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NOTE

Studies on Monobutyltin(IV) Derivatives of 3-Hydroxy-2-naphthoic Acid

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Some new monobutyltin(IV) derivatives of 3-hydroxy-2-naphthoic acid in different molar ratios, *viz.*, 1 : 1, 1 : 2, 1 : 3 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 were screened for pesticidal activities against the pest called *Tribolium castaneum* (red flour beetle). The monobutyltin(IV) derivatives exhibited enhanced pesticidal effect as compared to the ligand fragments alone.

Key Words: Monobutyltin, PMR, Pesticidal.

The organotin derivatives are of paramount importance both from theoretical and practical points of view. Several reviews[1-3] have comprehensively dealt with this emphasized work on organotin compounds. These compounds have been extensively used as biocidals[4-6]. The present work deals with the synthesis, structural and pesticidal studies of monobutyltin(IV) derivatives of 3-hydroxy-2-naphthoic acid.

Synthesis of monobutyltin triisopropoxide[7] (MBTTIP): 0.69 g (0.03 M) of sodium metal suspended in 10 mL dry benzene was taken in a round-bottomed flask having two-way adapter connected with water condenser at one end and dropping funnel protected with guard tube of $CaCl_2$ at another end. Isopropanol solution (2.4 mL, 0.03 M) in 5 mL dry benzene was taken in a dropping funnel and added dropwise into the round-bottomed flask with continuous shaking; a white crystalline precipitate of sodium chloride was separated. The reaction mixture was refluxed for about 3.5 h. 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: The derivatives were synthesized by refluxing monobutyltin triisopropoxide with 3-hydroxy-2-naphthoic acid (3,2-HNA) in 1 : 1, 1 : 2, 1 : 3 and 2 : 1 molar ratios, respectively.

A mixture of 1.1 mL (0.003 M)/1.1 mL (0.003 M)/0.75 mL (0.002 M)/1.4 mL (0.004 M) monobutyltin triisopropoxide and 0.56 g (0.003 M)/1.13 g (0.006 M)/1.13 g (0.006 M)/0.38 g (0.002 M) 3,2-HNA was suspended in 15 mL dry benzene in a round-bottomed flask. The reaction mixture was refluxed for about 10–14 h on a wax bath using water condenser. A solid product was obtained on azeotropic distillation. It was filtered, washed with dry benzene followed by dry ether, recrystallized with DMF and dried in vacuum desiccator over anhydrous $CaCl_2$.

The purity of all the 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. All the synthesized compounds were analyzed for carbon and hydrogen on Carlo Erba Micro Analyzer-1108 at the Regional Sophisticated Instrumentation Centre, CDRI, Lucknow. Tin(IV) metal was estimated by decomposing the compounds with conc. HNO_3 followed by conc. H_2SO_4 and then neutralized and precipitated by liquid NH_3 as tin oxide. IR spectra were recorded on Perkin-Elmer RX-1 in KBr pellets. PMR spectra were recorded on PMR Brucker-AC 300 MHz spectrometer using TMS as a reference material. The molar conductance was determined by using Systronics conductivity meter 306.

The physical and analytical data of monobutyltin triisopropoxide and its tin(IV) derivatives are given (Table-1). All the synthesized compounds were found coloured and stable at room temperature.

TABLE-1
PHYSICAL, ANALYTICAL AND PESTICIDAL DATA OF MONOBUTYLTIN TRIISOPROPOXIDE AND ITS DERIVATIVES

Compound (Colour)	m.f.	m.p./b.p. (°C)(±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 (Light brown liquid)	$C_{13}H_{30}O_3Sn$	94 at 0.3 mm	45.05 (44.23)	9.00 (8.51)	32.40 (33.65)	33	30	17
BuSn(L)(OPr^i) (1 : 1) (Mustard solid)	$C_{18}H_{22}O_4Sn$	196	51.75 (51.34)	5.80 (5.23)	28.00 (28.21)	45	32	20
BuSn(LH)$_2$(OPr^i) (1 : 2) (Mustard green solid)	$C_{29}H_{30}O_7Sn$	200	57.80 (57.17)	5.35 (4.93)	19.15 (19.50)	40	30	18
BuSn(LH)$_3$ (1 : 3) (Light parrot green solid)	$C_{37}H_{30}O_9Sn$	295	60.85 (60.27)	4.82 (4.07)	15.80 (16.11)	42	32	20
(BuSn)$_2$(L)(OPr^i)$_4$ (2 : 1) (Yellowish green solid)	$C_{31}H_{52}O_7Sn_2$	242	48.65 (48.10)	7.20 (6.72)	30.20 (30.69)	48	38	28

