



Short Communication

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

Mittal Pankaj* and Pachouri Manoj Kumar

Department of Applied Sciences (Chemistry), B.M.A.S. Engineering College, Keetham, Agra, INDIA

Available online at: www.isca.in

(Received 15th April 2011, revised 21st April 2011, accepted 21st February 2012)

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 biocidals¹⁻³ as well as pesticides⁴⁻⁶. 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 diisopropoxide⁷ (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 1-hydroxy-2-naphthoic acid (1,2-HNA): Dibutyltin (IV) derivatives of 1,2-HNA were synthesized by refluxing DBTDIP with 1,2-HNA in dry benzene in 1:1, 1:2 and 2:1 molar ratios. A mixture of DBTDIP {1.1 ml (0.003 M)/ 0.9 ml (0.0025 M)/ 1.7 ml (0.0048 M)} and 1-hydroxy-2-naphthoic acid {0.56 g (0.003 M)/ 1.0 g (0.0050 M)/ 0.45 g (0.0024 M)} was suspended in 15 ml dry benzene in a round bottom flask fitted with water

condenser and a guard tube containing anhydrous CaCl₂. The reaction mixture was refluxed for about 18 hrs/ 20 hrs/ 17 hrs on a wax bath. A creamish-brown solid / sandy brown solid / reddish-brown sticky 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 oxide⁸.

IR spectra of compounds were recorded on Perkin Elmer RX-1 spectrometer as KBr pellets and PMR spectra were recorded on PMR Bruker 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⁻¹cm²mol⁻¹) indicate their behaviour as non-electrolytes.⁹

Table-1
Physical, Analytical and Pesticidal Data of DBTDIP and its derivatives with 1-hydroxy-2-naphthoic acid (L)

S. No.	Compound (Molecular Formula) Ratio	Colour	m.p./ b.p. ($\pm 2^\circ\text{C}$)	% 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 ₂ Sn)	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 ₂ Sn(L) (C ₁₉ H ₂₄ O ₃ Sn) 1:1	Creamish - brown solid	205	54.95 (54.46)	6.10 (5.73)	28.05 (28.35)	50	42	32
3	Bu ₂ Sn(LH) ₂ (C ₃₀ H ₃₂ O ₆ Sn) 1:2	Sandy brown solid	199	59.70 (59.34)	5.52 (5.27)	19.25 (19.56)	48	38	28
4	(Bu ₂ Sn) ₂ (OPr) ₂ (C ₃₃ H ₅₆ O ₅ Sn ₂) 2:1	Reddish-brown sticky solid	--	51.92 (51.47)	7.60 (7.28)	30.20 (30.85)	55	45	35

Infra-red spectral analysis: In the IR spectrum of DBTDIP, the weak bands at 2910 cm⁻¹ and 2865 cm⁻¹ indicate ν C-H of ν -CH₂- and ν -CH₃ of the butyl group^{10,11}. The strong peak at 1370 cm⁻¹ occurs due to ν C-H bending of gem dimethyl structure of the isopropoxy group¹². A weak band at 1145 cm⁻¹ is due to ν 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 ν Sn-C¹³. The weak band at 535 cm⁻¹ and a strong band at 460 cm⁻¹ may be due to ν 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 ν C-H of the aromatic ring.^{10,12} The weak bands at 2920 cm⁻¹ and 2860 cm⁻¹ indicate ν C-H of -CH₂- and -CH₃ of the butyl group^{10,11}. The weak band in the region 1145 cm⁻¹ corresponds to the ν C-O of the isopropoxy group in 2:1 derivative¹². A strong band around 1425 cm⁻¹ corresponds to ν _sCOO stretching vibrations while a strong band around 1625 cm⁻¹ may be due to ν _{as}COO stretching vibrations¹⁵. The separation value, $\Delta\nu$ COO of about 200 cm⁻¹ suggested the presence of bridged carboxylate group¹⁶.

A strong band around 1360 cm⁻¹ is due to ν 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 ν Sn-C¹³, while weak bands around 530 cm⁻¹ and strong band around 460 cm⁻¹ occur due to ν 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

1. Arakawa Y., *Main Group Metal Chem.*, **12**, 1 (1989)
2. Saxena A.K., *Appl. Organometal. Chem.*, **1**, 39 (1987)
3. Dey K. and Mukhopadhyay S., *J. Ind. Chem. Soc.*, **78**, 73 (2001)
4. Gupta P.R., Mishra R.C. and Dogra G.S., *Ind. J. Agric. Sci.*, **51**, 514 (1981)

5. Mittal P., Pachouri M.K. and Sharma R.C., *Asian J. of Chem.*, **18(1)**, 737 (2006)
6. Mittal P., Pachouri M.K. and Sharma R.C., *J. Ind. Council Chem.*, **23(2)**, 23 (2006)
7. Gaur D.P., Srivastava G. and Mehrotra R.C., *J. Organometal. Chem.*, **63**, 221 (1973)
8. Vogel A.I., *Quantitative Inorganic Analysis*, Longmans, London, (1975)
9. Kettle S.F.A., *Coordination Compounds*, Thomas Nelson and Sons, 168 (1975)
10. Bellamy L.J., *The Infra-red Spectra of Complex Molecules*, Methuen, London, (1962)
11. Nakanishi K. and Solomon P.H., *Infra-red Absorption Spectroscopy* 2nd Ed., Holden-Day, London, (1962)
12. Silverstein R.M., Bassler G.C. and Morrill T.C., *Spectrometric Identification of Organic Compounds*, John Wiley, New York, (1981)
13. Brown M.P., Okawara R. and Rochow E.G., *Spectrochim. Acta*, **16**, 595 (1960)
14. Pardhy S.A., Gopinathan S. and Gopinathan C., *Synth. React. Inorg. Met. Org. Chem.*, **13**, 305 (1983)
15. Peruzzo V., Plazzogna G. and Tagliavini G., *Organometal. Chem.*, **24**, 347 (1970)
16. Srivastava T.N. and Singh J.D., *Ind. J. Chem.*, **24A**, 489 (1985)
17. Asahi Research Centre Co. Ltd. Tokyo, *Hand Book of Proton NMR Spectra and Data*, Vol. 2nd & 4th, Academic Press, Japan, (1985)
18. U.S. Environmental Protection Agency, *Report of DDT Advisory Committee* (2010)