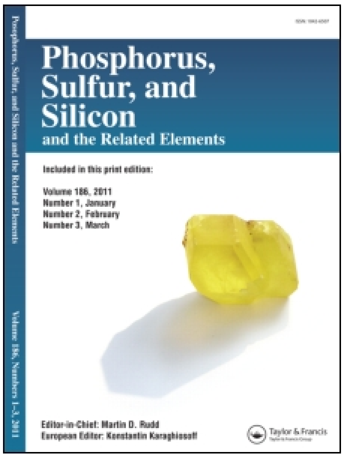

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ORGANIC DERIVATIVES OF ALKYLENE DITHIOPHOSPHATE: PART I. SYNTHESIS AND PROPERTIES OF 2-ACYL(BENZOYL) ALKYLENE DITHIOPHOSPHATES

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Organic derivatives of the type $[\overline{OGOP}(S)S(O)CR]$ (where G = —CMe_2CMe_2—, —$CH_2CMe_2CH_2$—, —CMe_2CH_2CHMe—, —CH_2CH_2CHMe—; R = —Me, —Ph) have been synthesized by the reactions of acetyl chloride/benzoyl chloride with O,O′-alkylene dithiophosphoric acids (or ammonium salts), which yields the red colored viscous liquids or sticky solids, soluble in common organic solvents. The newly synthesized derivatives have been characterized by elemental analysis, IR and NMR (^1H and ^{31}P) spectral studies. In contrast to the bidentate chelating behaviour of the ligand in metal and organometal derivatives of alkylene dithiophosphates, the behaviour of dithiophosphate moiety in these derivatives is found to be monodentate.

Key words: 2-Acyl(benzoyl)alkylene dithiophosphate; O,O′-alkylene dithiophosphates; acetyl chloride, benzoyl chloride.

INTRODUCTION

O,O′-alkylene dithiophosphoric acids[1] contribute an important series of ligands and behave either as unidentate[2] or bidentate[3,4] ligand. The use of organophosphorus specially as pesticides[5–8] in general and specially as organic derivatives of O,O′-dialkyl dithiophosphate and their derivatives, well known as contact insecticides, acaricide and ovicide.[9–11] A lot of work had been reported from our laboratories on the metal and organometal derivatives of -phosphonate and phosphate esters.[12–14] No information is available in the literature on the organic derivatives of alkylene dithiophosphates. In view of the above it was considered of interest to synthesize and characterized the compounds of the type $[\overline{OGOP}(S)S(O)CR]$.

RESULTS AND DISCUSSION

Acyl and benzoyl derivatives of O,O′-alkylene dithiophosphates have been synthesized by the following routes.

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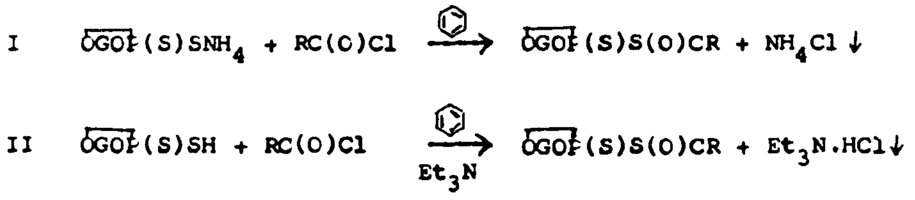

[where G= $-CMe_2CMe_2-$, $-CH_2CMe_2CH_2-$, $-CMe_2CH_2CHMe-$,
$-CH_2CH_2CHMe-$;
R = Me, Ph]

The reaction (I) has been completed by refluxing the reactant in benzene for ≈25 hours with the precipitation of ammonium chloride while the reaction (II) completes by mixing and stirring the reactant at room temperature. It has been observed that the color of the reaction medium changes from colorless to reddish yellow as reaction progressed and it becomes dark red at the completion of the reaction. The products have been isolated after filtering $NH_4Cl/Et_3N \cdot HCl$ under anhydrous reaction condition and are found to be red colored viscous liquids or sticky solids, which are soluble in common organic solvents.

