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SYNTHESIS AND CHARACTERISATION OF SOME ANTIMICROBIAL O-ALKYL/ARYL TRITHIOPHOSPHATE DERIVATIVES OF TIN

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ABSTRACT

A series of novel complexes have been synthesized with an objective for evaluation of antimicrobial property. Reaction of diorganotin (IV) dichloride with potassium salts of alkyl/aryl trithiophosphate in 1 : 1 and 2 : 1 molar ratio respectively was studied, which gave products of type $[ROPS_3K_2]$ where R = Me, Et, Pr^i, Bu^i and Ph, by solvent free microwave assisted procedure. These derivatives have been characterized by elemental analysis, molecular weight determination and spectroscopic (IR, ^1H and ^{31}P NMR) studies. Interestingly, these new synthesized derivatives showed good activity against some bacteria and some fungal strains.

Key words: Diorganotin (IV), O-alkyltrithiophosphates.

INTRODUCTION

The last decade has been witnessing a keen interest in the field of chemistry of moieties bonded to sulphur, nitrogen and oxygen containing ligands. A persual of the literature revealed that organic trithiophosphate esters[1-4] have been used as insecticides, nematodicials and defoliants[5-8]. So in continuation of our investigation on metals and organic derivatives of phosphate and dithiophosphate, the proposed work has been extended to investigate the effect of the bonding modes of o-alkyltrithiophoshate towards the metal ion. Microwave chemistry is nowadays gaining popularity, as it is a much "greener approach" to the reaction which is free of environmental impacts; thus, leading to rapid, reproducible and scaleable analysis. Under mild conditions, it gives higher yield with less energy as it causes polarization of the irradiated molecule[9].

The complexes isolated are coloured crystalline solids, soluble in common organic solvents, non-volatile, monomeric in nature and sensitive towards atmospheric moisture.

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Conventional method was also used for synthesis of these derivatives.

EXPERIMENTAL

Ligand-potassium salt of O-alkyltrithiophosphate

Dipotassium salts of O-alkyltrithiophosphates were synthesized by reacting respective alcohol on phosphorus pentasulphide in the presence of base (triethylamine).

A mixture of 0.2 mole triethylamine and 0.6 mole of respective alcohol was added dropwise with vigorous stirring to a suspension of 0.3 mole of phosphorus pentasulphide in 30 mL of anhydrous benzene at such a rate that the solvent is boiled until phosphorus pentasulphide is dissolved completely. The upper layer is separated out and a solution of 1 mole of potassium hydroxide in methanol is added to the lower layer. Dipotassium O-alkyl trithiophosphates precipitates immediately, washed with acetone and dried in vacuo.

Its derivatives are formed in the manner as -

Compound	Triethylamine	Alcohol	P_2S_5 /(benzene)	KOH
O-Methyl	15.60 g	Methanol 4.31 g	10 g (30 mL)	7.54 g
O-Ethyl	15.60 g	Ethanol 6.19 g	10 g (30 mL)	7.54 g
O-Isopropyl	15.60 g	Isopropanol 8.08 g	10 g (30 mL)	7.54 g
O-Isobutyl	15.60 g	Isobutanol 9.96 g	10 g (30 mL)	7.54 g
O-Phenyl	15.60 g	Phenol 12.67 g	10 g (30 mL)	7.54 g

Synthesis of bis (O-alkyltrithiophosphate) derivatives of tin

A mixture of tin tetrachloride (2.41 g, 9.25 m mol) and dipotassium O-alkyltrithiophosphate (respective ratios) were taken in dry benzene (30 mL) and was then refluxed for 8-10 hrs. The completion of the reaction takes place after complete dissolution of trithiophosphates. KCl was removed by filteration and the compounds were dried.

Derivatives of bis-(O-alkyltrithiophosphate) derivatives of tin

Compounds	Tin chloride		$K_3S_3POCH_3$		Benzene (mL)
	g	mmol	g	m mol	
O-Methyl	2.42	9.25	4.06	19.50	30
O-Ethyl	2.20	9.00	3.95	18.00	30
O-Isopropyl	2.02	8.50	3.85	16.60	30
O-Isobutyl	1.90	7.25	3.80	15.00	30
O-Phenyl	2.15	8.10	4.50	16.50	30

$$P_2S_5 + 3\ ROH + 3\ Et_3N \xrightarrow[(R = Me, Et, Pr^i, Bu^i, Ph)]{KOH} ROPS_3K_2$$

$$SnCl_4 + 2\ K_2S_3POCH_3 \xrightarrow[8\text{-}10\ hrs.]{C_6H_6} (CH_3OPS_3)_2Sn + 4\ KCl$$

RESULTS AND DISCUSSION

The physical and analytical parameters are given in Table 1.

Table 1: Physical and analytical data of potassium salt and tin bis O-alkyltrithiophosphates

Compound	Colour	Yield (%)	Mol weight	Sulphur % Found (calc.)
$MeOPS_3K_2$	Light blue	85	235	39.83 (40.85)
$EtOPS_3K_2$	Blue	88	249	37.68 (38.55)
$Pr^iOPS_3K_2$	Blue	90	263	35.42 (36.50)
$Bu^iOPS_3K_2$	Blue	82	277	33.82 (34.65)

Cont…

Compound	Colour	Yield (%)	Mol weight	Sulphur % Found (calc.)
$PhOPS_3K_2$	Blue	80	297	31.53 (32.32)
$[CH_3OP(S)S_2]_2Sn$	Dark blue	70	432	43.21 (44.44)
$[C_2H_5OP(S)S_2]_2Sn$	Dark blue	80	460	40.32 (41.73)
$[^iC_3H_7OP(S)S_2]_2Sn$	Yellow	88	488	38.27 (39.34)
$[^iC_4H9OP(S)S_2]_2Sn$	Dark yellow	85	516	36.15 (37.20)
$[C_6H_5OP(S)S_2]_2Sn$	Pale yellow	80	556	33.71 (34.53)

Spectral analysis

IR: The tentative assignments of some of the important bands have been made and are recorded in Table 2, which reveals the characteristic features of the compounds.

