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Some Mono-, Di- and Triphenyl Substituted Tin Derivatives of 1-Hydroxy-2-Naphthoic and 3-Hydroxy-2-Naphthoic Acids

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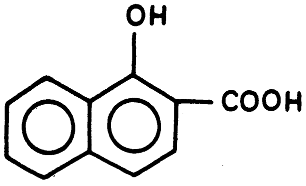
Several mono-, di- and triphenyl substituted tin derivatives of 1-hydroxy-2-naphthoic and 3-hydroxy-2-naphthoic acids have been prepared by alcoholysis reaction involving the interaction of the latter with the corresponding monophenyltin triisopropoxide, diphenyltin diisopropoxide or triphenyltin isopropoxide in 1:1, 1:2, 1:3 or 2:1 molar ratios in benzene/toluene. The various compounds thus prepared were obtained as coloured solids out of which some were hygroscopic. All these compounds were characterized by azeotrope and elemental analysis, as well as by IR spectral measurement.

INTRODUCTION

The ligating properties of 1-hydroxy-2-naphthoic acid (LH_2)(I) and 3-hydroxy-2-naphthoic acid ($L'H_2$)(II) have widely been examined in solution[1–6]. Their metal complexes have also been isolated in solid state and characterized in several cases[7,8]. The work described here the preparation of several mono-, di- and triphenyl substituted tin derivatives of LH_2 and $L'H_2$ adopting alcoholysis reactions involving the interaction of the corresponding phenyltin isopropoxide with the latter in appropriate stoichiometric ratios *viz.* 1:1, 1:2, 1:3 or 2:1 in suitable reaction medium *viz.* benzene/toluene. The various compounds thus prepared, were obtained as coloured solids and amongst them those containing isopropoxy group(s) were found to be hygroscopic. All these compounds were characterized by azeotrope and elemental analyses, as well as by IR spectral measurement.



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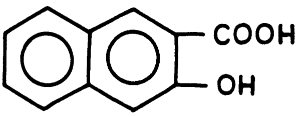


(II)

EXPERIMENTAL

The details of glass apparatus and reagents are described elsewhere[9]. Monophenyltin trichloride was prepared by a known method[10], while diphenyltin dichloride (Aldrich) and triphenyltin chloride (Fluka) were used, as such, Monophenyltin triisopropoxide, diphenyltin diisopropoxide and triphenyltin isopropoxide were prepared by sodium method[11,12] from their corresponding chlorides. Tin was determined by direct ignition of the sample after digestion with nitric and sulphuric acids, followed by neutralization and precipitation by ammonia solution[13].

Reaction of Monophenyltin Triisopropoxide and LH_2; 1:1 Molar Ratio

A mixture of $PhSn(OPr^i)_3$ (2.4760 g; 6.64 m mole) and LH_2 (1.2502 g; 6.64 m mole) in toluene (60 ml) taken in a R.B. flask was refluxed on a wax bath (125–130°), using a fractionating column. After *ca.* 16 h of reflux the isopropanol toluene azeotrope was fractionated out azeotropically and estimated by an oxidimetric method[14,15] to monitor the completion of the reaction. On completion of the reaction, the excess of solvent from the reaction mixture was removed in *vacuo*, when the product, $PhSn(L)(OPr^i)$ isolated as a grey coloured solid. The product was purified by washing with dry toluene followed by washing with dry ether to remove unreacted $PhSn(OPr^i)_3$ and LH_2, if any and finally dried in *vacuo*. The compound was found to be insoluble in common organic solvents like ethanol, benzene, toluene, chloroform, ether etc. (yield ~ 93.1–96.3%).

Identical procedure was adopted for the preparation of the other derivatives. The relevant analytical details and characteristic IR bands are summarized in Tables 1 and 2, respectively.

It may be mentioned here that compounds 1, 3, 4, 6, 7 and 10–13 (Table 1) were found to be soluble in ethanol but insoluble in other common organic solvents. Hence, these compounds were purified by recrystallization from ethanol. On the other hand, compounds 5, 8, 9, 14 and 15 (Table 1) were found to be insoluble in common organic solvents, similar to $PhSn(L)(OPr^i)$ (compound 2, Table 1) and hence their purification by recrystallization was not possible.

