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Substitution Reactions of Mono- and Trichloro Acetic Acids with Ammonium Dialkyl (Alkylene) Dithiophosphates

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A reaction of mono- and trichloro acetic acid with ammonium salts of alkylene (dialkyl) dithiophosphate; $[\overline{OGOP}S_2NH_4$; $G = —CH_2CH_2CHMe—$, $—C(Me)_2C(Me)_2—$, $—CH_2C(Me)_2CH_2—$, *and* $—C(Me)_2CH_2CHMe—$; $(RO)_2PS_2$-NH_4; *and* $R = C_2H_5$, C_3H_7, i-C_3H_7;] *in a 1:1 molor ratio in refluxing benzene solution yields low melting solids and light-yellow oily liquids of the type* $[(RO)_2PS_2R'$ *and* $\overline{OGOP}S_2R'$, *where* $R' = CH_2COOH$ *and* Cl_2CCOOH], *which are hygroscopic in nature. These newly synthesized complexes have been characterized by physicochemical and spectroscopic techniques (MW, IR,* ^1H, *and* $^{31}PNMR$*) On the basis of the previously discussed studies, the formation of a P—S—C chemical bond has been established.*

Keywords [(Dialkoxyphosphorothioyl)thio]acetic acid; Dichloro alkylene dithiophosphato acetic acid; IR spectra; NMR spectra

INTRODUCTION

Earlier investigations on a variety of metal, organometal, and organic derivatives of alkylene(dialkyl)dithiophosphates[1–17] yielded interesting chemical-bonding patterns as well as biological applications. It has been observed that biological activity is markedly governed by the nature of alkyl/aryl(substituted) groups substituted on an alkylene(alkyl) dithiophosphato moiety.

In view of this, it was considered of interest to extend the present course of investigations on the syntheses of mono-, chloro-, and trichloro acetic acid derivatives of ammonium alkylene(dialkyl) dithiophosphates.

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RESULTS AND DISCUSSION

Dialkyl dithiophosphato acetic acid and alkylene dithiophosphato acetic acid have been synthesized by reacting monochloroacetic acid with ammonium dialkyl (alkylene) dithiophosphates in refluxing benzene (8–6 h). These displacement reactions appear to be slow due to the high acidic strength of monochloro acetic acid, which generates chloride ions very slowly. No change in the reactivity has been observed even when using acetonitrile as a solvent.

$$(RO)_2P(S)\overset{-}{S}\overset{+}{N}H_4 + ClCH_2COOH \longrightarrow (RO)_2P(S)SCH_2COOH + NH_4Cl\downarrow$$

$$\overline{OGOP}(S)\overset{-}{S}\overset{+}{N}H_4 + ClCH_2COOH \longrightarrow \overline{OGOP}(S)SCH_2COOH + NH_4Cl\downarrow \qquad (1)$$

These new derivatives are white-colored low-melting solids that are hygroscopic in nature and are soluble in common organic solvents. Similarly, compounds of the type dichlro dialkyl dithiophosphato acetic acid and dichlro dialkylene dithiophosphato acetic acid have been synthesized by reacting trichloroacetic acid with ammonium dialkyl/alkylene dithiophosphates in refluxing benzene for 20∼22 h. Due to the high acidic strength of trichloroacetic acid, the substitution of a chloride ion is difficult and thus requires a longer time refluxing for completion.

$$(RO)_2P(S)\overset{-}{S}\overset{+}{N}H_4 + Cl_3CCOOH \longrightarrow (RO)_2P(S)SCCl_2COOH + NH_4Cl\downarrow$$

$$\overline{OGOP}(S)\overset{-}{S}\overset{+}{N}H_4 + Cl_3CCOOH \longrightarrow \overline{OGOP}(S)SCCl_2COOH + NH_4Cl\downarrow \qquad (2)$$

An attempt has been made to synthesize 1:2 and 1:3 derivatives of trichloroacetic acid, but it has been observed that in this reaction, always and only 1:1 product has been isolated. The products formed are pale-yellow oily liquids that are hygroscopic in nature and are soluble in common organic solvents (tetrahydrofurane, ethanol, acetone etc.).

IR Spectra

IR spectra of the newly synthesized derivatives show the following characteristic changes (Table I).

1. A broad and intense νOH absorption band has been present at 3520 cm^{-1} for the –COOH group of monochloro acetic acid derivatives, and a broad and intense absorption band for the νOH group has been observed in the region 3300–3000 cm^{-1} for trichloro acetic acid derivatives.

