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Characterization and Pesticidal Studies of Dibutyltin (IV) Derivatives of diphenylamine-2-hydroxy-2'-carboxylic acid

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Abstract

Organotin (IV) compounds of diphenylamine derivatives have synthesized by the reaction of dibutyltin diisopropoxide with diphenylamine-2-hydroxy-2'-carboxylic acid in 1:1, 1:2 and 2:1 molar ratios. These compounds have been characterized by elemental analyses, IR spectral analyses, ^{1}H NMR spectral analyses and molar conductance measurements. The products are screened for pesticidal activities against the pest 'Red Flour Beetle' (Tribolium castaneum). The compounds exhibited enhanced pesticidal effects as compared to the ligand.

Keywords: Dibutyltin, Diphenylamine, IR, ^{1}H NMR, Pesticidal.

Introduction

The organotin comounds are of paramount importance from academic point of view as well as tin may form coordination complexes with suitable ligands displaying enhanced its coordination number. The organotin compounds have been used as biocidals[1-3] as well as pesticidals[4-8]. The present work deals with the synthesis, characterization and pesticidal studies of dibutyltin (IV) compounds of diphenylamine-2-hydroxy-2'-carboxylic acid.

Material and Methods

Experimental: Synthesis of dibutyltin diisopropoxide[9] (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. 6.1 g of dibutyltin dichloride (0.02 M) in 15 ml dry benzene was mixed drop-wise in the reaction mixture 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 Diphenylamine-2-hydroxy-2'-carboxylic acid (dphc): 1.56 gm (0.01 M) o-chlorobenzoic acid and 1.09 gm (0.01 M) o-amino phenol were taken in 100 ml of distilled water in a flask. This mixture was made slightly alkaline with K_2CO_3 solution and a little copper oxide was mixed in the reaction mixture. The reaction mixture was refluxed on an oil bath for about 4 hours and cooled. One gram activated charcoal was added and boiled for about one hour to decolourise the product. It was filtered, concentrated and cooled. The obtained solution was acidified with dil. HCl in excess till the precipitation of the resultant product was complete. The obtained crude product was dissolved in ethyl alcohol for recrystallization and the recrystallized compound was dried over anhydrous calcium chloride in a desiccator to get brown powder.

Synthesis of Dibutyltin (IV) derivatives of Diphenylamine-2-hydroxy-2'-carboxylic acid: Dibutyltin (IV) derivatives of Diphenylamine-2-hydroxy-2'-carboxylic acid were synthesized by refluxing DBTDIP with dphc in dry toluene 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 dphc {0.92 g (0.004 M)/ 1.84 g (0.008 M)/ 0.46 g (0.002 M)} was suspended in 30 ml dry toluene in a round bottom flask fitted with water condenser and a guard tube containing anhydrous $CaCl_2$. The solution was condensed for about 12-16 hrs on a wax bath. On cooling in a desiccator for over night, the coloured solid was separated out which was filtered and washed with dry ether. The obtained product was recrystallized from DMSO and dried under reduced pressure over anhydrous $CaCl_2$ to get coloured crystalline solid.

Physical and Analytical Measurements: The purity of derivatives was determined 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[10].

Infra-red spectrum of compounds was recorded by Perkin Elmer RX-1 spectrometer and ^{1}H NMR spectrum was recorded by 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 dibutyltindiisopropoxide 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 (3.8 – 4.9 $ohm^{-1}cm^2mol^{-1}$) indicate their behaviour as non-electrolytes[11].

Infra-red spectral analysis: In the IR spectrum of DBTDIP, the weak peaks around 2910 cm^{-1} and 2865 cm^{-1} indicate υ C-H of υ $–CH_2-$ and υ $–CH_3$ of the butyl group[12,13]. The strong peak at 1370 cm^{-1} occurs due to υ C-H bending vibration of geminal dimethyl structure of the isopropoxy group[14]. A weak peak at 1145 cm^{-1} occurs due to υ C-O present in isopropoxy group.[14] The medium peak around 645 cm^{-1} and a weak peak around 620 cm^{-1} may be due to υ Sn-C.[15] The weak peak around 535 cm^{-1} and a strong peak around 460 cm^{-1} may be due to υ Sn-O[16].

