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Mono-, Di- and Tributyltin Derivatives of 1-Hydroxy-2-Naphthoic and 3-Hydroxy-2-Naphthoic Acids

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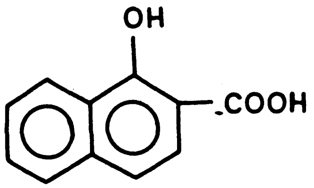
Several organotin derivatives of 1-hydroxy-2-naphthoic and 3-hydroxy-2-napththoic acids have been prepared by the interaction of monobutyltin triisopropoxide, dibutyltin diisopropoxide or tributyltin isopropoxide with the latter in various stoichiometric ratios *viz.* 1 : 1, 1 : 2, 1 : 3 and 2 : 1 in benzene/toluene medium. The compounds thus prepared were obtained generally as coloured solids, excepting the tributyltin derivatives which isolated as dark viscous liquids. However, amongst them those containing isopropoxy group(s) were found to be hygroscopic in nature. All these compounds were characterized by azeotrope and elemental analyses, as well as by IR and PMR spectral measurements.

INTRODUCTION

The facile reactivity of metal alkoxides towards protonated organic ligands provides a convenient method of preparing a variety of metallo-organic/organometallic derivatives. However, practically no attempt has been made to prepare such derivatives of hydroxy naphthoic acids which do contain replaceable hydrogen(s), despite their ligating properties having been extensively studied[1–6]. A systematic programme of work towards the preparation of their organotin derivatives *via* the reactivity of the corresponding organotin alkoxide has now been undertaken in these laboratories.

The work described here thus deals with the preparation and characterization of several mono-, di- and tributyltin derivatives of 1-hydroxy-2-naphthoic acid (abbreviated as LH_2) [I] and 3-hydroxy-2-naphthoic acid (abbreviated as $L'H_2$) [II]. These derivatives were prepared by alcoholysis reactions involving the interaction of mono-, di- or tributyltin isopropoxide with LH_2 or $L'H_2$ in appropriate stoichiometric ratios *viz.* 1:1, 1:2, 1:3 and 2:1 in benzene/toluene medium. The compounds thus prepared were obtained as coloured solids, excepting the tributyltin derivatives which isolated as dark viscous liquids. However, amongst them those conaining isopropoxy group(s) were observed to be hygroscopic. All these compounds were characterized by azeotrope and



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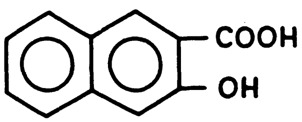


(II)

elemental analyses, as well as by IR and PMR (in several representative cases) spectral measurements.

EXPERIMENTAL

Owing to highly hygroscopic nature of the organotin isopropoxides, special precautions were taken to exclude moisture throughout the experiments. The alcoholysis reactions were performed in a fractionating column packed with Raschig rings and fitted to a total condensation variable take-off stillhead. Special weighing tubes and measuring pipettes with standard joints were used for the analytical sampling of the compounds. For filtration purposes, a especially designed G_4 sintered glass filtration funnel fitted to a guard tube at the upper end and filled with fused calcium chloride, was used.

Benzene (BDH,AR), toluene (E.Merck, GR), *iso*propanol (BDH, Glaxo AnalaR) and solvent ether (E. Merck) were dried by standard procedures[7]. 1-Hydroxy-2-naphthoic acid (E. Merck) and 3-hydroxy-2-naphthoic acid (Koch-Light) were used after recrystallization from 50% (v/v) aqueous-ethanol. Monobutyltin trichloride was prepared by already reported method[8], while dibutyltin dichloride (Fluka) and tributyltin chloride (Fluka) were used, as such Mono-, di- and tributyltin isopropoxides were prepared from their corresponding chlorides by sodium method[9-11].

Melting points were determined in open capillary tubes, using a digital m.pt. apparatus and are uncorrected. Tin was estimated by direct ignition of the sample after digestion with nitric and sulphuric acids followed by neutralization and precipitation by ammonia solution[12].

