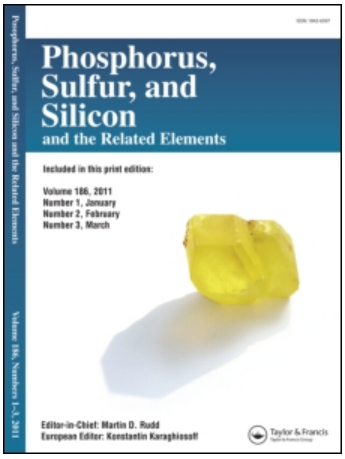

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DIALKYL(ARYL) PHOSPHORYL DERIVATIVES OF ALKYLENE DITHIOPHOSPHATES

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DIALKYL(ARYL) PHOSPHORYL DERIVATIVES OF ALKYLENE DITHIOPHOSPHATES

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Dialkyl(aryl) phosphoryl derivatives of alkylene dithiophosphates of general formula $\overline{OGOP}(S)SP(O)(OR)_2$*: R =* Pr^i*, Ph and G =* $-CMe_2CMe_2-$, $-CH_2CH_2CHMe-$, $-CH_2CH_2CH_2CH_2-$, $-CMe_2CH_2CHMe-$, *and* $-CH_2CMe_2CH_2-$*; have been synthesized by reacting dialkyl and diaryl phosphoryl chloride with ammonium salts of alkylene dithiophosphates in 1:1 molar ratio in refluxing benzene. The products formed are yellow-colored viscous liquids and white-colored waxy solids; they are soluble in common organic solvents and are nonvolatile, even under reduced pressure. The new compounds have been characterized by elemental analysis, molecular weight measurements and spectroscopic (IR,* ^1HNMR*, and* $^{31}PNMR$*)] data.*

Keywords: Ammonium alkylene dithiophosphate; dialkyl phosphoryl chloride; diphenyl phosphoryl chloride

INTRODUCTION

Dialkyl phosphonates, dialkyl thiophosphonates[1,2], dialkyldithiophosphates, and O,O′-alkylene dithiophosphates are well known for their utility as active pesticides. Numerous metal derivatives of alkylene dithiophosphates have been reported from our laboratory in the last 15 years.[3–12] In view of their strong pesticidal activity, recently the organic derivatives[13–15] of alkylene dithiophosphates have attracted the attention of chemists.

In view of the above it was considered of interest to extend the investigations for the synthesis of alkylene dithiophosphate derivatives, which contain more then one phosphorus atom.

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RESULTS AND DISCUSSION

Reactions of dialkyl phosphoryl and diaryl phosphoryl chlorides with ammonium alkylene dithiophosphates in 1:1 molar ratio have been carried out in refluxing benzene for ~10 h and ~8 h, respectively:

$$\overline{OGOP}(S)SNH_4 + (RO)_2P(O)Cl \rightarrow \overline{OGOP}(S)SP(O)(OR)_2 + NH_4Cl\downarrow$$

where G = $-CMe_2CMe_2-$, $-CH_2CH_2CHMe-$, $-CH_2CH_2CH_2CH_2-$, $-CMe_2CH_2CHMe-$, $-CH_2CMe_2CH_2-$ and R = Pr^i and Ph.

These derivatives are nonvolatile, soluble in benzene, chloroform, methanol, and dichloromethane, and are found to be monomeric in nature.

Infrared (IR) Spectra

The relevant infrared (IR) spectral data of dialkyl(aryl) phosphoryl derivatives of alkylene dithiophosphate with tentative assignments on the basis of published literature[3–5] are given in Table I.

The absorption bands present in the region 1025–985 and 870–840 cm^{-1} may be assigned to ν(P)—O—C and νP—O—(C) vibrations, and these show a slight shift towards lower wave numbers. A sharp absorption band present in the region 710–645 cm^{-1} has been assigned to νP=S vibration.[11] The phosphoryl νP=O absorption band is observed in the region 1300–1250 cm^{-1}, which shows a slight shift (~30 cm^{-1}) towards higher wave numbers in comparison to the νP=O absorption band present in dialkyl(aryl) phosphoryl chlorides.