TABLE I IR Spectral Data of Mono and Tri Chloro Acetic Acid Derivatives of Ammonium Dialkyl/alkylene Dithiophosphate

S. No.	Compounds	ν(P)O—C	νP—O(C)	Ring vibrations	νP=S	νP—S	νC=O	νC—S	νC—Cl
1	$\overline{OCH_2CH_2CHMeOP}(S)SCH_2COOH$	1065	820	970	650	580	1716	625	
2	$\overline{OCH_2C(Me)_2CH_2OP}(S)SCH_2COOH$	1070	830	960	655	535	1716	610	
3	$\overline{OC(Me)_2CH_2CHMeOP}(S)SCH_2COOH$	1025	830	915	665	570	1716	610	
4	$\overline{OC(Me)_2C(Me)_2OP}(S)SCH_2COOH$	1075	820	955	665	580	1720	620	
5	$(i\text{-}C_3H_7O)_2P(S)SCH_2COOH$	1025	770	—	655	560	1726	562	
6	$(C_2H_5O)_2P(S)SCH_2COOH$	1035	815	—	655	550	1726	555	
7	$(n\text{-}C_3H_7O)_2P(S)SCH_2COOH$	1025	810	—	660	530	1726	560	
8	$\overline{OCH_2CH_2CHMeOP}(S)SCCl_2COOH$	1070	850	990	660	590	1720	700	770
9	$\overline{OCH_2C(Me)_2CH_2OP}(S)SCCl_2COOH$	1060	840	960	675	540	1720	680	770
10	$\overline{OC(Me)_2CH_2CHMeOP}(S)SCCl_2COOH$	1060	840	920	675	540	1716	690	770
11	$\overline{OC(Me)_2C(Me)_2OP}(S)SCCl_2COOH$	1070	845	950	675	590	1730	685	780
12	$(i\text{-}C_3H_7O)_2P(S)SCCl_2COOH$	1040	810	—	645	545	1730	675	750
13	$(C_2H_5O)_2P(S)SCCl_2COOH$	1045	815	—	640	550	1725	675	755
14	$(n\text{-}C_3H_7O)_2P(S)SCCl_2COOH$	1040	815	—	650	555	1725	675	750

2. A comparison of the νC=O absorption band present in monochloro acetic acid at 1736 cm^{-1} indicates a slight shift toward lower wave numbers (10–20 cm^{-1}). Similarly, a νC=O absorption band of trichloroacetic acid present at 1740 cm^{-1} shows a slight shift toward lower wave numbers (10–20 cm^{-1}) due to a lower electrical effect of the chlorine atom.
3. The ν(P)—OC and νP—O(C) absorption band appears in the regions 1075–1025 cm^{-1} and 830–770 cm^{-1}, respectively, while a broad absorption band around 915–970 cm^{-1} is due to ring vibrations in monochloro acetic acid derivatives. For trichloro acetic acid derivatives, the absorption band appears in the regions 1070–1040 cm^{-1} and 850–810 cm^{-1}, respectively.
4. The νC–Cl absorption band present in the region 720–715 cm^{-1} has disappeared in monochloro acetic acid derivatives, and in trichloro acetic acid derivatives, the νC—Cl absorption band present in the region 750–780 cm^{-1} has shifted toward lower wave numbers (10–15 cm^{-1}) in comparison to its position in trichloroacetic acid.
5. νP=S and νP—S absorption bands have been observed at 665–650 cm^{-1} and 580–530 cm^{-1}, respectively, in monochloro acetic acid derivatives. The νP=S and νP=S absorption bands have been observed in the region 675–640 cm^{-1} and 590–540 cm^{-1}, respectively, in trichloro acetic acid derivatives.
6. A new medium intensity absorption band has been observed in the region 560–675 cm^{-1}, which was tentatively assigned to phosphorus-sulfur-carbon(S=P—S—C) chemical linkage in these derivatives.

PMR Spectra

PMR spectra of these derivatives have been recorded in $CDCl_3$, and these are tabulated in Table II. The PMR spectra show a multiplet for OCH_2 and OCH protons due to long range coupling with the magnetically active phosphorus atom. In addition to this, the PMR signal presented at δ 12–11.5 ppm is due to an acidic proton of substituted acetic acid. Deammonization has been observed in the PMR spectra of these derivatives, thus showing the formation of the (S=P—S—C) chemical bond.

^{31}P NMR Spectra

A ^{31}P NMR resonance signal in dialkyl (alkylene) dithiophosphato acetic acid has been observed in the range 50.4 to 62.4 ppm, which exhibits deshielding (δ 13–19 ppm) in the ^{31}P chemical shift value in comparison to dithiophosphates (70–104 ppm).