The absorption band at 710-660 cm^{-1} and 550-520 cm^{-1} were assigned to ν P = S and ν P-S linkage, respectively. Shifting of bands towards lower frequency (30-40 cm^{-1}) indicates that chelation of thiophosphoryl group to metal atom has taken place.

Another important linkages ν (P)-O-C and ν P-O-(C) were present in the region 1020-970 cm^{-1} and 880-830 cm^{-1}, respectively[10].

A significant 395 cm^{-1} band can be attributed to Sn-S bond.

Table 2: IR data of bis O-alkyltrithiophosphate

Compunds	ν(P)-O-C	νP-O-(C)	ν P = S	νP-S	νSn-S
$[CH_3OP(S)S_2]_2Sn$	1010 s	880 s	700 s	545 s	390 w
$[C_2H_5OP(S)S_2]_2Sn$	990 s	865 s	690 s	540 s	385 w
$[^iC_3H_7OP(S)S_2]_2Sn$	980 s	850 s	680 s	530 s	380 w
$[^iC_4H_9OP(S)S_2]_2Sn$	970 s	830 s	665 s	520 s	370 w
$[C_6H_5OP(S)S_2]_2Sn$	1020 s	860 s	710 vs	550 s	395 w

NMR: Characteristic signals in the ^{1}H NMR spectra of these complexes are summarized in tabular form. Signals were observed due to alkyl and aryl protons present.

Proton	δ
$[CH_3OP(S)S_2]_2Sn$	3.6, s, 3H (OCH_3)
$[C_2H_5OP(S)S_2]_2Sn$	1.6, t, 3H (CH_3)
	3.0, q, 2H (OCH_2)
$[^{i}C_3H_7OP(S)S_2]_2Sn$	1.5, d, 6H (CH_3)
	3.0-3.4, m, 1H (OCH)
$[^{i}C_4H_9OP(S)S_2]_2Sn$	1.1, d, 6H (CH_3)
	2.2-2.5, m, 1H (CH)
	3.4, d, 2H (OCH_2)
$[C_6H_5OP(S)S_2]_2Sn$	6.7-6.9, m, 5H (OC_6H_5)

$^{31}P_1$ NMR: In parent trithiophosphate, a value of δ = 71.25-72.55 ppm was observed which showed a downfield shift in the case of derivatives (Table 3).

^{119}Sn NMR: The ^{119}Sn spectrum showed resonance signals in the range 136.67-152.34 ppm. Chemical shift values were observed in all the derivatives (Table 3).

Table 3: NMR (^{31}P and ^{119}Sn) spectral data of tin bis (O-alkyltrithiophosphate)

Compounds	(Chemical shift ppm)	
	^{31}P	^{119}Sn
$[CH_3OP(S)S_2]_2Sn$	98.74	145.23
$[C_2H_5OP(S)S_2]_2Sn$	94.63	138.09
$[^{i}C_3H_7OP(S)S_2]_2Sn$	102.17	136.67
$[^{i}C_4H_9OP(S)S_2]_2Sn$	102.98	141.70
$[C_6H_5OP(S)S_2]_2Sn$	103.47	152.34

Antimicrobial activity

All the synthesized compounds were screened for their antibacterial and antifungal activity. Zone of inhibition was measured in mm. DMF was used as a solvent. The micro organisms used were *Escherichia coli*, *Bacillus subtilis* and *Proteus mirabilis* for bacterial

activity and *Pseudomonas aeruginosa*, *Candida albicans* and *Aspergillus fumigatus* as fungal strains. The compounds were tested at 100 μg/mL concentration

Observations

Compound bis (O-isobutyl trithiophosphate) tin was found to exhibit maximum activity against bacteria and compound bis(O-ethyl trithiophosphate) tin showed maximum activity against all the fungi.

Table 5: Antibacterial activity

Compound	*E. coli*	*B. subtilis*	*P. mirabilis*
Me	24	18	18
Et	20	28	15
^{i}Pr	18	16	14
^{i}Bu	28	20	12
Ph	19	18	20
Ciprofloxacin	16	18	17

Table 6: Antifungal activity

Compound	*P. aeruginosa*	*C. albicans*	*A. fumigatus*
Me	26	30	32
Et	27	32	34
^{i}Pr	25	31	25
^{i}Bu	20	30	30
Ph	25	25	28
Ciprofloxacin	20	22	22

The observations reveal that the compounds have more comprehensive fungus inhibiting properties than that of bacteria.

Application

Podosphaera pannosa is a plant pathogen (fungi), which produces powdery mildew in roses, looks like white powdery spots over the surface area of the leaves. It may spread to stem and to new rose buds too. It is prevalent in dry hot conditions (i.e when the root area is dry and is lacking moisture).

A moderate dose (50 g/L) of bis (O-methyl trithiophosphate) tin was given to the moderately mildew affected rose plant after 8 hr interval regularly for 7 days.

Observation

Significant changes were observed. The spotty surface of the leaf started turning green again.

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