TABLE I IR Spectra of Dialkyl(aryl) Phosphoryl Derivatives of Alkylene Dithiophosphates

No.	Compound	ν(P)—O—C	νP—O—(C)	Ring vibrations	νP=S	νP=O	νP—S
1.	$\overline{OCH_2CH_2CHMeOP}(S)SP(O)(OPr^i)_2$	990	865	980	654	1280	590
2.	$\overline{OCH_2CH_2CH_2CH_2OP}(S)SP(O)(OPr^i)_2$	990	860	972	710	1310	605
3.	$\overline{OCMe_2CH_2CHMeOP}(S)SP(O)(OPr^i)_2$	985	840	964	695	1305	613
4.	$\overline{OCMe_2CMe_2OP}(S)SP(O)(OPr^i)_2$	1020	862	965	645	1290	572
5.	$\overline{OCMe_2CMe_2OP}(S)SP(O)(OPh))_2$	1025	870	965	650	1300	565
6.	$\overline{OCH_2CMe_2CH_2OP}(S)SP(O)(OPh))_2$	1020	850	960	670	1280	555
7.	$\overline{OCMe_2CH_2CHMeOP}(S)SP(O)(OPh))_2$	1010	860	970	665	1250	580
8.	$\overline{OCH_2CH_2CHMeOP}(S)SP(O)(OPh)_2$	1000	865	975	655	1265	575

The disappearance of the νP(O)—Cl absorption band in the region 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 the above derivatives show a multiplet for —OCH_2 and —OCH protons due to long-range coupling with the phosphorus atom (Table II). In addition to this, ^{1}H NMR signals are also present due to alkyl and aryl protons present in the molecules.

The ^{31}P chemical shift for the phosphoryl group (P=O) is observed in the range of δ −0.19 to +3.8 ppm, which suggests a phosphate structure

TABLE II NMR ^{1}H and ^{31}P Spectral Data of Dialkyl(aryl)phosphoryl Derivatives of Alkylene Dithiophosphates

No.	Compound	^{1}H (δ, ppm)	^{31}P (δ ppm) P=O (P=S)
1.	$\overline{OCH_2CH_2CHMeO}P(S)SP(O)(OPr^i)_2$	1.26, d, 3H (CH_3); 4.12–4.76, m, 5H(—OCH_2, —OCH); 2.04–2.71, m, 2H(CH_2); 1.32, d, 12H(CH_3)	1.1 (78.27)
2.	$\overline{OCH_2CH_2CH_2CH_2O}P(S)SP(O)(OPr^i)_2$	1.58–1.67, m, 4H (CH_2); 3.9–4.02, m, 6H (—OCH_2, —OCH); 1.36, d, 12H(CH_3)	0.53 (82.31)
3.	$\overline{OCMe_2CH_2CHMeO}P(S)SP(O)(OPr^i)_2$	1.34, s, 6H (CH_3); 1.65, d, 2H (CH_2); 4.51–5.14, m, 3H(—OCH); 1.2, d, 12H(CH_3)	0.84 (83.0)
4.	$\overline{OCMe_2CMe_2O}P(S)SP(O)(OPr^i)_2$	1.55, s, 12H(CH_3); 1.32, d, 12H(CH_3); 4.53–5.06, m, 2H(—OCH)	−0.19 (80.25)
5.	$\overline{OCMe_2CMe_2O}P(S)SP(O)(OPh))_2$	1.58, s, 12H (CH_3); 7.8, m, 10H (C_6H_5)	3.2 (94.23)
6.	$\overline{OCH_2CMe_2CH_2O}P(S)SP(O)(OPh))_2$	1.20, s, 6H (CH_3); 4.04, d, 4H (—OCH_2); 7.90, m, 10H (C_6H_5)	3.0 (87.04)
7.	$\overline{OCMe_2CH_2CHMeO}P(S)SP(O)(OPh))_2$	1.28, s, 6H (CH_3); 1.58, d, 2H (CH_2); 1.38, d, 3H (CH_3), 4.98–5.06, m, 1H (—OCH); 7.7, m, 10H (C_6H_5)	3.8 (92.6)
8.	$\overline{OCH_2CH_2CHMeO}P(S)SP(O)(OPh)_2$	1.27, d, 3H (CH_3); 4.27–4.35, m, 3H(—OCH_2, —OCH); 2.04, m, 2H(CH_2); 7.85, m, 10H (C_6H_5)	2.9 (88.68)

with a slight negative shift with respect to its position in the free $(RO)_2P(O)Cl$ (δ 7–10 ppm). The thiophosphoryl signal shows a slight negative shift (δ 78–88 ppm) in comparison to alkylene dithiophosphate (δ 77–92 ppm) ligand.[16–17] On the basis of above observations, it appears that there is formation of >P(S)S(O)P< linkage in these derivatives.