TABLE I

Reactions of CH_3COCl and C_6H_5COCl with alkylene dithiophosphate in 1:1 molar ratio

	Reactants g (mmoles)		Product		Analysis Found/(calcd.) (%)		
S. No.	$\overline{OGOP}(S)SNH_4$ G = ...	RC(O)Cl R = ...	.... g;	..... %	C	H	S
1.	$-CMe_2CMe_2-$ 1.40 (6.11)	Me 0.48 (6.11)	$\overline{OCMe_2CMe_2OP}(S)SC(O)Me$ 1.11	 78	37.20 (37.80)	5.86 (5.90)	24.98 (25.20)
2.	$-CH_2CMe_2CH_2-$ 1.18 (5.48)	Me 0.43 (5.48)	$\overline{OCH_2CMe_2CH_2OP}(S)SC(O)Me$ 1.12	 84	34.85 (35.00)	5.38 (5.42)	26.40 (26.67)
3.	$-CMe_2CH_2CHMe-$ 1.4 (6.11)	Me 0.49 (6.11)	$\overline{OCMe_2CH_2CHMeOP}(S)SC(O)Me$ 1.15	 83	37.25 (37.80)	5.85 (5.90)	25.01 (25.20)
4.	$-CH_2CH_2CHMe-$ 1.40 (6.92)	Me 0.54 (6.92)	$\overline{OCH_2CH_2CHMeOP}(S)SC(O)Me$ 1.23	 80	31.50 (31.85)	4.84 (4.86)	27.96 (28.32)
5.	$-CMe_2CMe_2-$ 1.14 (4.98)	Ph 0.70 (4.98)	$\overline{OCMe_2CMe_2OP}(S)SC(O)Ph$ 0.94	 80	48.85 (49.37)	5.30 (5.38)	19.95 (20.25)
6.	$-CH_2CMe_2CH_2-$ 1.02 (4.74)	Ph 0.67 (4.74)	$\overline{OCCH_2CMe_2CH_2OP}(S)SC(O)Ph$ 1.19	 82	47.40 (47.68)	4.95 (4.97)	20.98 (21.19)
7.	$-CMe_2CH_2CHMe-$ 1.24 (5.41)	Ph 0.76 (4.51)	$\overline{OCMe_2CH_2CHMeOP}(S)SC(O)Ph$ 0.93	 80	49.05 (49.36)	5.35 (5.38)	20.03 (20.25)
8.	$-CH_2CH_2CHMe-$ 0.97 (4.83)	Ph 0.68 (4.83)	$\overline{OCH_2CH_2CHMeOP}(S)SC(O)Ph$ 1.16	 79	45.10 (45.81)	4.48 (4.51)	22.09 (22.22)

TABLE II

IR Spectra of Acyl/benzoyl derivative of alkylene dithiophosphates

S. No.	Product	ν C=O	ν (P)—O—C	ν P—O—(C)	ν Ring vibration	ν P=S/C—S	ν P—S
1.	$\overline{\text{OCMe}_2\text{CMe}_2\text{OP}}\text{(S)SC(O)Me}$	1630s	1010b	860m	955s	650b	550m
2.	$\overline{\text{OCH}_2\text{CMe}_2\text{CH}_2\text{OP}}\text{(S)SC(O)Me}$	1650s	1000s	840m	970s	660b	570m
3.	$\overline{\text{OCMe}_2\text{CH}_2\text{CHMeOP}}\text{(S)SC(O)Me}$	1660s	1040b	870s	930b	650b	530m
4.	$\overline{\text{OCH}_2\text{CH}_2\text{CHMeOP}}\text{(S)SC(O)Me}$	1680s	1015	820b	950b	640b	580b
5.	$\overline{\text{OCMe}_2\text{CMe}_2\text{OP}}\text{(S)SC(O)Ph}$	1640s	1020b	880m	960s	660b	560m
6.	$\overline{\text{OCH}_2\text{CMe}_2\text{CH}_2\text{OP}}\text{(S)SC(O)Ph}$	1690s	1050b	850s	980b	680b	580m
7.	$\overline{\text{OCMe}_2\text{CH}_2\text{CHMeOP}}\text{(S)SC(O)Ph}$	1670s	1040b	830m	950s	640b	550b
8.	$\overline{\text{OCH}_2\text{CH}_2\text{CHMeOP}}\text{(S)SC(O)Ph}$	1675s	1020b	860b	970b	650m	570b

