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Short Communication

Synthetic, Characterization and Pesticidal Studies of Dibutyltin (IV) Derivatives of Salicylic acid

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Abstract

Dibutyltin (IV) derivatives of salicylic acid in different molar ratios viz., 1:1, 1:2 and 2:1 have been synthesized. These synthesized derivatives have been characterized by elemental analyses, IR spectral data, ^{1}H NMR spectral data and molar conductance measurements. The products are screened for pesticidal activities against the pest 'Red Flour Beetle' (Tribolium castaneum). These derivatives exhibited enhanced pesticidal effects as compared to the ligand.

Keywords: Dibutyltin, IR, ^{1}H NMR, Pesticidal, Salicylic acid

Introduction

The organotin compounds have been used as biocidals[1-3] as well as pesticidals[4-7]. The chemistry of organotin compounds is extensive which was developed largely due to greater tendency of tin (IV) to show coordination number higher than four. The present work deals with the synthesis, characterization and pesticidal studies of dibutyltin(IV) derivatives of salicylic acid.

Material and Methods

Experimental: Synthesis of dibutyltin diisopropoxide[8] (DBTDIP): Isopropanol (3.1 ml, 0.04 M) in 10 ml dry benzene was mixed and stirred with sodium metal (0.92 g, 0.04 M) under anhydrous condition till the complete dissolution of sodium metal. Dibutyltin dichloride (6.1 g, 0.02 M) in 15 ml dry benzene was added drop-wise to it with continuous shaking by using dropping funnel. The reaction mixture was refluxed for about 2.5 hours. The product so obtained was filtered and the filtrate was distilled under reduced pressure on a wax bath. On distillation, a colourless liquid was obtained which changed to light brown upon standing.

Synthesis of Dibutyltin (IV) derivatives of salicylic acid: Dibutyltin (IV) derivatives of salicylic acid were synthesized by refluxing DBTDIP with salicylic acid in dry benzene in 1:1, 1:2 and 2:1 molar ratios. A mixture of DBTDIP { 1.4 ml (0.004 M)/ 1.4 ml (0.004 M)/ 1.4 ml (0.004 M) } and salicylic acid { 0.55 g (0.004 M)/ 1.1 g (0.008 M)/ 0.27 g (0.002 M)} was suspended in 15 ml dry benzene in a round bottom flask fitted with water condenser and a guard tube containing anhydrous $CaCl_2$. The reaction mixture was refluxed for about 11 hrs/ 10 hrs/ 14 hrs on a wax bath. A light brown solid / dirty cream solid / brownish-white solid was obtained on azeotropic distillation. The product was filtered, washed with dry benzene followed by dry ether, recrystallized with DMF and dried in vacuum desiccator over anhydrous $CaCl_2$.

Physical and Analytical Measurements: The purity of all the synthesized compounds was checked by running their TLC for single spot on silica gel-G plate and by the repeated melting point determination of recrystallized samples taken in open capillary tube and thus uncorrected. These compounds were analyzed for elemental analysis on Carlo Erba Micro Analyser-1108 at the RSIC, CDRI, Lucknow. Tin (IV) metal was estimated by decomposing the compound with conc. HNO_3 followed by conc. H_2SO_4 and then neutralized and precipitated by liq. NH_3 as tin oxide[9].

IR spectra of compounds were recorded on Perkin Elmer RX-1 spectrometer as KBr pellets and ^{1}H NMR spectra were recorded on PMR Brucker AC 300 MHz spectrometer at RSIC, CDRI, Lucknow. The molar conductance was determined by using Systronics conductivity meter 306.

Results and Discussion

The physical and analytical data of DBTDIP and its derivatives are given in Table-1. All the synthesized derivatives were found stable and hygroscopic at room temperature. They are soluble in DMF and DMSO and insoluble in water. The low values of molar conductance of these derivatives (4.4 – 5.7 $ohm^{-1}cm^2mol^{-1}$) indicate their behaviour as non-electrolytes[10].

Infra-red spectral analysis: In the IR spectrum of DBTDIP, the weak bands at 2910 cm^{-1} and 2865 cm^{-1} indicate υ C-H of υ $–CH_2-$ and υ $–CH_3$ of the butyl group[11,12]. The strong peak at 1370 cm^{-1} occurs due to υ C-H bending of gem dimethyl structure of the isopropoxy group[13]. A weak band at 1145 cm^{-1} is due to υ C-O of the isopropoxy group[13]. The medium band at 645 cm^{-1} and a weak band at 620 cm^{-1} may be due to υ Sn-C[14]. The weak band at 535 cm^{-1} and a strong band at 460 cm^{-1} may be due to υ Sn-O[15].