Reaction between Tributyltin Isopropoxide and LH_2; 1 : 1 Molar Ratio

A mixture of $Bu_3Sn(OPr^i)$ (1.7791 g; 5.10 mmol) and LH_2 (0.9566 g; 5.08 mmol) suspended in dry benzene (60 ml) taken in a R.B. flask was refluxed on a wax bath (95–100°C), using a fractionating column. After *ca.* 2 h of reflux, the *iso*propanol liberated during the course of reaction was removed azeotropically and determined by an oxidimetric method[13, 14]. On completion of the reaction, the excess of solvent from the reaction mixture was removed *in vacuo*, when the product $Bu_3Sn(LH)$ isolated as a dark tan coloured liquid. The product was purified by washing with carbon tetrachloride (2–3 times) and then dried under suction. The compound was found to be soluble in benzene, toluene, ethanol, ether, chloroform, dimethylformamide and dimethylsulphoxide but insoluble in carbon tetrachloride. Attempted distillation of the compound resulted in its decomposition and thus further purification was not possible.

Since $Bu_3Sn(OPr^i)$ is soluble in carbon tetrachloride while LH_2 is insoluble, the latter was taken in slightly less than the required stoichiometric amount (as evident from the weights given above) in order to avoid impurities likely to occur by unreacted LH_2. The amount of *iso*propanol liberated was, therefore, calculated according to the amount of LH_2 taken. Identical procedure was adopted for the preparation of other tributyltin derivatives, which all isolated as dark tan coloured liquids and showed identical solubility/insolubility.

The various dibutyltin and monobutyltin derivatives were also prepared similarly but the product in each case isolated as a coloured solid. Here, in view of the purity considerations, the various reactants were taken strictly according to their stoichiometric amounts in each case. The various compounds isolated were washed under suction with dry solvent ether in order to remove unreacted LH_2 or $L'H_2$ and butyltin isopropoxide, if any, before drying them *in vacuo*. All the di- and monobutyltin derivatives were found to be soluble in ethanol, and hence these derivatives were purified by recrystallization from dry ethanol.

The relevant analytical details, characteristic IR frequencies and PMR data (in several representative cases) are summarized in Tables 1–3, respectively.

RESULTS AND DISCUSSION

The reactions occurring between the various butyltin *iso*propoxides and LH_2 may be illustrated as:

$$BuSn(OPr^i)_3 + LH_2 \rightarrow BuSn(LH)(OPr^i)_2 + Pr^iOH \quad (1)$$

$$BuSn(OPr^i)_3 + LH_2 \rightarrow BuSn(L)(OPr^i) + 2Pr^iOH \quad (2)$$

$$BuSn(OPr^i)_3 + 2LH_2 \rightarrow BuSn(LH)_2(OPr^i) + 2Pr^iOH \quad (3)$$

$$BuSn(OPr^i)_3 + 3LH_2 \rightarrow BuSn(LH)_3 + 3Pr^iOH \quad (4)$$

$$Bu_2Sn(OPr^i)_2 + LH_2 \rightarrow Bu_2Sn(L) + 2Pr^iOH \quad (5)$$

$$Bu_2Sn(OPr^i)_2 + 2LH_2 \rightarrow Bu_2Sn(L)_2 + 2Pr^iOH \quad (6)$$

$$Bu_3Sn(OPr^i) + LH_2 \rightarrow Bu_3Sn(LH) + Pr^iOH \quad (7)$$

$$2Bu_3Sn(OPr^i) + LH_2 \rightarrow (Bu_3Sn)_2L + Pr^iOH \quad (8)$$

Identical reactions occurred in case of $L'H_2$, excepting the reaction (1), which did not occur at all even after controlled reflux and fractionation.

