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Spectroscopic and elemental analysis studies of the reactions of triiodomethane with dialkyl and alkylenedithiophosphate Salts and acids

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Abstract

Methyl tris-dialkyl and alkylenedithiophosphates, $\text{HC}[\text{S}_2\text{P}(\text{OR})_2]_3$ where $\text{R} = \text{Et}, n\text{-Pr}, i\text{-Pr}, i\text{-Bu}$ and Ph and $\text{HC}[\text{S}_2\text{POGO}]_3$, where $\text{G} = -\text{CMe}_2, \text{CMe}_2, -, \text{CH}_2\text{CMe}_2\text{CH}_2-,$ and $-\text{CH}_2\text{CET}_2\text{CH}_2-$, have been synthesized for the first time by the reactions of iodoform with the alkali metal salt of the corresponding ligand in anhydrous toluene in 1:3 molar ratio respectively. These compounds are powdery solids or viscous liquids and are soluble in common organic solvents, in which they show monomeric behavior. Based on elemental analyses, molecular weight determinations, IR and NMR (^1H and ^{31}P) spectral data, chelate tetrahedral structures have been proposed for these derivatives

Keywords: Spectroscopic, elemental analysis, triiodomethane, alkylenedithiophosphate Salts

Introduction

As compared to the chemistry of metal-sulfur bonded compounds, that of carbon-sulfur bonded compounds has been little explored. Open and cyclic O, O-dialkyl and alkylenedithiophosphoric acids act as versatile mono and bidentate dithio ligands and form a variety of stable complexes with main group and transition elements ^[1-6]. The increase of using these organosulfur compounds in the industrial use is due to the diverse technical applications, ^[7-8] toxicological ^[9] and environment ^[10-11] properties. Methyl tris dialkyl and alkylenedithiophosphates are surprisingly still unknown. The latter derivatives appear to be monomeric, containing three sulfur atoms bonded to the carbon. In view of the above, it was considered of interest to synthesize and characterize methyl tris dialkyl- as well as alkylenedithiophosphates and compare their containing structural features with the known complexes with other dithio ligands.

Experiment

Moisture was carefully excluded throughout the experimental manipulations. All alcohol glycol and solvents were dried before use, by standard methods. CHI_3 (Merck) was used as such. Dialkyl and alkylenedithiophosphoric acids ^[12-13] or their potassium salts were prepared by the methods reported in the literature. Sulfur were estimated gravimetrically as barium sulfate. Molecular weights were determined by the "Knaur Vapor pressure Osmometer" using a chloroform solution at 45°C Infrared spectra were recorded as Nujol mulls using CsI cells in the region $4000\text{--}200\text{ cm}^{-1}$ on an FT-IR 8201PC spectrophotometer. ^1H and ^{13}C , spectra were recorded on a Jeol-FT NMR spectrometer-LA300 and using TMS as the internal reference. ^{31}P NMR spectra were recorded in CHCl_3 using H_3PO_4 as an external reference on the same instrument.

Triiodomethane was mixed with acid or potassium salt derivatives in 1:3 ratio. The reaction mixture was stirred and refluxed for ~6 hours in toluene. Then the reaction was allowed to continue with no heat but at the same stirring speed. Potassium chloride separated by filtration funnel. Solutions were then washed repeatedly by n-hexane and the desired products were finally dried under reduced pressure. The samples were spectroscopically analyzed using ^1H NMR, ^{13}C , ^{31}P NMR, and FT-IR.

Results & Discussion

Methyl tris O, O-dialkyl and alkylenedithiophosphate compounds have been synthesized by the reactions of the corresponding potassium salt of dithiophosphoric acid with trimethyl,

iodide in 1:3 molar ratio. These reactions are quite facile, but, to ensure completion of the reaction, solutions were refluxed with stirring for ~6 h in anhydrous toluene. All these newly synthesized derivatives are green powdery solids and are soluble in common organic solvents. Table 1

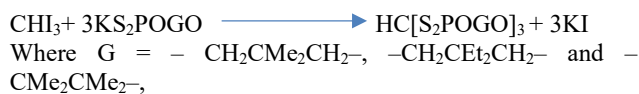
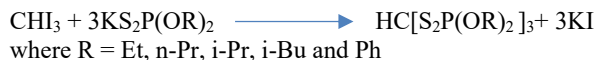


Table 1: Physical Data of methyl tris dialkyl and alkylenedithiophosphate derivatives