Table-1
Physical, Analytical and Pesticidal Data of DBTDIP and its derivatives of salicylic acid

S. No.	Compound (Molecular Formula) Ratio	Colour	m.p./ b.p. (±2°C)	% Analysis Found/ (Calcd.)			% mortality data at different concentrations		
				C	H	Sn	0.08% (w/v)	0.06% (w/v)	0.03% (w/v)
1	DBTDIP ($C_{14}H_{32}O_2Sn$)	Light brown liquid	130.5 at 10 mm	48.40 (47.90)	9.80 (9.12)	32.95 (33.84)	40	33	18
2	$Bu_2Sn(L)$ ($C_{15}H_{22}O_3Sn$) 1:1	Light brown solid	110	49.05 (48.82)	6.10 (5.97)	31.94 (32.19)	48	38	28
3	$Bu_2Sn(LH)_2$ ($C_{22}H_{28}O_6Sn$) 1:2	Dirty cream solid	95	52.50 (52.10)	5.85 (5.53)	23.52 (23.42)	45	35	27
4	$(Bu_2Sn)_2L(OPr^i)_2$ ($C_{29}H_{54}O_5Sn_2$) 2:1	Brownish white solid	92	48.74 (48.37)	7.88 (7.51)	32.74 (32.99)	53	42	33

In the IR spectra of dibutyltin(IV) derivatives of salicylic acid, a medium band at 3030 cm^{-1} may be due to υ C-H of the aromatic ring[11,13]. The weak bands at 2930 cm^{-1} and 2855 cm^{-1} indicate υ C-H of $–CH_2$- and $–CH_3$ of the butyl group[11,12]. The weak band in the region 1140 cm^{-1} corresponds to the υ C-O of the isopropoxy group in 2:1 derivative[13]. A strong band around 1430 cm^{-1} corresponds to $υ_s$COO stretching vibrations while a strong band around 1620 cm^{-1} may be due to $υ_{as}$COO stretching vibrations[16]. The separation value, ΔυCOO of about 190 cm^{-1} suggested the presence of bridged carboxylate group[17].

A strong band around 1370 cm^{-1} is due to υ C-H bending of the gem dimethyl structure of the isopropoxy group[12] in 2:1 derivative. The medium bands around 635 cm^{-1} and weak bands around 625 cm^{-1} occur due to υ Sn-C[14], while weak bands around 525 cm^{-1} and strong band around 470 cm^{-1} occur due to υ Sn-O.[15] The absence of free hydroxyl (-OH) band in the region 3500-3200 cm^{-1} in 1:1 and 2:1 derivatives suggests possible bonding of hydroxyl oxygen to tin, while this band is appeared in 1:2 derivative at 3480 cm^{-1}.

^{1}H NMR spectral analysis: In the nmr spectrum of DBTDIP, a multiplet between 1.20 – 1.60 ppm may be due to protons of butyl group[18] attached with tin. A multiplet between 0.70 – 1.20 ppm may be due to protons of isopropoxy group.

In the nmr spectra of synthesized dibutyltin (IV) derivatives of salicylic acid, a multiplet between 6.90 – 7.70 ppm corresponds to aromatic protons. The multiplet in the region 1.00 – 1.40 ppm in 1:1 and 1:2 derivatives and 0.50 – 1.20 ppm in 2:1 derivative may be due to protons of butyl group[17] attached with tin. A hump around 6.50 ppm is obtained in 1:2 derivative which corresponds to –OH group proton which is absent in 1:1 and 2:1 derivatives.

Pesticidal activity: All the synthesized compounds have been screened for their pesticidal activities on a Red Flour Beetle (*Tribolium castaneum*), a storage food grain pest adopting bio-assay technique.[19] A comparative study of % pest mortality (table-1) indicates the enhancement of pesticidal activity of derivatives as compared to ligand.

Conclusion

From the above analysis, it has been found that all the synthesized derivatives are stable at room temperature. The pesticidal activity of dibutyltin(IV) derivatives of salicylic acid is higher as compared to ligand fragments.

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