972	710	1280	602

4. The disappearance of the νP (O)Cl absorption band from the region of 650–630 cm^{-1} supports the formation of the > (S) P—S—P(O)< chemical linkage in these derivatives.

NMR (^{1}H & ^{31}P) SPECTRA

The ^{1} H NMR spectra of these derivatives shows a multiplet for —OCH_2 and —OCH protons due to long-range coupling with a magnetically active phosphorus atom (Table II). In addition to the ^{1}H NMR, signals also are present due to dialkyl and alkylene protons present in the molecules.

The ^{31}P chemical shift for the phosphoryl group (P=O) has been observed in the range of 0.84–3.8 ppm, which indicates the presence of pentavalent phosphorus with the phosphoryl group (P=O) with an upfield shift with respect to its position in the free $\overline{\text{OGOP}}$ (O)Cl (δ 7–10 ppm). The thiophosphoryl (P=S) signal shows a slight negative shift (δ 78–88 ppm) in comparison to dialkyl/alkylene dithiophophates (δ 77–92 ppm)[17,18] ligand. On the basis of these observations, it appears that there is the formation of a >P(S)S(O)P< linkage in these derivatives.

It also has been postulated in some publications[19] that there is a tendancy of isomerization from S=P—S—P=O to S=P—O—P=S. On the basis of these observations, it appears that there is no possibility of isomerisation in these derivatives because of the presence of a strong phosphoryl (νP=O) absorption band in the region of 1300–1159 cm^{-1} in the IR spectra as well as a ^{31}P resonance signal in the phosphoryl region 0.84–3.8 ppm. It appears that there is no possibility of isomerisation [P—S—P(O) → P—O—P(S)] in these derivatives.

EXPERIMENTAL

Solvents were dried by standard methods. Ammonium dialkyl/alkylene dithiophosphate[20] and 2-chloro-2-oxo-1,3,2-dioxaphosphorinanes $\overline{\text{OGOP}}$ (O)Cl were prepared by the methods reported in the literature.[12] Sulphur was estimated gravimetrically as barium sulphate (messenger method).[21] Molecular weight was determined by the Knaur Vapour Pressure Osmometer using a chloroform solution at 45°C. IR spectra were recorded in Nujol mull. (4000–200 cm^{-1}) on an FTIR spectrophotometer model Megna-IR-550 MICOLAC-USA. Carbon and hydrogen analysis was performed on a Perkin Elemer CHN/O analyzer. ^{1}H NMR spectra were recorded in a $CDCl_3$ solution on a 90 MHz JEOL FX 90 spectrometer using TMS as an internal reference. ^{31}P NMR were recorded in C_6H_6 using H_3PO_4 as an external reference

TABLE II NMR ^{1}H and ^{31}P Spectral Data of 2-Alkylene/Dialkyl Dithiophosphato-2-Oxo-1,3,2-dioxaphosphorinanes

