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# Structural and Pesticidal Studies of Monobutyltin (IV) Derivatives of 1-Hydroxy-2-Naphthoic Acid

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## Abstract

*Some organotin (IV) derivatives have prepared by treating the monobutyltin triisopropoxide with 1-hydroxy-2-naphthoic acid in 1:1, 1:2, 1:3 and 2:1 molar ratios. The synthesized derivatives are characterized by their elemental analyses, IR spectral analyses, $^1$HNMR spectral analyses and molar conductance measurements. The products are screened for their pesticidal activities against the pest 'Red Flour Beetle' (Tribolium castaneum). The derivatives so obtained shown increased pesticidal activities as compared to the ligand.*

**Keywords:** Monobutyltin, IR, $^1$HNMR, Pesticidal.

## Introduction

The organotin compounds are important 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[4-10]. The present work deals with the synthesis, structural and pesticidal studies of monobutyltin (IV) derivatives of 1-hydroxy-2-naphthoic acid (1,2-HNA).

## Materials and Methods

**Experimental: Synthesis of Monobutyltin triisopropoxide[11] (MBTTIP):** 0.69 g (0.03 M) of sodium metal suspended in dry benzene was taken in round bottom flask having two-way adapter connected with water condenser at one end and a dropping funnel protected with guard of $CaCl_2$ at another end. 2.4 ml (0.03 M) of isopropanol solution in 5 ml dry benzene was taken in dropping funnel and added drop wise in to round bottom flask with continuous stirring. The reaction content was refluxed till the complete dissolution of sodium pieces. After dissolution, 2.8 ml (0.01 M) of monobutyltin trichloride solution in 10 ml dry benzene was taken in dropping funnel. The solution was poured drop wise in to R.B. flask with continuous stirring; a white crystalline precipitate of sodium chloride was separated. The reaction mixture was refluxed for about three and half hours. The product so obtained 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 Monobutyltin (IV) derivatives of 1-hydroxy-2-naphthoic acid:** Monobutyltin (IV) derivatives of 1-hydroxy-2-naphthoic acid were synthesized by refluxing MBTTIP with 1,2-HNA in dry benzene in 1:1, 1:2, 1:3 and 2:1 molar ratios. A mixture of MBTTIP {1.1 ml (0.003 M)/ 1.1 ml (0.003 M)/ 0.75 ml (0.002 M)/1.4 ml (0.004 M)} and 1,2-HNA {0.56 g (0.003 M)/ 1.13 g (0.006 M)/ 1.16 g (0.006 M)/0.38 g (0.002 M)} was suspended in 20 ml dry benzene in a R. B. flask connected with water condenser and a guard tube containing anhydrous $CaCl_2$. The solution was condensed for about 10-14 hrs on a wax bath. On cooling in a desiccator for overnight, the coloured solid was separated out, which was filtered and washed with dry ether. The obtained product was recrystallized from dimethylformamide 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 compounds 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 concentrated nitric acid followed by concentrated sulphuric acid and then neutralized and precipitated by liquid ammonia as tin oxide[12].

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 monobutyltin triisopropoxide 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 solvents and insoluble in water. The low values of molar conductance of these derivatives (3.9 – 4.6 $ohm^{-1}cm^2mol^{-1}$) indicate their behaviour as non-electrolytes[13].