s = sharp, m = medium, b = broad.

IR SPECTRA

A comparison of the IR spectra of the 2-acyl(benzoyl)alkylene dithiophosphates with those of the starting materials, alkylene dithiophosphate, acetyl chloride, benzoyl chloride show the following characteristic features (Table II).

1. IR spectra of these derivatives show disappearance of the ν S—H absorption band from the region 2500–2400 cm^{-1}.

2. The ν C=O absorption band in these compounds is appeared in the range 1680 cm^{-1} to 1630 cm^{-1}. A comparison of the position ν C=O absorption in acetyl chloride (≃1760 cm^{-1}) and in benzoyl chloride (≃1740 cm^{-1}) with those of the new derivatives shows marked shifting of the ν C=O (≃50 cm^{-1}) absorption band towards lower wave numbers. It may be due to lesser nucleophilicity of -dithio moiety in comparison to chlorine atom.

3. Two strong bands in the region 1130–970 cm^{-1} and 880–810 cm^{-1} are observed and assigned to ν (P)—O—C and ν P—O—(C).

4. A sharp absorption band in the region 660–630 cm^{-1} and 715–630 cm^{-1} have been observed and assigned to ν P=S and ν C—S stretching mode.

5. Absorption band of ν P—S occurs in region 580–530 cm^{-1}.

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

^1H

PMR spectra (Table III) shows the characteristic resonance signals of the protons present on alkylene and benzoyl groups. The sharp singlet in the region 3.10–3.70 ppm characteristic of the S—H proton in O,O′-alkylene dithiophosphoric acids is absent in the PMR spectra. A multiplet is observed for P—O—CH$_2$ and P—O—CH

TABLE III

NMR (^1H and ^{31}P) spectral data (δ ppm) for Acyl/benzoyl dithiophosphates

S. No.	Compound	^1H	^{31}P
1.	$\overline{\mathrm{OCMe_2CMe_2OP}}\mathrm{(S)SC(O)Me}$	1.52, 2, 12H (CH_3) 2.15, s, 3H ($OCCH_3$)	97.59
2.	$\overline{\mathrm{OCH_2CMe_2CH_2OP}}\mathrm{(S)SC(O)Me}$	1.07, s, 6H (CH_3) 3.98, s, 4H (OCH_2) 2.19, s, 3H ($OCCH_3$)	82.92
3.	$\overline{\mathrm{OCMe_2CH_2CHMeOP}}\mathrm{(S)SC(O)Me}$	1.24–1.70, m, 11H (CH_2 + CH_3) 4.79, m, 1H (POCH, J = 14 Hz) 2.25, s, 3H ($OCCH_3$)	92.88
4.	$\overline{\mathrm{OCH_2CH_2CHMeOP}}\mathrm{(S)SC(O)Me}$	1.42, s, 3H (CH_3) 4.80, m, 1H (POCH, J = 14 Hz) 2.06, s, 3H ($OCCH_3$) 4.01, m, 2H ($POCH_2$, J = 16 Hz)	82.91
5.	$\overline{\mathrm{OCMe_2CMe_2OP}}\mathrm{(S)SC(O)Ph}$	1.37, s, 12H (CH_3) 7.33, m, 5H (C_6H_5)	99.48
6.	$\overline{\mathrm{OCH_2CMe_2CH_2OP}}\mathrm{(S)SC(O)Ph}$	1.10, s, 6H (CH_3) 3.90, s, 4H (OCH_2) 7.20, m, 5H (C_6H_5)	85.61
7.	$\overline{\mathrm{OCMe_2CH_2CHMeOP}}\mathrm{(S)SC(O)Ph}$	1.52–1.99, m, 11H (CH_2 + CH_3) 4.62, m, 1H (POCH, J = 14 Hz) 7.30, m, 5H (C_6H_5)	92.61
8.	$\overline{\mathrm{OCH_2CH_2CHMeOP}}\mathrm{(S)SC(O)Ph}$	1.30, d, 3H (CH_3, J = 7 Hz) 7.45, m, 5H (C_6H_5) 4.05, m, 2H ($POCH_2$, J = 16 Hz) 4.80, m, 1H (POCH, J = 14 Hz)	85.45