TABLE II NMR ^{1}H and ^{31}P Spectral Data of Mono and Tri Chloro Acetic Acid Derivatives of Ammonium Dialkyl/alkylene Dithiophosphate

S. No.	Compounds	^{1}H (δ ppm)	^{31}P (δ ppm)
1	$OCH_2CH_2CHMeOP(S)SCH_2COOH$	1.35, d, 3H (CH_3); 2.75–2.98, m, 2H(CH_2); 4.2–4.5, m, 3H (OCH, OCH_2); 12.5, S, 1H(COOH)	62.31
2	$OCH_2C(Me)_2CH\ OP(S)SCH_2COOH$	1.5–1.6, S, 6H(CH_3); 4.1–4.2, d, 4H(CH_2O);11.3, S, 1H (COOH)	60.40
3	$OC(Me)_2CH_2CHMeOP(S)SCH_2COOH$	1.99–2.2, m, 11H (CH_3, CH_2); 4.0–4.5, m, 1H(CHO); 12.5, S, 1H (COOH)	62.45
4	$OC(Me)_2C(Me)_2OP(S)SCH_2COOH$	1.80, S, 12H (CH_3); 12.5, S, 1H (COOH)	61.35
5	$(i\text{-}C_3H_7O)_2P(S)SCH_2COOH$	1.48–2.1, d, 12H (CH_3); 11.9, S, 1H (COOH)	56.49
6	$(C_2H_5O)_2P(S)SCH_2COOH$	2.28–3.3, t, 6H (CH_3); 3.7–4.5, m, 4H(OCH_2); 12.3, S, 1H (COOH)	55.70
7	$(n\text{-}C_3H_7O)_2P(S)SCH_2COOH$	1.52–1.58, t, 6H (CH_3); 2.27–3.1, m, 4H(CH_2); 3.5–4.2, m, 4H(OCH_2); 12.3, S, 1H(COOH)	54.51
8	$OCH_2CH_2CHMeOP(S)SCCl_2COOH$	1.4, d, 3H(CH_3); 3.0–2.8, m, 2H (CH_2); 4.5–4.9, m, 3H(OCH, OCH_2); 12.1, S, 1H (COOH)	56.59
9	$OCH_2C(Me)_2CH_2OP(S)SCCl_2COOH$	1.24, s, 6H(CH_3); 4.2–4.5, d, 4H(CH_2O); 11.9, S; 1H(COOH)	60.21
10	$OC(Me)_2CH_2CHMeOP(S)SCCl_2COOH$	2.0–2.5, m, 11H (CH_3, CH_2); 5.0–5.2, m, 1H(CHO); 12.1, S, 1H (COOH)	59.41
11	$OC(Me)_2C(Me)_2OP(S)SCCl_2COOH$	1.52, S, 12 H (CH_3); 4.6, m, 2H(CHOP); 11.9, S, 1H (COOH)	58.51
12	$(i\text{-}C_3H_7O)_2P(S)SCCl_2COOH$	1.46–1.5, d, 12 H (CH_3); 11.5, S, 1H(COOH)	50.41
13	$(C_2H_5O)_2P(S)SCCl_2COOH$	1.67–1.98, t, 6H (CH_3); 5.01–5.2, m, 4H (OCH_2) 11.9–12.0, s, 1H (COOH)	55.52
14	$(n\text{-}C_3H_7O)_2P(S)SCCl_2COOH$	1.57–1.70, t, 6H (CH_3); 2.75–3.01, m, 4H (CH_2); 5.5–5.7, m, 4H (OCH_2); 11.9, S, 1H (COOH)	50.61

^{31}P NMR spectra of dichloro dialkyl (alkylene) dithiophosphato acetic acid have been recorded in benzene. In a proton-decoupled ^{31}P spectra, one sharp signal has been observed at δ 50–60 ppm, which indicates a presence of one type of phosphorus atom (Table II). The ^{31}P NMR chemical shift values observed in ammonium dialkyl (alkylene) dithiophosphate (77–102 ppm) was shifted upfield ($\delta = 18$–28 ppm) in the corresponding trichloro acetic acid derivatives, which indicates the covalent character of a sulphur-carbon linkage as well as an absence of coordinating tendency in these derivatives.

On the basis of the previously discussed studies, the formation of a phosphorus-sulfur-carbon (S=P—S—C) chemical linkage with a free thiophosphoryl group has been tentatively proposed.