Compound No	Compound formula	Physical state	Mol Weight Found/Cal.	%P Found/Cal.	%S Found/Cal.	%C Found/Cal.	%H Found/Cal.
1	HC[(EtO) ₂ PS ₂] ₃	Green powdery solids	567.45/568.69	16.44/16.33	33.76/33.83	27.65/27.45	5.39/5.49
2	HC[(nPrO) ₂ PS ₂] ₃	Green powdery solids	650.78/652.85	13.89/14.23	29.76/29.46	34.76/34.95	6.23/6.63
3	HC[(iPrO) ₂ PS ₂] ₃	Green powdery solids	654.65/652.85	13.98/14.23	29.07/29.46	34.75/34.95	6.87/6.63
4	HC[(iBuO) ₂ PS ₂] ₃	Green powdery solids	737.65/737.01	12.97/12.60	25.76/26.10	40.35/40.74	7.09/7.52
5	HC[(PhO) ₂ PS ₂] ₃	Green powdery solids	856.12/856.94	10.32/10.84	22.81/22.45	51.43/51.85	3.76/3.64
6	HC[OCMe ₂ CMe ₂ OPS ₂] ₃	Green powdery solids	645.73/646.80	14.66/14.36	29.35/29.74	35.46/35.28	5.21/5.765
7	HC[OCH ₂ CMe ₂ CH ₂ OPS ₂] ₃	Green powdery solids	605.12/604.72	15.34/15.36	31.44/31.81	32.04/31.77	5.64/5.16
8	HC[OCH ₂ Ce _t CH ₂ OPS ₂] ₃	Viscous liquid	676.57/688.88	13.68/13.48	27.56/27.92	37.68/38.35	6.84/6.29

IR Spectra

The IR spectra of the new complexes were explained on the comparison basis with pertinent literature reports. [14–16] Only small shifting of bands in the IR spectra was observed compared to free acids. The IR spectra of these new derivatives recorded in the region 4000–400 cm⁻¹. In case of using the dithiophosphoric acids, the S-H stretching band at 2544 – 2400 cm⁻¹ which has been observed for the parent acid disappeared in the derivative spectra indicating the formation of C-S which appeared as new bands in the region 402–486

cm⁻¹. Two bands corresponding to ν(P)–O–C and ν P–O–(C) vibration at the region 994.0–1150.0 cm⁻¹ and 820.0 – 864.1 cm⁻¹ respectively. A band in the region 880.0 – 940.0 cm⁻¹ is most probably due to dioxaphospholane and dioxaphosphorinane ring vibrations [17–19]. A band present in the region 505.0– 681.0 cm⁻¹ can be assigned to ν P=S vibrations [20]. Bands with medium to weak intensities in the region 513.0 – 586.0 cm⁻¹ may be attributed to vibration of ν P–S asymmetric and symmetric vibrations [21]. Detailed peak data is recorded in table 2.

Table 2: IR spectral data (cm⁻¹) of methyl tris dialkyl and alkylenedithiophosphate derivatives

Sr. No	Compound	ν (P)–O–C	ν P–O–(C)	Ring Vibration	ν P=S	ν P–S	ν (C–S)
1	HC[(EtO) ₂ PS ₂] ₃	1022s	964s		681s	521m	478w
2	HC[(nPrO) ₂ PS ₂] ₃	1002s	913m		644m	589m	414w
3	HC[(iPrO) ₂ PS ₂] ₃	1028s	960m		645s	555w	486w
4	HC[(iBuO) ₂ PS ₂] ₃	1022s	958m		617m	581m	426w
5	HC[(PhO) ₂ PS ₂] ₃	994s	891m		655m	580m	478w
6	HC[OCMe ₂ CMe ₂ OPS ₂] ₃	1020	850 m	940 m	532 m	542 m	402 m
7	HC[OCH ₂ CMe ₂ CH ₂ OPS ₂] ₃	1030	860 m	908m	513w	532 m	413 w
8	HC[OCH ₂ Ce _t CH ₂ OPS ₂] ₃	1150	820 s	880	505 m	513w	405 m

¹H NMR Spectra

¹H spectra of methyl tris (dialkyl and alkylene dithiophosphate), recorded in CDCl₃, show the characteristic resonance due to alkoxy and glycoxy (dithio moiety) protons. Singlet peak at ~4.1ppm in the parent dithiophosphoric acid assigned to SH proton is absent from the spectrum of these new complexes; indicating deprotonation of the SH group. The singlet peak appears at ~3.1ppm assigned to H-C bond [22].

¹³C NMR Spectra

The ¹³C NMR spectra of methyl tris (dialkyl and alkylene

dithiophosphate compared to those obtained for the parent dithiophosphoric acids indicate no substantial difference [23]. The ¹³C NMR spectra of all derivative complexes were recorded in deuterated chloroform. Table 4

³¹P NMR

The ³¹P NMR spectra for these compounds give a singlet indicating the purity of these complexes. However, no notable difference was observed in comparison to the parent acids. [24, 25]. The values of chemical shifts according to Glidewell's [26] observation indicates monodentate chelating behavior of the ligand (Table 3).