EXPERIMENTAL

Solvents were dried by standard methods. Alkylene dithiophosphates[3] and dialkyl phosphoryl chlorides[10] were prepared by the methods reported in the literature.[3] Sulphur was estimated gravimetrically as barium sulphate (messenger Method).[18] Molecular weights were determined by the Knauer vapor pressure osmometer using a chloroform solution at 45°C. IR spectra were recorded in Nujol mull (4000–200 cm^{-1}) on a Perkin Elmer 577 spectrophotometer. Carbon and hydrogen analyses were performed on a Perkin Elmer CHN/O analyzer. ^1H NMR spectra were recorded in $CDCl_3$ solution on a 90 MHz JEOL FX 90 spectrometer using TMS as an internal reference. ^{31}P NMR were recorded in $CHCl_3$ using H_3PO_4 as an external reference. The experimental details of a representative complex are described below. Analytical results are summarized in Table III.

Preparation of $\overline{OCH_2CH_2CHMeOP}(S)SP(O)(OPr^i)_2$

The ammonium alkylene dithiophosphate (1.00 g) was taken up in 30 ml of benzene and refluxed with diisopropyl phosphoryl chloride (1.01) for ~10 h. After removing the ammonium chloride, the solvent was distilled off under reduced pressure. A colorless viscous liquid was obtained. The above procedure was adopted for all other preparations. Relevant data are given in Table III.

Preparation of $\overline{OCMe_2CMe_2OP}(S)SP(O)(OPh)_2$

The ammonium alkylene dithiophosphate (0.98) was taken up in ~30 ml of benzene. The diphenyl phosphoryl chloride (0.11 g) in ~20 ml of benzene was added slowly with stirring and then refluxed for ~8 h. The precipitated ammonium chloride was filtered off. The solvent was removed from the filtrate under reduced pressure to obtain the desired product, a white-colored semisolid.

TABLE III Synthetic and Analytical Data of Dialkyl(aryl)phosphoryl Derivatives of Alkylene Dithiophosphates

No.	Reactants (g): $\overline{OGOP(S)SNH_4}$	Reactants (g): $(RO)_2P(O)Cl$ R=	Product: $\overline{OGOP(S)SP(O)(OR)_2}$ (g %)		Found (calcd.) % C	Found (calcd.) % H	Found (calcd.) % S	M. wt. found (calcd.)
1.	$\overline{OCH_2CH_2CHMeOP(S)SNH_4}$	Pri	$\overline{OCH_2CH_2CHMeOP(S)SP(O)(OPr^i)_2}$		40.90	6.95	20.15	368
	1.0	1.00	1.42	82	(41.23)	(7.56)	(21.9)	(348)
2.	$\overline{OCH_2CH_2CH_2CH_2OP(S)SNH_4}$	Pri	$\overline{OCH_2CH_2CH_2CH_2OP(S)SP(O)(OPr^i)_2}$		41.12	7.68	21.12	—
	1.25	1.24	1.54	71	(43.95)	(8.05)	(23.44)	(348)
3.	$\overline{OCMe_2CH_2CHMeOP(S)SNH_4}$	Pri	$\overline{OCMe_2CH_2CHMeOP(S)SP(O)(OPr^i)_2}$		45.19	7.97	18.05	—
	1.19	1.03	1.60	82	(45.14)	(8.15)	(20.56)	(376)
4.	$\overline{OCMe_2CMe_2OP(S)SNH_4}$	Pri	$\overline{OCMe_2CMe_2OP(S)SP(O)(OPr^i)_2}$		45.11	8.75	19.45	304
	1.40	1.22	1.86	81	(45.14)	(8.15)	(20.96)	(376)
5.	$\overline{OCMe_2CMe_2OP(S)SNH_4}$	Ph	$\overline{OCMe_2CMe_2OP(S)SP(O)(OPh)_2}$		50.28	3.84	14.12	421
	0.98	1.11	1.60	77	(51.30)	(4.95)	(14.41)	(444)
6.	$\overline{OCH_2CMe_2CH_2OP(S)SNH_4}$	Ph	$\overline{OCH_2CMe_2CH_2OP(S)SP(O)(OPh)_2}$		46.54	3.91	14.35	—
	1.29	1.14	1.68	81	(47.44)	(4.65)	(14.88)	
7.	$\overline{OCMe_2CH_2CH_2CH_2CHMeOP(S)SNH_4}$	Ph	$\overline{OCMe_2CH_2CH_2CH_2CHMeOP(S)SP(O)(OPh)_2}$		47.32	5.31	12.90	—
	1.12	1.14	1.62	78	(49.78)	(5.24)	(13.97)	
8.	$\overline{OCH_2CH_2CHMeOP(S)SNH_4}$	Ph	$\overline{OCH_2CH_2CHMeOP(S)SP(O)(OPh)_2}$		45.84	5.12	14.31	398
	1.05	1.14	1.53	74	(46.15)	(46.15)	(15.38)	(416)

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