EXPERIMENTAL

Solvents were dried by standard methods. Ammonium salt of dialkyl/alkylene dithiophosphates have been prepared by the method reported in the literature.[17] Sulphur was estimated gravimetrically as barium sulphate (messenger method)[17] and has been purified by vacuum distillation. Molecular weights were 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 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 300 Mhz FT NMR spectrometer using TMS as an internal reference. ^{31}P NMR were recorded in C_6H_6using H_3PO_4 as an external reference. The experimental details of representative compounds are described in the following sections. Analytical results are summarized in Table III.

Preparation of Ammonium Dialkyl (Alkylene) Dithiophosphate Ligands[17]

These ligands can be prepared by the reactions of P_2S_5 with the corresponding alcohol/1,2 or 1,3 glycols in anhydrous benzene by passing dry ammonia gas.

These may be purified by washing with benzene or ether or may be crystallized from a benzene parent alcohol mixture.

Preparation of [(Diisopropoxyphosphorothioyl) thio] Acetic Acid

A mixture of ammonium diisopropyl dithiophosphate (2.42 g, 10.47 mmole) and monochloro acetic acid (0.98 g, 10.37 mmole) in

TABLE III Synthetic and Analytical Data of Mono and Tri Chloro Acetic Acid Derivatives of Ammonium Dialkyl/alkylene Dithiophosphate

	Reactant g, (mMole)				Found (Calculated) (in % age)			
	$\overline{OGO}P(S)SNH_4/(RO)_2P(S)SNH_4$			Product				M. Wt. Found
S.No.	G=	R=	$ClCH_2COOH$	g, %	C	H	S	(Calculated)
1	$—CH_2CH_2CHMe—$ 2.20 (10.94)		1.02 (1079)	$OCH_2CH_2CHMeOP(S)SCH_2COOH$ 2.22, 85.12	30.15 (29.75)	5.12 (4.54)	25.76 (26.44)	— (242)
2	$—CH_2C(Me)_2CH_2—$ 5.20 (24.18)		2.31 (24.44)	$OCH_2C(Me)_2CH_2OP(S)SCH_2COOH$ 4.94, 79.16	33.35 (32.81)	4.52 (5.07)	24.61 (25.00)	246 (256)
3	$—C(Me)_2CH_2CHMe—$ 2.60 (11.35)		1.09 (11.53)	$OC(Me)_2CH_2CHMeOP(S)SCH_2COOH$ 2.24, 72.12	36.12 (35.55)	6.01 (5.55)	24.12 (23.70)	— (270)
4	$—C(Me)_2C(Me)_2—$ 5.19 (22.66)		2.15 (22.75)	$OC(Me)_2C(Me)_2OP(S)SCH_2COOH$ 5.46, 89.01	34.92 (35.55)	4.88 (5.55)	24.32 (23.70)	255 (270)
5		$i\text{-}C_3H_7—$ 2.42 (10.47)	0.98 (10.37)	$(i\text{-}C_3H_7O)_2P(S)SCH_2COOH$ 1.70, 78.01	34.81 (35.42)	7.02 (6.64)	24.10 (23.61)	— (271)
6		$C_2H_5—$ 2.91 (14.33)	1.33 (14.07)	$(C_2H_5O)_2P(S)SCH_2COOH$ 2.51, 73.34	30.01 (29.52)	4.91 (5.33)	25.79 (26.24)	230 (243)
7		$n\text{-}C_3H_7—$ 3.51 (15.91)	1.40 (14.81)	$(n\text{-}C_3H_7O)_2P(S)SCH_2COOH$ 3.03, 75.54	34.61 (35.42)	5.69 (6.64)	24.12 (23.61)	— (271)
8	$—CH_2CH_2CHMe—$ 1.36 (6.76)		1.1 (6.72)	$OCH_2CH_2CHMeOP(S)SCCl_2COOH$ 1.56, 75.00	22.61 (23.15)	3.10 (2.89)	21.10 (20.57)	— (311)
9	$—CH_2C(Me)_2CH_2—$ 1.30 (6.04)		0.98 (5.99)	$OCH_2C(Me)_2CH_2OP(S)SCCl_2COOH$ 1.64, 85.01	26.15 (25.84)	2.79 (3.38)	20.13 (19.69)	308 (325)
10	$—C(Me)_2CH_2CHMe—$ 1.70 (7.42)		1.21 (7.33)	$OC(Me)_2CH_2CHMeOP(S)SCCl_2COOH$ 2.23, 89.22	27.61 (28.31)	4.20 (3.83)	19.20 (18.87)	— (339)
11	$—C(Me)_2C(Me)_2—$ 1.60 (6.98)		1.15 (7.03)	$OC(Me)_2C(Me)_2OP(S)SCCl_2COOH$ 1.90, 79.92	27.99 (28.31)	4.02 (3.83)	19.30 (18.87)	303 (339)
12		$i\text{-}C_3H_7—$ 1.40 (6.06)	0.99 (6.05)	$(i\text{-}C_3H_7O)_2P(S)SCCl_2COOH$ 2.23, 90.12	27.65 (28.15)	5.11 (4.69)	19.20 (18.76)	— (341)
13		$C_2H_5—$ 1.60 (7.88)	1.30 (7.95)	$(C_2H_5O)_2P(S)SCCl_2COOH$ 1.79, 72.45	22.79 (23.00)	4.02 (3.51)	21.13 (20.44)	— (313)
14		$n\text{-}C_3H_7—$ 1.77 (7.66)	1.25 (7.64)	$(n\text{-}C_3H_7O)_2P(S)SCCl_2COOH$ 2.08, 80.12	27.61 (28.15)	5.15 (4.69)	19.21 (18.76)	328 (341)