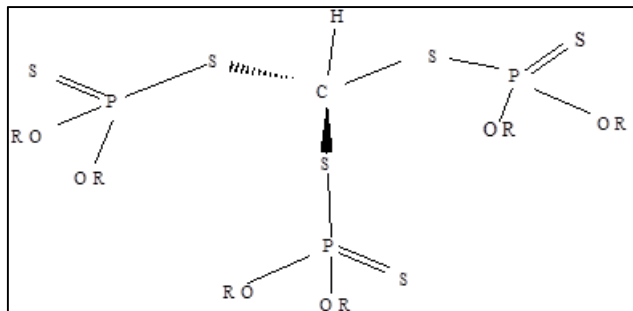
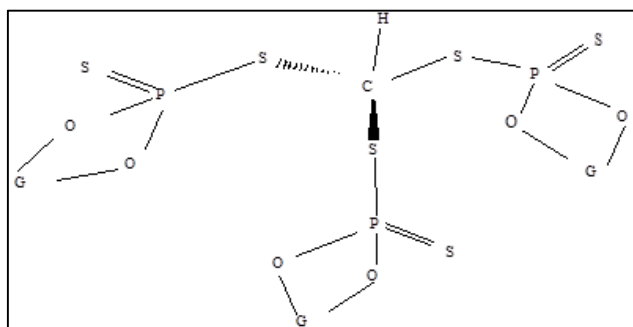
Table 3: ¹H, ³¹P NMR of methyl tris dialkyl and alkylenedithiophosphate derivatives

Comp. No	Compound	¹ H chemical shift in δ ppm in CDCl ₃	³¹ P chemical shift
1	HC[(EtO) ₂ PS ₂] ₃	1.39 (t, J = 6Hz, 6H, 3xCH ₃); 4.33 (q, J = 6Hz, 4H, 2xCH ₂)	86.8(85.7)
2	HC[(nPrO) ₂ PS ₂] ₃	1.08 (t, J = 5.8Hz, 18H, 6xCH ₃), 1.84 (m, 12H, 6xCH ₂); 4.25 (J = 5.3 Hz, 12H, 6xCH ₂)	86.9(86.1)
3	HC[(iPrO) ₂ PS ₂] ₃	1.52 (d, J = 5.5Hz, 18H, 6xCH ₃); 4.90 (m, 3H, 3xCH)	82.6(82.3)
4	HC[(iBuO) ₂ PS ₂] ₃	0.98 (d, J = 3.6Hz, 18H, 6xCH ₃); 2.0 (m, 3H, 3xCH); 4.05 (d, J = 6.4Hz, 6H, 3xCH ₂)	85.9(85.7)
5	HC[(PhO) ₂ PS ₂] ₃	7.24 (m, ArH)	78.6(79.9)
6	HC[OCMe ₂ CMe ₂ OPS ₂] ₃	1.60 (s, 36H, 12xCH ₃)	94.2(93.1)
7	HC[OCH ₂ CMe ₂ CH ₂ OPS ₂] ₃	12, d, 12H(OCH ₂), J(PH) = 15.5 Hz 1.12, s, 18H(CH ₃)	78.7(77.3)
8	HC[OCH ₂ Ce _t CH ₂ OPS ₂] ₃	0.71, t (J = 7.5 Hz), 12H(CH ₃), 1.11, q (J = 7.5 Hz), 8H(CH ₂) 4.02, d, 8H(OCH ₂), J(PH) = 16 Hz	79.1(78.5)

Table 4: ^{13}C NMR spectral data of methyl tris dialkyl and alkylenedithiophosphate derivatives

S. NO	Compound	CH_3	OCH_2	OCH	C	OC
1	$\text{HC}[(\text{EtO})_2\text{PS}_2]_3$	15.81s	64.13 s			
2	$\text{HC}[(i\text{-PrO})_2\text{PS}_2]_3$	23.17s		72.35s		
3	$\text{HC}[(n\text{PrO})_2\text{PS}_2]_3$	10.01s	23.07s	70.23s		
4	$\text{HC}[(i\text{BuO})_2\text{PS}_2]_3$	18.90	28.52s	74.27s		
6	$\text{HC}[(\text{PhO})_2\text{PS}_2]_3$			121.49s, 129.54s,		150.37 s
7	$\text{HC}[\text{OCMe}_2\text{CMe}_2\text{OPS}_2]_3$	24.51 s			35.44 s	91.32 s

Molecular weight determination of methyl tris-dialkyl and alkylenedithiophosphates showed monomeric nature of these compounds in benzene. Thus, on the basis of our observations for IR, NMR (^1H and ^{31}P) and molecular weight determinations, the following structure (in which carbon is tetracoordinated) is proposed for the tris-derivatives: Fig 1

**Fig 1:** Open chain structure of methyl tris dithiophosphate**Fig 1:** Cyclic structure of methyl tris dithiophosphate

Conclusion

In this study, we have shown the facile synthesis of dialkyl and alkylene dithiophosphate derivatives triiodomethane. All these new compounds were characterized using ^1H NMR, ^{13}C , ^{31}P NMR and IR. Results showed that dialkyl and alkylene dithiophosphoric salts and acids react as a monodentate with methine atoms.

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