TABLE 1

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

S. No.	Compound (molar ratio)	Reflux time (hrs)	Yield (%)	Physical state		Azeotrope analysis Pr^iOH(g) found (calcd)	Elemental analysis		
				Colour	m. pt. (°C)		C% found (calcd)	H% found (calcd)	Sn% found (calcd)
1.	$BuSn(LH)(OPr^i)_2$ (1 : 1)	3	91.6	buff (solid)	280	0.2317 (0.2321)	52.08 (52.37)	6.20 (6.23)	24.57 (24.67)
2.	$BuSn(L)(OPr^i)$ (1:1)	8	93.4	buff (solid)	130	0.8870 (0.9028)	51.05 (51.30)	5.19 (5.22)	28.02 (28.19)
3.	$BuSn(LH)_2(OPr^i)$ (1 : 2)	6	95.8	greenish yellow (solid)	>300	0.7982 (0.8184)	56.88 (57.12)	4.90 (4.92)	19.35 (19.48)
4.	$BuSn(LH)_3$ (1 : 3)	6	92.7	buff (solid)	250	0.3406 (0.3473)	59.77 (60.06)	4.03 (4.06)	15.94 (16.05)
5.	$Bu_2Sn(L)$ (1 : 1)	6	96.5	brown (solid)	160	0.6258 (0.6728)	54.21 (54.41)	5.70 (5.73)	28.16 (28.32)
6.	$Bu_2Sn(LH)_2$ (1 : 2)	8	92.3	buff (solid)	150	0.7529 (0.7684)	59.05 (59.28)	5.24 (5.27)	19.48 (19.55)
7.	$^*Bu_3Sn(LH)$ (1 : 1)	1	97.2	dark tan (viscous liquid)	. . .	0.3002 (0.3050)	57.60 (57.84)	7.09 (7.13)	24.76 (24.87)
8.	$^*(Bu_3Sn)_2(L)$ (2 : 1)	1/2	93.1	dark tan (viscous liquid)	. . .	0.2131 (0.2133)	54.60 (54.82)	7.80 (7.83)	30.84 (30.98)

S. No.	Compound (molar ratio)	Reflux time (hrs)	Yield (%)	Physical state		Azeotrope analysis Pr^iOH(g) found (calcd)	Elemental analysis		
				Colour	m. pt. (°C)		C% found (calcd)	H% found (calcd)	Sn% found (calcd)
9.	$BuSn(L')(Opr^i)$ (1 : 1)	8	95.2	buff (solid)	220	0.7504 (0.7580)	51.10 (51.35)	5.24 (5.26)	28.05 (28.19)
10.	$BuSn(L'H)_2(Opr^i)$ (1 : 2)	6	93.3	pale yellow (solid)	150	0.8297 (0.8389)	56.85 (57.12)	4.89 (4.92)	19.39 (19.48)
11.	$BuSn(L'H)_3$ (1 : 3)	8	93.2	greenish yellow (solid)	240d	0.4229 (0.4442)	59.91 (60.06)	4.04 (4.06)	15.99 (16.05)
12.	$Bu_2Sn(L')$ (1 : 1)	8	97.1	greenish yellow (solid)	220	0.3495 (0.3516)	54.20 (54.41)	5.70 (5.73)	28.10 (28.32)
13.	$Bu_2Sn(L'H)_2$ (1 : 2)	7	95.3	pale yellow (solid)	150	0.3542 (0.3561)	59.00 (59.28)	5.24 (5.27)	19.47 (19.55)
14.	*$Bu_3Sn(L'H)$ (1 : 1)	1	96.2	dark tan (viscous liquid)	. . .	0.1560 (0.1567)	57.60 (57.84)	7.10 (7.13)	23.82 (24.87)
15.	*$(Bu_3Sn)_2(L')$ (2 : 1)	1/2	94.3	dark tan (viscous liquid)	. . .	0.3969 (0.3973)	54.60 (54.82)	7.80 (7.83)	30.83 (30.96)

*The b. ps. could not be determined.

Abbreviations: Bu = C_4H_9, Opr^i = OC_3H_7, LH_2 or $L'H_2$ = $C_{11}H_8O_3$.