RESULTS AND DISCUSSION

The reactions of various phenyltin isopropoxides with LH_2 were observed to occur as follows:

$$PhSn(OPr^i)_3 + LH_2 \longrightarrow PhSn(LH)(OPr^i)_2 + Pr^iOH \qquad (1)$$

$$PhSn(OPr^i)_3 + LH_2 \longrightarrow PhSn(L)(OPr^i) + 2Pr^iOH \qquad (2)$$

$$PhSn(OPr^i)_3 + 2LH_2 \longrightarrow PhSn(LH)_2(OPr^i) + 2Pr^iOH \qquad (3)$$

$$PhSn(OPr^i)_3 + 3LH_2 \longrightarrow PhSn(LH)_3 + 3Pr^iOH \qquad (4)$$

$$Ph_2Sn(OPr^i)_2 + LH_2 \longrightarrow Ph_2Sn(L) + 2Pr^iOH \qquad (5)$$

$$Ph_2Sn(OPr^i)_2 + 2LH_2 \longrightarrow Ph_2Sn(LH)_2 + 2Pr^iOH \qquad (6)$$

TABLE 1
ANALYTICAL DETAILS OF THE VARIOUS PHENYL SUBSTITUTED TIN DERIVATIVES OF 1-HYDROXY-2- NAPHTHOIC AND 3-HYDROXY-2-NAPHTHOIC ACIDS

S. No.	Compound/ (molar ratio)/colour	M.p. °C	Azeotrope analysis Pr^iOH(g) found (calcd)	Analysis % found(calcd)		
				C	H	Sn
1.	$PhSn(LH)(OPr^i)_2$ (1:1) (off white)	290	0.3477 (0.3484)	55.32 (55.08)	5.17 (5.19)	23.57 (23.69)
2.	$PhSn(L)(OPr^i)$ (1:1) (grey)	>300	0.7954 (0.7966)	54.20 (54.41)	4.08 (4.08)	27.01 (26.91)
3.	$PhSn(LH_2)(OPr^i)$ (1:2) (buff)	220	0.4106 (0.4124)	58.42 (59.13)	4.12 (4.13)	18.89 (18.87)
4.	$PhSn(LH)_3$ (1:3) (light buff)	240	0.5889 (0.5987)	61.52 (61.80)	3.42 (3.43)	15.59 (15.67)
5.	$Ph_2Sn(L)$ (1:1) (brownish black)	>300	0.6354 (0.6389)	46.16 (46.24)	2.68 (2.68)	19.79 (19.88)
6.	$Ph_2Sn(LH)_2$ (1:2) (yellowish brown)	>300	0.4744 (0.4759)	62.80 (63.06)	3.70 (3.71)	18.40 (18.34)
7.	$Ph_3Sn(LH)$ (1:1) (brownish black)	145	0.3861 (0.3877)	65.10 (64.82)	4.11 (4.10)	22.20 (22.12)
8.	$(Ph_3Sn)_2L$ (2:1) (yellowish green)	285	0.5199 (0.5235)	63.92 (63.69)	4.05 (4.07)	26.71 (26.81)
9.	$PhSn(L')(Opr^i)$ (1:1) (off white)	>300	0.7884 (0.7966)	54.63 (54.41)	4.09 (4.08)	26.87 (26.91)
10	$PhSn(L'H)_2(OPr^i)$ (1:2) (yellowish grey)	>300	0.4809 (0.4813)	59.40 (59.13)	4.12 (4.13)	18.75 (18.67)
11.	$PhSn(L'H)_3$ (1:3) (light yellow)	>300	0.5561 (0.5581)	62.06 (61.80)	3.42 (3.43)	15.62 (15.67)
12.	$Ph_2Sn(L')$ (1:1) (pale yellow)	>300	0.6492 (0.6527)	46.16 (46.24)	2.67 (2.68)	19.96 (19.88)
13.	$Ph_2Sn(L'H)_2$ (1:2) (yellow)	>300	0.5792 (0.5845)	62.86 (63.06)	3.17 (3.17)	18.26 (18.34)
14.	$Ph_2Sn(L'H)$ (1:1) (pale yellow)	>300	0.5200 (0.5207)	65.05 (64.82)	4.07 (4.09)	22.09 (22.11)
15.	$(Ph_2Sn)_2(L')$ (2:1) (cream)	>300	0.3104 (0.3170)	63.59 (63.68)	4.05 (4.07)	26.92 (26.80)