S. no.	Compounds	^{1}H (δ ppm)	31p (δppm) P=O (P=S)
1.	$\overline{OCH_2CH_2CH(CH_3)O}P(S)S(O)P\overline{O(CH_3)CHCH_2CH_2O}$	1.25, d, 3H(CH_3); 4.12–4.76, m, 3H(—OCH_2,—OCH); 1.27, d, 3H(CH_3); 4.27–4.35, m, 3H(—OCH_2,—OCH)	2.9 (86.92)
2.	$\overline{OCH_2CH_2CH(CH_3)O}P\ (S)S(O)P\overline{OCH(CH_3)CH_2(CH_3)_2CO}$	1.26, d, 3H(CH_3); 4.12–4.76, m, 5H(—OCH_2,—OCH); 1.34, s, 6H(CH_3); 1.65, d, 2H(CH_2); 4.51–5.14, m, 3H(—OCH)	3.8 (85.51)
3.	$\overline{OC(CH_3)_2CH_2(CH_3)CHO}P\ (S)S(O)P\overline{OCH(CH_3)CH_2(CH_3)_2CO}$	1.33, s, 6H(CH_3); 1.58, d, 2H(CH_2); 1.38, d, 3H(CH_3), 4.98–5.06m, 1H(—OCH); 1.28, s, 6H(CH_3); 1.68, d, 2H(CH_2); 4.51–5.14, m, 3H(—OCH)	3.5 (85.19)
4.	$\overline{OCH_2C(CH_3)_2CH_2O}P(S)S(O)P\overline{OCH(CH_3)CH_2(CH_3)_2CO}$	1.20, s, 6H(CH_3); 4.04, d, 4H(—OCH_2); 1.32, s, 6H(CH_3); 1.62, d, 2H(CH_2); 4.50–5.12, m, 3H(—OCH).	3.1 (87.20)
5.	$\overline{OCH_2C(CH_3)_2CH_2O}P(S)S(O)P\overline{OCH(CH_3)CH_2(CH_3)_2CO}$	1.22, s, 6H(CH_3); 4.12, d, 4H(—OCH_2); 1.25, d, 3H(CH_3); 4.10–4.67, m, 5H(—OCH_2,—OCH)	2.7 (86.19)
6.	$(C_2H_5O)_2P(S)S(O)P\overline{O(CH_3)CHCH_2CH_2O}$	1.28, t, 6H(CH_3), 4.12–4.8, m, 4H(—OCH_2); 1.24, d, 3H(CH_3); 4.9–4.51, m, 5H(—OCH_2—OCH)	1.7 (79.26)
7.	$(C_2H_5O)_2P(S)S(O)P\overline{OCH(CH_3)CH_2(CH_3)_2CO}$	1.26, t, 6H(CH_3), 4.10–4.7m, 4H(—OCH_2); 1.32, s, 6H(CH_3); 1.65, d, 2H(CH_2); 4.49–5.10, m, 3H(—OCH)	0.89 (82.15)
8.	$(i{-}C_3H_7O)_2P(S)S(O)P\overline{O(CH_3)CHCH_2CH_2O}$	4.30–4.7, m, 6H(—OCH,—OCH_2)1.20, d, 12H(CH_3); 1.26, d, 3H(CH_3); 4.11–4.76, m, 5H(—OCH_2—OCH); 2.04–2.61, m, 2H(CH_2)	1.1 (78.27)
9.	$(i{-}C_3H_7O)_2P(S)S(O)P\overline{OCH(CH_3)CH_2(CH_3)_2CO}$	4.20–4.60, m, 6H(—OCH,—OCH_2), 1.22, d, 12H(CH_3); 1.34, s, 6H(CH_3); 1.62, d, 2H(CH_2); 4.49–5.12, m, 3H(—OCH)	0.84 (83.01)

TABLE III Synthetic and Analytical Data of 2-Alkylene/dialkyl Dithiophosphato-2-Oxo-1,3,2-dioxaphosphorinanes