TABLE 2

CHARACTERISTIC INFRARED FREQUENCIES (in cm^{-1}) OF 1-HYDROXY-2-NAPHTHOIC AND 3-HYDROXY-2-NAPHTHOIC ACIDS AND THEIR BUTYL SUBSTITUTED TIN DERIVATIVES

S. No.	Compound	νOH	νC–H	ν_{as}COO	ν_sCOO	$\Delta\nu$ (COO)	νC–O	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)	1670(b)	1405(m)	—	1260(m) 1225(s)	—	—
3.	$BuSn(LH)(OPr^i)_2$	3450(b)	3050(s), 2940(s), 2920(m)	1580(s)	1400(s)	180	1260(s) 1210(s)	580(s)	500(w)
4.	$BuSn(L)(OPr^i)$	—	3050(s), 2940(s), 2920(m)	1580(s)	1400(s)	180	1250(m) 1220(s)	610(m) 570(s)	500(w) 470(m)
5.	$BuSn(LH)_2(OPr^i)$	3600(w)	3200(m), 3040(m), 2940(s), 2840(w)	1570(b)	1390(w)	180	1250(w) 1220(m)	620(mb) 550(m)	530(m) 470(s)
6.	$BuSn(LH)_3$	3600–3300(wb)	3040(m), 2940(s), 2910(s), 2850(m)	1590(m)	1420(s)	170	1250(s) 1210(sh)	580(m)	520(m) 480(b)
7.	$Bu_2Sn(L)$	—	3060(m), 2950(s), 2920(s), 2850(s)	1580(s)	1380(s)	200	1270(b) 1215(m)	580(m) 540(m)	510(s) 470(s)
8.	$Bu_2Sn(LH)_2$	3220(w)	3060(m), 2950(s), 2920(s), 2850(s)	1600(s)	1400(mb)	200	1260(m) 1210(s)	580(s) 540(m)	480(s)
9.	$Bu_3Sn(LH)$	3500–3400(b)	3060(m), 2950(s), 2860(s), 2840(m)	1590(s)	1390(m)	200	1260(s) 1210(s)	590(m) 520(m)	480(w)
10.	$(Bu_2Sn)_2(L)$	3400(wb)	3040(m), 2940(s), 2910(m), 2840(m)	1580(mb)	1400(sh)	180	1260(s) 1210(s)	580(m)	490(s)

S. No.	Compound	νOH	νC–H	ν_{as}COO	ν_sCOO	Δν (COO)	νC–O	νSn–C	νSn–O
11.	$BuSn(L')(OPr^i)$	3600(wb)	3200–2900(wb)	1610(w)	1410(sh)	200	1330(s) 1280(vb)	610(s) 560(m)	530(w) 470(vs)
12.	$BuSn(L'H)_2(OPr^i)$	3280(m)	3200(m), 3040(m), 2950(s), 2840(s)	1610(s)	1420(s)	190	1320(m) 1280(b)	580(s)	510(w) 480(s)
13.	$BuSn(L'H)_3$	3300(s)	3040(s), 2950(s), 2910(s), 2840(s)	1610(s)	1385(b)	225	1280(b)	550(sh)	480(s)
14.	$Bu_2Sn(L')$	—	3040(s), 2950(s), 2920(s), 2850(m)	1580(b)	1380(s)	200	1290(s)	550(s)	500(sh) 475(s)
15.	$Bu_2Sn(L'H)_2$	3500(wb)	3040(s), 2950(s), 2950(vs), 2840(s)	1610(s)	1380(s)	230	1325(m) 1285(s)	550(sh)	470(vs)
16.	$Bu_3Sn(L'H)$	3500–3200(b)	3050(s), 2940(s), 2920(s), 2840(s)	1580(s)	1400(s)	180	1280(s)	570(m) 530(s)	480(m)
17.	$(Bu_3Sn)_2(L')$	—	3040(s), 2940(s), 2910(s), 2840(s)	1610(s)	1380(s)	230	1300(b)	600(s) 530(m)	475(s) 460(w)

Abbreviations: w = weak, m = medium, wb = weak broad, mb = medium broad, b = broad, vb = very broad, s = sharp, vs = very sharp, sh = shoulder
*Overlapping of ν(OH) and ν(C–H).