Abbreviations: $Ph = C_6H_5$, $OPr^i = OC_3H_7$, LH_2 or $L'H = C_{11}H_8O_3$

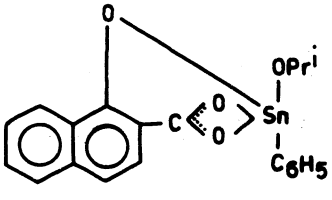
$$Ph_3Sn(OPr^i) + LH_2 \longrightarrow Ph_3Sn(LH) + Pr^iOH \quad (7)$$

$$2Ph_3Sn(OPr^i) + LH_2 \longrightarrow (Ph_3Sn)_2L + 2Pr^iOH \quad (8)$$

Similar reactions followed in case of $L'H_2$ excepting reaction (1) which did not occur even after controlled reflux and fractionation.

Infrared spectra

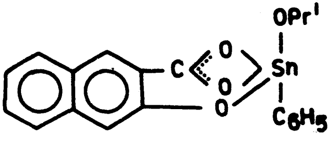
The compound, PhSn(L)(OPr^i) displays a very broad band between 3200–3000 cm^{-1}, which may be assigned to νC–H of the aromatic rings and the isopropoxy group^{16,17}. A broad band appearing at 1600 cm^{-1} indicates the overlapping of ν_{as}COO and aromatic νC=C, while a medium band at 1405 cm^{-1} arises because of ν_sCOO. The separation value, $\Delta\nu$COO (ν_{as}COO–ν_sCOO) of 195 cm^{-1} suggests the presence of a bridged or coordinated carboxylate group$^{18-20}$. An absence of free hydroxy band, together with the fact that νC–O and O–H bending modes show a shift of 5–10 cm^{-1}, as compared to LH_2, indicates the participation of the hydroxy oxygen in bonding with tin. A band observed at 1390 cm^{-1} may be ascribed to the *gem* dimethyl structure of the isopropoxy group^{17}, while a strong band at 1140 cm^{-1} may be attributed to νC–O of the isopropoxy group. In addition, the bands at 1060 cm^{-1} and 665 cm^{-1} may be assigned to νSn–C^{21,22}, while the weak bands at 550 cm^{-1} and 470 cm^{-1} to νSn–O^{22,23}. The overtones in the region 2000–1700 cm^{-1} occur possibly owing to the substitution in the aromatic ring^{16}. Characteristic absorption bands of weak to strong intensities exclusively shown by the aromatic compounds appear here in the region 1200–650 cm^{-1}, while the bands due to the skeletal vibrations^{16} occur below 650 cm^{-1}. These observations show that both the oxygens from the carboxylate group and the oxygen from the hydroxy group, along with an isopropoxy and a phenyl group are bonded to tin. Thus, tin atom in PhSn(L)(OPr^i) exhibits penta-coordination(III).



(III)

The IR spectra of other compounds were similarly interpreted and the main findings are as under:

The tin atom in PhSn(L')(OPr^i), PhSn(LH)(OPr^i)$_2$, Ph_2Sn(L), Ph_2Sn(L'), Ph_3Sn(LH) and Ph_3Sn(L'H)(IV–IX), show penta-coordination in each case, as a



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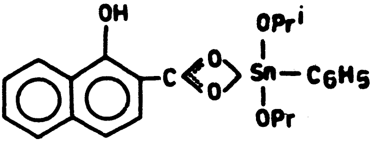


(V)

TABLE 2

CHARACTERISTIC INFRARED BANDS (in cm^{-1}) OF THE VARIOUS PHENYL SUBSTITUTED TIN DERIVATIVES OF 1-HYDROXY -2-NAPHTHOIC AND 3-HYDROXY-2-NAPHTHOIC ACIDS AND THEIR ASSIGNMENTS.