**Table-1**
**Physical, Analytical and Pesticidal Data of MBTTIP and its derivatives with 1-hydroxy-2-naphthoic acid**

| 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) |
| MBTTIP ($C_{13}H_{30}O_3Sn$) | Light brown liquid | 94 at 0.03 mm | 45.05 (44.23) | 9.00 (8.51) | 32.40 (33.65) | 33 | 30 | 17 |
| $BuSn(L)(OPr^i)$ ($C_{18}H_{22}O_4Sn$) **1:1** | Sand- stone solid | 190 | 51.92 (51.34) | 5.98 (5.23) | 27.90 (28.21) | 45 | 32 | 20 |
| $BuSn(LH)_2(OPr^i)$ ($C_{29}H_{30}O_7Sn$) **1:2** | Light brown solid | 142 | 57.80 (57.17) | 5.25 (4.93) | 19.05 (19.50) | 38 | 32 | 18 |
| $BuSn(LH)_3$ ($C_{37}H_{30}O_9Sn$) **1:3** | Dirty-white solid | 195 | 60.85 (60.27) | 4.95 (4.07) | 15.88 (16.11) | 40 | 30 | 22 |
| $(BuSn)_2L(OPr^i)_4$ ($C_{31}H_{52}O_7Sn_2$) **2:1** | Muddy brown solid | 162 | 48.75 (48.10) | 7.18 (6.72) | 29.90 (30.69) | 47 | 35 | 23 |

**Infra-red spectral analysis:** In the Infra-red spectrum of MBTTIP, the weak bands around 2920 $cm^{-1}$ and 2860 $cm^{-1}$ indicate υ C-H of υ $–CH_2$- and υ $–CH_3$ of the butyl group[14,15]. The strong peak at 1390 $cm^{-1}$ occurs due to υ C-H bending vibration of geminal dimethyl structure of the isopropoxy group[16]. A weak peak at 1150 $cm^{-1}$ occurs due to υ C-O present in isopropoxy group[16]. The medium peak around 645 $cm^{-1}$ and a weak peak around 610 $cm^{-1}$ may be due to υ Sn-C[17]. The weak peak around 540 $cm^{-1}$ and a strong peak around 470 $cm^{-1}$ may be due to υ Sn-O[18].

In the IR spectra of monobutyltin(IV) derivatives of 1-hydroxy-2-naphthoic acid, a medium band at 3040 $cm^{-1}$ may be due to υ C-H of the aromatic ring.[14,16] The weak bands at 2950 $cm^{-1}$ and 2850 $cm^{-1}$ indicate υ C-H of $–CH_2$- and $–CH_3$ of the butyl group[14,15]. The weak band in the region 1160 $cm^{-1}$ corresponds to the υ C-O of the isopropoxy group in 2:1 derivative.[16] A strong band around 1425 $cm^{-1}$ corresponds to $υ_sCOO$ stretching vibrations while a strong band around 1630 $cm^{-1}$ may be due to $υ_{as}COO$ stretching vibrations[19]. The separation value, ΔυCOO of about 200 $cm^{-1}$ suggested the presence of bridged carboxylate group[20].

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 1:1, 1:2 and 2:1 derivative. The medium bands around 635 $cm^{-1}$ and weak bands around 615 $cm^{-1}$ occur due to υ Sn-C[17], while weak bands around 540 $cm^{-1}$ and strong band around 460 $cm^{-1}$ occur due to υ Sn-O[18].

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 and 1:3 derivatives around 3480 $cm^{-1}$.

**$^1$H NMR spectral analysis:** In the nmr spectrum of MBTTIP, a multiplet between 1.30 – 1.80 ppm may be due to protons of butyl group[21] attached with tin. A multiplet between 0.50 – 1.20 ppm may be due to protons of isopropoxy group.

In the nmr spectra of synthesized monobutyltin (IV) derivatives of 1,2-HNA, a multiplet between 7.70 – 7.70 ppm corresponds to aromatic protons. The multiplet in the region 0.70 – 1.30 ppm in 1:1, 1:2 and 1:3 derivatives and 0.45 – 1.10 ppm in 2:1 derivative may be due to protons of butyl group[21] attached with tin. A hump around 6.40 ppm is obtained in 1:2 and 1:3 derivatives which corresponds to –OH group proton which is absent in 1:1 and 2:1 derivatives.

**Pesticidal activity:** All the synthesized derivatives have been screened for their pesticidal activities on a Red Flour Beetle (*Tribolium castaneum*), a storage food grain pest adopting bio-assay technique[22]. 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 monobutyltin (IV) derivatives of 1-hydroxy-2-naphthoic acid is higher than ligand fragments.

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