s = singlet, m = multiplet, d = doublet.

protons due to 3-bond coupling of the protons with phosphorus atom. The value of coupling constants ranges between 14–16 Hz.

^{31}P

The ^{31}P spectra for these derivatives have been recorded in benzene and show one resonance signal 82 to 99 pp'm in all the derivatives thus indicating magnetic equivalent of the dithiophosphate ligand on one hand and on the other hand purity of the compounds, there is slight shifting of the resonance signal towards down field by 5–10 ppm. A comparison of the ^{31}P chemical shift value of these derivatives with (S)P—S—C(O) linkage (^{31}P δ: 82 to 99 ppm) with those of the $\mathrm{(S)P{-}S{-}\overset{/}{\underset{\backslash}{Si}}{-}}$ (^{31}P δ: 78–90 ppm),[15,16] $\mathrm{(S)P{-}S{-}\overset{/}{\underset{\backslash}{Ge}}{-}}$ (^{31}P: 85–90 ppm)[15], and $\mathrm{(S)P{-}S{-}\overset{/}{\underset{\backslash}{Sn}}{-}}$ (^{31}P δ: 76–90 ppm)[15,17] linkage is also clearly indicative of upfield shift and thus indicative absence of any coordinating tendencies in these derivatives.

EXPERIMENTAL

Stringent precautions were taken to exclude moisture during the experimental manipulation. Solvent was dried by standard method. Acetyl chloride and benzoyl chloride were distilled before use. Alkylene dithiophosphoric acids and their ammonium salts have been prepared by the methods[1] reported in the literature. Sulfur was estimated gravimetrically as barium sulphate (Messenger's method).[18]

IR spectra were recorded as nujol mulls using CsI pellets on a Perkin-Elmer 577 spectrophotometer in the range 4000–200 cm^{-1}. PMR spectra were recorded in $CDCl_3$ and ^{31}P NMR spectra recorded in benzene on JEOL FX 90Q spectrometer using TMS (^1H) as internal and H_3PO_4 (^{31}P) as external references.

Reaction of acetyl chloride with ammonium salts of O,O'-alkylene dithiophosphoric acid in 1:1 molar ratio: Acetyl chloride (0.47 g, 6.11 mmole) in benzene (20 ml) was added to a $[\overline{OCMe_2CMe_2OP}(S)SNH_4]$ (1.39 g, 6.11 mmole) in benzene (30 ml) and the mixture was refluxed for ≈25 hours. The precipitated ammonium chloride was filtered off and the solvent was removed under reduced pressure to yield the product (1.22 g, 78%) as viscous liquid.

The above procedure was adopted for all the reactions of various ammonium salts of alkylene dithiophosphate $[(\overline{OGOP}S_2)NH_4$, G = $-CH_2CMe_2CH_2-$, $-CMe_2CH_2CHMe-$, $-CH_2CH_2CHMe-]$ with acetyl chloride and benzoyl chloride. Relevant data are given in Table I.

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