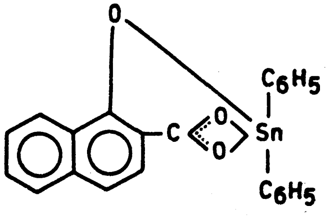
S.N.	Compound	νOH	νC–H	ν_{as}COO	ν_sCOO	ΔνCOO	νC–O (Hydroxy)	νSn–C	νSn–O
1.	LH_2	3200–2400 (mb)*	—	1640 (vsb)	1420 (m)	—	1260 (m)	—	—
2.	$L'H_2$	3300 (mb)	3100–2780 (mb)	1610 (b)	1405 (m)	—	1260 (m) 1225 (s)	—	—
3.	$PhSn(LH)(OPr^i)_2$	3600 (b)	3100–2900 (wb)	1610 (w)	1410 (sh)	200	1265 (s) 1210 (m)	1080 (s) 660 (s)	550 (s) 470 (s)
4.	$PhSn(L)(OPr^i)$	—	3200–3000 (vb)	1600 (b)	1405 (m)	195	1265 (s) 1220 (s)	1060 (m) 665 (s)	550 (w) 470 (w)
5.	$PhSn(LH)_2(OPr^i)$	3600–3300 (wb)	3300–2700 (b)	1600 (b)	1400 (sh)	200	1250 (b) 1200 (s)	1075 (w) 650 (s)	540 (s) 460 (s)
6.	$PhSn(LH)_3$	3600–3300 (b)	3140 (m) 3000–2800 (b)	1590 (s)	1405 (m)	195	1250 (m) 1205 (s)	1080 (s) 640 (s)	540 (s) 480 (m)
7.	$Ph_2Sn(L)$	—	3060 (b) 2970 (s) 2930 (w) 2860 (w)	1590 (s)	1405 (m)	185	1270 (m) 1220 (s)	1080 (m) 640 (m)	535 (s) 460 (s)
8.	$Ph_2Sn(LH)_2$	3400 (b)	2940 (w)	1600 (mb)	1400 (m)	200	1265 (s) 1205 (m)	1070 (s) 660 (w)	550 (s) 460 (m)
9.	$Ph_3Sn(LH)$	3440 (b)	3080 (sh) 2960 (w) 2940 (w)	1585 (s)	1400 (m)	185	1265 (s) 1210 (m)	1080 (s) 650 (sh)	530 (m) 460 (s)

Contd . . .

10. $(PH_3Sn)_2(L)$	—	3200 (b) 3060 (s) 2950 (m) 2940 (m)	1600 (m)	1400 (m)	200	1270 (s) 1220 (s)	1080 (b) 650 (m)	520 (m) 450 (m)
11. $PhSn(L')(OPr^i)$	—	3060 (s) 2960 (w) 2860 (w)	1590 (s)	1400 (s)	190	1260 (s) 1220 (s)	1070 (sh) 660 (s)	550 (m) 470 (s)
12. $PhSn(L'H)_2(OPr^i)$	3400 (vw)	3060 (s)	1590 (b)	1390 (m)	200	1290 (b) 1220 (b)	1080 (s) 650 (s)	560 (s) 465 (m)
13. $PhSn(L'H)_3$	3500 (vw)	3300 (s) 3060 (s)	1600 (s)	1400 (m)	200	1280 (s) 1215 (s)	1070 (s) 660 (s)	560 (w) 480 (s)
14. $Ph_2Sn(L')$	—	3060 (s) 2960 (w) 2950 (m)	1580 (b)	1385 (s)	205	1265 (s) 1230 (s)	1080 (s) 675 (s)	540 (s) 480 (s)
15. $Ph_2Sn(L'H)_2$	3400 (s)	3060 (s) 2960 (w) 2940 (w)	1600 (s)	1390 (s)	190	1260 (m) 1220 (s)	1080 (s) 660 (s)	480 (s)
16. $Ph_3Sn(L'H)$	3450 (wb)	3060 (s) 2960 (s) 2930 (s) 2860 (m)	1580 (s)	1380 (s)	200	1260 (w) 1230 (s)	1080 (s) 675 (s)	540 (m) 460 (s)
17. $(Ph_3Sn)_2(L')$	—	3060 (s) 3010 (w) 2940 (s) 2860 (s)	1575 (s)	1380 (s)	205	1270 (w) 1230 (s)	1080 (s) 670 (sh)	540 (s) 465 (s)

*Overlapping of νO–H and νC–H

Abbreviations: vw = very weak, w = weak, m = medium, wb = weak broad, mb = medium broad, b = broad s = sharp, vs = very sharp, sh = shoulder.