L = 3-hydroxy-2-naphthoic acid, Bu = butyl, OPr^i = isopropoxy group.

In the IR spectrum of monobutyltin triisopropoxide, the weak bands at 2920 and 2865 cm^{-1} indicate ν(C—H) of —CH_2— and —CH_3 of the butyl group. The strong band at 1390 cm^{-1} occurs due to C—H bending of the *gem*-dimethyl structure of the isopropoxy group. A weak band at 1150 cm^{-1} corresponds to ν(C—O) of the isopropoxy group. The medium band at 645 cm^{-1} and a weak band at 610 cm^{-1} occur due to ν(Sn—C). The weak band at 540 cm^{-1} and a strong band at 470 cm^{-1} occur due to ν(Sn—O).

In the IR spectra of monobutyltin(IV) derivatives of 3,2-HNA, a medium band at 3080–3035 cm^{-1} may be assigned to ν(C—H) of aromatic ring. A weak band at 2960–2935 cm^{-1} and a medium band at 2860–2840 cm^{-1} occur due to ν(C—H) of —CH_2— and —CH_3 of the butyl group. The weak bands in the region 1950–1715 cm^{-1} indicate the overtones due to substitution in the aromatic ring[8]. A strong band around 1640 cm^{-1} and a strong band around 1430 cm^{-1} may be due to ν_{asym}(COO)

and $\nu_{sym}(COO)$[9], respectively. A shift of 15 cm^{-1} in $\nu_{sym}(COO)$, as compared to 3,2-NHA [$\nu_{sym}(COO)$ stretching in 3,2-HNA appeared at 1415 cm^{-1}] indicates the bonding of the carboxylate oxygen to tin. The separation value, $\Delta\nu(COO)$ of 210 cm^{-1} suggests the presence of bridged or coordinated carboxylate group[10, 11]. A strong band at 1360 cm^{-1} may be due to C—H bending of *gem*-dimethyl group, while a strong band at 1250 cm^{-1} may be attributed to ν(C—O) of the isopropoxy group except 1 : 3 molar ratio. The medium band at 635 cm^{-1} and weak band at 615 cm^{-1} correspond to ν(Sn—C)[12] while the weak band at 540 cm^{-1} and the strong band at 445 cm^{-1} correspond to ν(Sn—O)[13]. The absence of free —OH band in the region 3325–2810 cm^{-1} in 1 : 1 and 2 : 1 derivatives suggests possible bonding of the hydroxy oxygen to tin.

In the PMR spectra of synthesized derivatives, a multiplet between δ 6.95–7.75 may be due to aromatic ring protons. A multiplet in the region δ 0.40–1.40 may be due to the overlapping of protons of the butyl group and isopropoxy group[14]. This overlapping is absent in 1 : 3 derivative. A hump of δ 6.35 and δ 6.30 in 1 : 2 and 1 : 3 derivatives may be due to —OH group proton, while it is absent in 1 : 1 and 2 : 1 derivatives indicating the participation of —OH proton in bonding with tin.

The molar conductance of 10^{-3} M solution of monobutyltin(IV) derivatives in DMF (4.6–5.7 Ω^{-1} cm^2 mol^{-1}) indicates their behaviour as non-electrolytes[15].

Pesticidal Activity: Pesticidal activities of all the synthesized compounds have been determined on a red flour beetle (*Tribolium castaneum*), a storage food grain pest adopting bio-assay technique. A comparative study of % pest mortality indicates the enhancement of pesticidal activity of monobutyltin(IV) derivatives as compared to ligand fragments.

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