S. no.	Reactant (g)		Product	Found (calcd)%			M.wt.
	$OGOP(O)S(S)NH_4$/$(RO)_2P(S)SNH_4$	>POCI	$OGOP(O)S(S)O<$ g, %	C	H	S	found (calcd)
1.	$OCH_2CH_2CH(CH_3)OP(S)SNH_4$ (1.01)	$OCH_2CH_2CH(CH_3)OP(O)Cl$ (0.86)	$OCH_2CH_2CH(CH_3)OP(S)S(O)PO(CH_3)CHCH_2CH_2O$ (1.34) 84.27	30.12 (30.18)	4.98 (5.03)	19.89 (20.12)	320 (318)
2.	$OCH_2CH_2CH(CH_3)OP(S)SNH_4$ (1.05)	$O(CH_3)_2CH_2(CH_3)CHOP(O)Cl$ (1.09)	$OCH_2CH_2CH(CH_3)OP(S)S(O)POCH(CH_3)CH_2(CH_3)_2CO$ (1.54) 89.01	33.98 (34.68)	6.01 (5.78)	17.99 (18.49)	352 (346)
3.	$OC(CH_3)_2CH_2(CH_3)CHOP(S)SNH_4$ (1.16)	$OC(CH_3)_2CH_2(CH_3)CHOP(O)Cl$ (0.98)	$OC(CH_3)_2CH_2(CH_3)CHOP(S)S(O)POCH(CH_3)CH_2(CH_3)_2CO$ (1.59) 85.02	39.01 (38.50)	5.98 (6.41)	16.88 (17.10)	368 (374)
4.	$OCH_2C(CH_3)_2OP(S)SNH_4$ (1.10)	$OC(CH_3)_2CH_2(CH_3)CHOP(O)Cl$ (0.96)	$OCH_2C(CH_3)_2CH_2CHOP(S)S(O)POCH(CH_3)CH_2(CH_3)_2CO$ (1.59) 88.33	37.12 (36.66)	5.78 (6.11)	16.85 (17.10)	— (360)
5.	$OCH_2C(CH_3)_2CH_2OP(S)SNH_4$ (1.09)	$OCH_2CH_2CH(CH_3)OPCl$ (0.87)	$OCH_2C(CH_3)_2CH_2OP(S)S(O)PO(CH_3)CHCH_2CH_2O$ (1.38) 83.13	33.21 (32.53)	4.99 (5.42)	17.65 (1849)	— (332)
6.	$(C_2H5O)_2P(S)SNH_4$ (1.05)	$OCH_2CH_2CH(CH_3)OPCl$ (0.87)	$(C_2H5O)_2P(S)S(O)PO(CH_3)CHCH_2CH_2O$ (1.26) 78.51	29.92 (30.00)	4.93 (5.62)	19.64 (20.01)	— (320)
7.	$(C_2H5O)_2P(S)SNH_4$ (1.09)	$OC(CH_3)_2CH_2(CH_3)CHOP(O)Cl$ (0.98)	$(C_2H5O)_2P(S)S(O)POCH(CH_3)CH_2(CH_3)_2CO$ (1.35) 77.58	33.76 (34.68)	5.62 (6.35)	17.61 (18.49)	352 (346)
8.	$(i{-}C_3H7O)_2P(S)SNH_4$ (1.15)	$OCH_2CH_2CH(CH_3)OPOCl$ (0.88)	$(i{-}C_3H7O)_2P(S)S(O)PO(CH_3)CHCH_2CH_2O$ (1.32) 75.86	35.01 (34.48)	7.01 (6.03)	18.01 (18.38)	356 (348)
9.	$(i{-}C_3H7O)_2P(S)SNH_4$ (1.17)	$OC(CH_3)_2CH_2(CH_3)CHOP(O)Cl$ (0.98)	$(i{-}C_3H7O)_2P(S)S(O)POCH(CH_3)CH_2(CH_3)_2CO$ (1.37) 77.87	39.10 (38.29)	7.11 (6.91)	16.92 (17.02)	— (376)

(CDRI Lucknow). The experimental details of representative compounds is described below. Analytical results are summarized in Table III.

Preparation of $\overline{OCH_2CH_2CH(CH_3)OP}(O)S$ $(S)\overline{PO(CH_3)CHCH_2CH_2O}$

Bis-(5-Methyl-2-oxo-1,3,2-dioxaphosphorinanyl) Sulphide

Ammonium 1,3-butylene dithiophosphate (1.01 g) was taken in anhydrous benzene (30 mL). To this, a solution of 2-chloro [5-methyl-2-oxo-1,3,2-dioxaphosphorinane $\overline{OCH_2CH_2CH(CH_3)OP}(O)Cl$ (0.86 g) was added slowly and refluxed 5–6 h. After removing the ammonium chloride, the solvent was distilled under reduced pressure. It was a yellow sticky liquid. This procedure was adopted for the rest of the compounds. Relevant data are given in Table III.

Preparation of $\overline{OCH_2CH_2CH(CH_3)OP}\ (O)S(S)(OC_3H_7{-}i)_2$

2-Isoprophyldithiophosphato [5-Methyl-2-oxo-1,3,2-dioxaphosphorinanyl] Sulphide

Ammonium diisopropyl dithiophosphate (1.15 g) was refluxed and stirred with 2-chloro [5-methyl-2-oxo-1,3,2-dioxaphosphorinane] (0.88 g) in benzene for 5–6 h. The precipitated ammonium chloride was filtered off. The solvent was removed from the filtrate under reduced pressure to obtain the desired product, a yellow sticky liquid.

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