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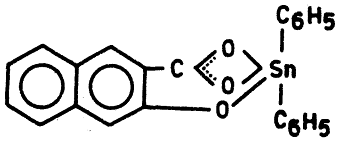

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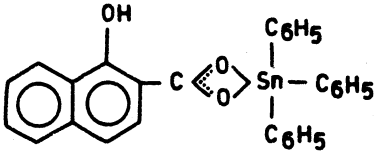

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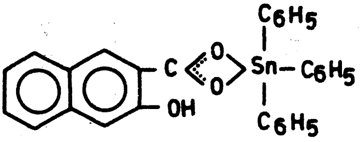
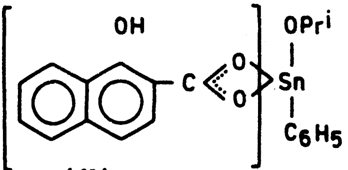


(IX)

consequence of bonding with both the oxygens from the carboxylate group or with both the oxygens from the carboxylate group, as well as the oxygen from the hydroxy group, along with phenyl group(s) or phenyl and isopropoxy groups both, as the case may be.

The derivatives $PhSn(LH)_2(OPr^i)$, $PhSn(L'H)_2(OPr^i)$, $Ph_2Sn(LH)_2$ and $Ph_2Sn(L'H)_2$ (X)–(XIII), possess a hexa-coordinated tin atom in each case, as a



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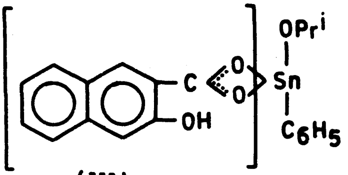

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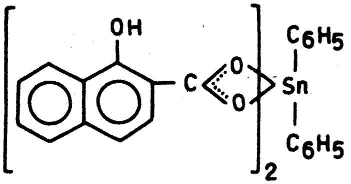

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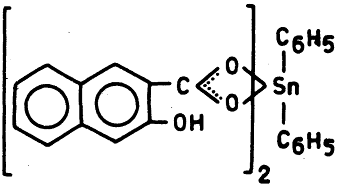
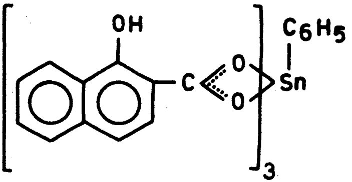


(XIII)

result of bonding with both the oxygens from each of the two carboxylate groups available from two moles of LH_2 of $L'H_2$, along with phenyl group(s) or phenyl and isopropoxy groups both, as the case may be.



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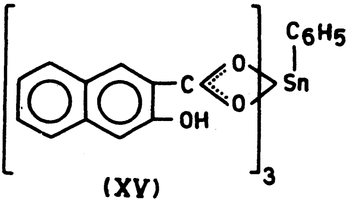
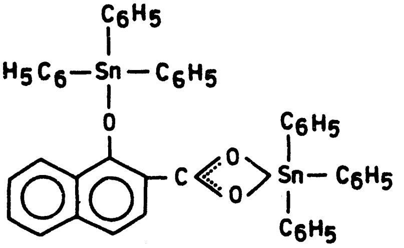


(XV)

$PhSn(LH)_3$ and $PhSn(L'H)_3$ (XIV and (XV), contain a hepta-coordinated tin atom in each case by way of bonding with both of the oxygens from each of the three carboxylate groups available from three moles of LH_2 or $L'H_2$, along with a phenyl group.



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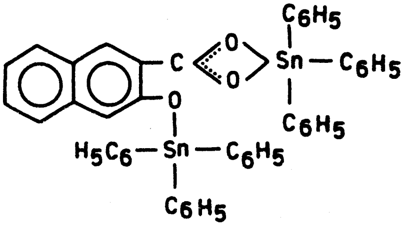

(XVII)

In the derivatives $(Ph_3Sn)_2(L)$ and $(Ph_3Sn)_2(L')$ (XVI) and (XVII), one of the tin atom is observed to be penta-coordinated as a result of bonding with both the oxygens from the carboxylate group along with three substituted phenyl group, while the other displays tetra-coordination as a consequence of bonding with the oxygen from the hydroxy group, along with three substituted phenyl groups.

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