Short Communication

Characterization and Pesticidal Studies of some new Dibutyltin (IV) Derivatives of 1-hydroxy-2-naphthoic acid

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Abstract

Some new dibutyltin (IV) derivatives of 1-hydroxy-2-naphthoic acid (1,2-HNA) in different molar ratios viz., 1:1, 1:2 and 2:1 have been synthesized. The synthesized derivatives have been characterized by elemental analyses, IR spectral data, PMR 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.

Key Words: Dibutyltin, 1,2-HNA, IR, PMR, Pesticidal

Introduction

The organotin compounds are the organo-metallic compounds in which the carbon atom of the organic group is directly attached with tin metal. These compounds have been used as biocidals as well as pesticidals. 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 characterization and pesticidal studies of some new synthesized dibutyltin (IV) derivatives of 1-hydroxy-2-naphthoic acid.

Material and Methods

Experimental: Synthesis of dibutyltin diisopropoxide (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. A creamish brown 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 CaCl₂.

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. HNO₃ followed by conc. H₂SO₄ and then neutralized and precipitated by liq. NH₃ as tin oxide.

IR spectra of compounds were recorded on Perkin Elmer RX-1 spectrometer as KBr pellets and PMR 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 (4.1 – 5.2 ohm cm²/mol) indicate their behaviour as non-electrolytes.
Table-1
Physical, Analytical and Pesticidal Data of DBTDIP and its derivatives with 1-hydroxy-2-naphthoic acid (L)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Compound (Molecular Formula) Ratio</th>
<th>Colour</th>
<th>m.p./ b.p. (±2°C)</th>
<th>% Analysis Found (Calcd.)</th>
<th>% mortality data at different concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>1</td>
<td>DBTDIP (C₁₄H₂₃O₂Sn)</td>
<td>Light brown liquid</td>
<td>130.5 at 10 mm</td>
<td>48.40 (47.90)</td>
<td>9.80 (9.12)</td>
</tr>
<tr>
<td>2</td>
<td>Bu₂Sn(L) (C₁₅H₂₇O₃Sn) 1:1</td>
<td>Creamish brown solid</td>
<td>205</td>
<td>54.95 (54.46)</td>
<td>6.10 (5.73)</td>
</tr>
<tr>
<td>3</td>
<td>Bu₂Sn(LH)₂ (C₁₇H₃₃O₄Sn) 1:2</td>
<td>Sandy brown solid</td>
<td>199</td>
<td>59.70 (59.34)</td>
<td>5.52 (5.27)</td>
</tr>
<tr>
<td>4</td>
<td>(Bu₂Sn)₂L(OPr)₂ (C₁₅H₂₉O₅Sn₂) 2:1</td>
<td>Reddish brown sticky solid</td>
<td>--</td>
<td>51.92 (51.47)</td>
<td>7.60 (7.28)</td>
</tr>
</tbody>
</table>

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 ν–CH₃ and ν–CH₂ of the butyl group¹⁰,¹¹. The strong peak at 1370 cm⁻¹ occurs due to υ C-H bending of gem dimethyl structure of the isopropoxy group¹². A weak band at 1145 cm⁻¹ is due to υ C-O of the isopropoxy group¹². The medium band at 645 cm⁻¹ and a weak band at 620 cm⁻¹ may be due to υ Sn-C.¹³ The weak band at 535 cm⁻¹ and a strong band at 460 cm⁻¹ may be due to υ Sn-O¹⁴.

In the IR spectra of dibutyltin(IV) derivatives of 1,2-HNA, a medium band at 3025 cm⁻¹ may be due to υ C-H of the aromatic ring.¹⁰,¹¹ The weak bands at 2920 cm⁻¹ and 2860 cm⁻¹ indicate υ C-H of ν–CH₂ and ν–CH₃ of the butyl group¹⁰,¹¹. The weak band in the region 1145 cm⁻¹ corresponds to the υ C-O of the isopropoxy group in 2:1 derivative¹². A strong band around 1425 cm⁻¹ corresponds to υSnCOO stretching vibrations while a strong band around 1625 cm⁻¹ may be due to υSnCOO stretching vibrations¹⁵. The separation value, ΔυSnCOO of about 200 cm⁻¹ suggested the presence of bridged carboxylate group¹⁶.

A strong band around 1360 cm⁻¹ is due to υ C-H bending of the gem dimethyl structure of the isopropoxy group¹² in 2:1 derivative. The medium bands around 635 cm⁻¹ and weak bands around 620 cm⁻¹ occur due to υ Sn-C¹³, while weak bands around 530 cm⁻¹ and strong band around 460 cm⁻¹ occur due to υ Sn-O¹⁴.

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 3430 cm⁻¹.

PMR spectral analysis: In the pmr spectrum of DBTDIP, a multiplet between 1.20 – 1.60 ppm may be due to protons of butyl group attached with tin¹⁷. A multiplet between 0.70–1.20 ppm may be due to protons of isopropoxy group.

In the pmr spectra of synthesized dibutyltin(IV) derivatives of 1,2-HNA, a multiplet between 6.85 – 7.85 ppm corresponds to aromatic protons. The multiplet in the region 1.10 – 1.40 ppm in 1:1 and 1:2 derivatives and 0.55 – 1.30 ppm in 2:1 derivative may be due to protons of butyl group attached with tin¹⁷. A hump around 6.40 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 technique¹⁸. A comparative study of % pest mortality (table-1) indicates the enhancement of pesticidal activity of derivatives as compared to ligand.

Conclusion
The pesticidal studies of Dibutyltin(IV) derivatives of 1-hydroxy-2-naphthoic acid have shown their enhanced pesticidal activities as compared to ligand.

References