TABLE 3

PROTON MAGNETIC RERSONANCE SPECTRAL DATA (δ Value) OF 1-HYDROXY-2-NAPHTHOIC AND 3-HYDROXY-2-NAPHTHOIC ACIDS AND SOME OF THEIR BUTYL SUBSTITUTED TIN DERIVATIVES

S. No.	Compound	–COOH and –OH protons (Hydrogen bonded)	Naphthyl ring protons	OH group proton	Butyl and *iso*proxy (*gem* dimethyl) / butyl group protons
1.	LH_2	9.90–10.50(m)	8.60(d), 7.40–7.90(m)	—	—
2.	$L'H_2$	9.90–12.90(m)	8.58(s), 7.34–7.99(m)	—	—
3.	$Bu(LH)_2(OPr^i)$	—	7.56–8.60(m)	6.00(s)	0.70–2.63(m)
4.	$Bu_3Sn(LH)$	—	6.82–8.15(m)	6.00(s)	2.27(s), 1.42(d), 0.92(d)
5.	$(Bu_3Sn)_2(L)$	—	6.96–7.99(m)	—	0.90–3.39(m)
6.	$Bu_2Sn(L')$	—	7.57–8.52(m)	—	0.70–3.20(m)
7.	$Bu_3Sn(L'H)$	—	7.20–8.90(m)	6.00(s)	0.90–2.35(m)
8.	$(Bu_3Sn)_2(L')$	—	8.32–9.61(m)	—	0.90–2.69(m)

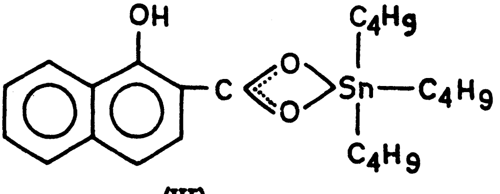
Abbreviations: s = singlet, d = doublet, m = multiplet

Infrared Spectra

The derivative $Bu_3Sn(LH)$ displays a broad band in the region 3500–3400 cm^{-1} which may be assigned to $\nu(OH)$ of the unbonded hydroxy group[15, 16]. Medium to strong intensity bands at 3060 cm^{-1}, 2950 cm^{-1}, 2860 cm^{-1} and 2840 cm^{-1} correspond to $\nu(C–H)$ of the aromatic ring and the butyl groups[15]. The bands in the region 2000–1700 cm^{1} indicate overtones due to substitution in the aromatic ring[17]. A sharp band at 1590 cm^{-1} occurs owing to $\nu_{as}(COO)$, while a medium band at 1390 cm^{-1} may be assigned to $\nu_s(COO)$. A shift of 30 cm^{-1} in $\nu_s(COO)$, as compared to LH_2 shows the bonding of the carboxylate oxygen to tin. Further, the separation value $[\nu_{as}(COO)–\nu_s(COO)]$, $\Delta\nu(COO)$ of 200 cm^{-1} suggests the presence of a bridged or coordinated carboxylate group[18–20]. The absorptions due to the overlapping of the aromatic skeletal stretchings and C–H bending of the butyl groups[16] appear at 1630 cm^{-1}, 1560 cm^{-1}, 1520 cm^{-1}, 1510 cm^{-1} and 1460 cm^{-1}. A medium band at 1355 cm^{-1} corresponds to O–H bending of the hydroxy group[17], while the bands owing to $\nu(C–O)$ of the hydroxy group occur at 1260 and 1210 cm^{-1}. The bands at 1190 cm^{-1}, 1170 cm^{-1}, 1145 cm^{-1}, 1085 cm^{-1}, 1075 cm^{-1} and 1040 cm^{-1} show the aromatic C–H-in-plane bending, while those in the region 1000–650 cm^{-1} may be assigned to the aromatic C–H out-of-plane bending. The medium bands at 590 cm^{-1} and 520 cm^{-1} appear because of $\nu_{as}(Sn–C)$ and

ν_s(Sn–C), respectively[20–22], while a weak band at 480 cm^{-1} corresponds to ν(Sn–O)[20, 22].