In the IR spectrum of dphc, a medium peak around 3440 cm^{-1} may be due to υ O-H stretching vibration and 2640 cm^{-1} due to υ O-H stretching of –COOH group. The sharp peak at 1685 cm^{-1} takes place for υ –CO stretching vibration of –COOH group.

In the IR spectra of dibutyltin(IV) derivatives of dphc, a medium band at 3040 cm^{-1} may be due to υ C-H of the aromatic ring[12,14]. The weak peaks at 2940 cm^{-1} and 2850 cm^{-1} indicate υ C-H of $–CH_2-$ and $–CH_3$ of the butyl group[12,13]. The weak peak in the region 1145 cm^{-1} corresponds for υ C-O of the isopropoxy group in 2:1 derivative[14]. A strong peak around 1435 cm^{-1} corresponds to υ_sCOO stretching vibrations while a strong peak around 1630 cm^{-1} may be due to υ_{as}COO stretching vibrations[17]. The separation value, ΔυCOO of about 195 cm^{-1} suggested the presence of bridged carboxylate group[18].

A strong peak around 1375 cm^{-1} occurs due to υ C-H bending of the geminal dimethyl structure of the isopropoxy group[14] in 2:1 derivative. The medium peak around 640 cm^{-1} and weak peak around 610 cm^{-1} occur due to υ Sn-C[15], while weak peak around 540 cm^{-1} and strong peak around 460 cm^{-1} occurs due to υ Sn-O[16].

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 3460 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[19] attached with tin. A multiplet between 0.70 – 1.20 ppm may be due to protons of isopropoxy group.

In the nmr spectrum of dphc, a multiplet is shown between 7.20 – 8.10 ppm, which corresponds for aromatic protons. A singlet at 10.50 ppm, 11.30 ppm and 3.45 ppm corresponds to –OH, -COOH and –NH- protons respectively.

In the nmr spectra of synthesized dibutyltin (IV) derivatives of dphc, a multiplet is shown between 7.10 – 8.20 ppm, which corresponds to aromatic protons. The multiplet between 1.00 – 1.40 ppm in 1:1 and 1:2 derivatives and 0.50 – 1.30 ppm in 2:1 derivative may be due to protons of butyl group[19] attached with tin. A hump around 10.70 ppm is obtained in 1:2 derivative which corresponds to –OH group proton which is absent in 1:1 and 2:1 derivatives. A singlet is obtained in the region 3.50 – 3.65 ppm corresponds to –NH- proton.

Table-1
Physical, Analytical and Pesticidal Data of DBTDIP and its derivatives with dphc

S. No.	Compound (Molecular Formula) Ratio	Colour	m.p./ b.p. (±2°C)	% Analysis Found/ (Calcd.)				% mortality data at different concentrations		
				C	H	N	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	dphc ($C_{13}H_{11}O_3N$)	Brown solid	144	68.75 (68.12)	5.24 (4.80)	6.85 (6.11)	--	17	10	8
3	$Bu_2Sn(L)$ ($C_{21}H_{27}O_3NSn$) 1:1	Dark brown solid	140	55.21 (54.78)	6.14 (5.80)	3.84 (3.04)	26.12 (25.87)	48	43	37
4	$Bu_2Sn(LH)_2$ ($C_{34}H_{38}O_6N_2Sn$) 1:2	Black solid	95	59.88 (59.22)	5.64 (5.52)	4.76 (4.06)	17.25 (17.27)	47	37	30
5	$(Bu_2Sn)_2L(OPr^i)_2$ ($C_{35}H_{55}O_5NSn_2$) 2:1	Brownish black solid	108	52.74 (52.05)	7.43 (6.82)	1.98 (1.73)	29.62 (29.49)	53	47	38

Pesticidal activity: All the synthesized derivatives were screened for their pesticidal activities on a Red Flour Beetle (*Tribolium castaneum*), a storage food grain pest adopting bio-assay technique[20]. 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 diphenylamine 2-hydroxy-2'-carboxylic acid is higher as compared to ligand fragments.

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