benzene (50–60 mL) were refluxed for 6–8 h. Ammonium chloride that precipitated was filtered off, and the product was obtained (1.70 g, 78.01%) after evaporating the solvent under reduced pressure; a white low-melting solid was obtained. Relevant data are tabulated in Table III.

Preparation of Dichloro [(4-Methyl-2-sulfido-1,3,2-dioxaphosphinane-2-yl)thio] Acetic Acid

A benzene solution of trichloro acetic acid (1.21 g, 7.33 mmole) was added into an ammonium salt of hexylene dithiophosphate (1.70 g, 7.42 mmole) and refluxed for 20–22 h. The ammonium chloride precipitated during the course of reaction was filtered off under anhydrous reaction conditions, and the product was isolated after evaporating the solvent under reduced pressure. A pale-yellow oily liquid was obtained (2.23 g, 89.22%). Relevant data are tabulated in Table III.

REFERENCES

[1] H. P. S. Chauhan, C. P. Bhasin, G. Srivastava, and R. C. Mehrotra, *Phosphorus, Sulfur, and Silicon*, **15,** 99 (1983).

[2] K. C. Molloy, M. B. Hossain, D. V. Helim, J. J. Zuckerman, and I. Haidue, *Inorg. Chem.*, **18,** 3507 (1979).

[3] K. C. Molloy, M. B. Hossain, D. V. Helim, J. J. Zuckerman, and I. Haidue, *Inorg. Chem.*, **19,** 3507 (1980).

[4] R. C. Mehrotra, G. Srivastava, and B. P. S. Chauhan, *Coord. Chem. Revs.*, **55,** 207 (1984).

[5] A. Chaturvedi, P. N. Nagar, and G. Srivastava, *Phosphorus, Sulfur, and Silicon*, **80,** 141 (1993).

[6] P. N. Nagar, *Phosphorus, Sulfur, and Silicon*, **79,** 207 (1993).

[7] A. Chaturvedi, P. N. Nagar, and G. Srivastava, *Main Group Met. Chem.*, **16,** 45 (1993).

[8] A. Chaturvedi, P. N. Nagar, and A. K. Rai, Synth. React., *Inorg. Met. Chem.*, **26,** 1025 (1996).

[9] A. Chaturvedi, R. K. Sharma, P. N. Nagar, and A. K. Rai, *Phosphorus, Sulfur, and Silicon*, **112,** 179 (1996).

[10] R. Purwar and P. N. Nagar, *Phosphorus, Sulfur, and Silicon*, **86,** 211 (1994).

[11] R. Purwar, M. K. Sharma, R. K. Sharma, and P. N. Nagar, *Phosphorus, Sulfur, and Silicon*, **174,** 15 (2001).

[12] N. Harkut and P. N. Nagar, *Phosphorus ,Sulfur, and Silicon*, **180,** 2517 (2005).

[13] N. Harkut, A. Keshawat, and P. N. Nagar, *Phosphorus, Sulfur, and Silicon*, **181,** 2177–2185 (2006).

[14] C. S. Sharma, M. K. Sharma, and P. N. Nagar, *Phosphorus, Sulfur, and Silicon*, **177,** 981 (2002)

[15] C. S. Sharma and P. N. Nagar, *Phosphorus, Sulfur, and Silicon*, **179,** 1793 (2004).

[16] C. S. Sharma and P. N. Nagar, *Phosphorus, Sulfur, and Silicon*, **181,** 1 (2006).

[17] A. I. Vogel, *A Textbook of Quantitative Inorganic Analysis*, 4th Ed. (ELBS, London 1973).