On the basis of above observations, it is evident that in $Bu_3Sn(LH)$ [III], both the oxygens from the carboxylate group along with three butyl groups are bonded with tin, while the hydroxy group remains intact, and thus the compound possesses a penta-coordinated tin atom.



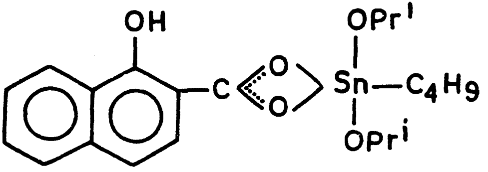
(III)

Proton Magnetic Resonance Spectra

The PMR spectrum of $Bu_3Sn(LH)$ shows signal due to the aromatic ring protons in form of a multiplet between δ6.82–8.15[16, 23]. The singlet at δ 2.27 and doublets at δ1.42 and δ0.92 may be assigned to the protons of the butyl groups[24, 25]. The signal at δ6.00 corresponds to the unbonded hydroxy group proton. The absence of any signal in the region δ9.90–10.50 together with the fact that hydroxy group remains intact shows that, the carboxylate group alone participates in bonding. Thus, the inferences drawn here are in conformity to those derived from the IR measurement earlier.

The IR and PMR spectral data were similarly interpreted for the other derivatives and the main findings in the context of their structure are as under:

The derivatives $BuSn(LH)(OPr^i)_2$, $BuSN(L)(OPr^i)$, $BuSn(L')(OPr^i)$, $Bu_2Sn(L)$, $Bu_2Sn(L')$ and $Bu_3Sn(L'H)$ [IV–IX], respectively contain a penta-coordinated tin



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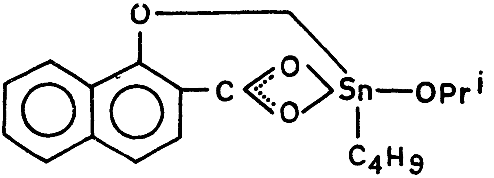

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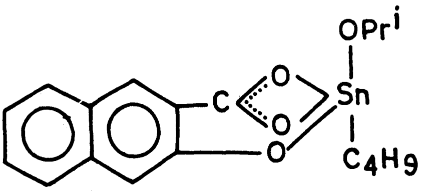

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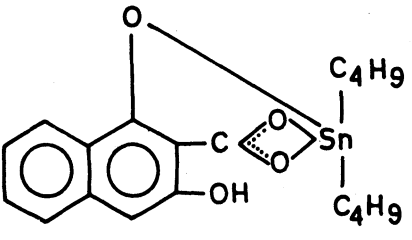

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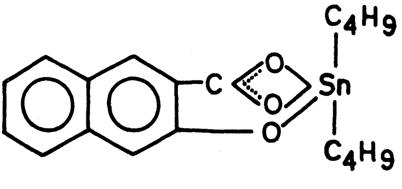

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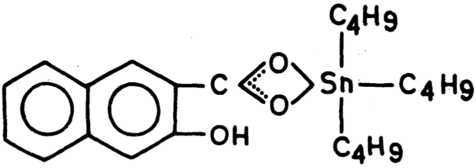
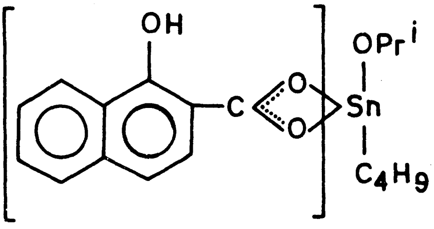


(IX)

atom in each case by way of bonding with both the oxygens from the carboxylate group or with both the oxygens from the carboxylate, as well as the oxygen from the hydroxy group, along with butyl and isopropoxy groups or butyl groups alone, as the case may be.

The tin atom in case of BuSn(LH)$_2$(OPr^i), BuSn(L'H)$_2$(OPr^i), BuSn(LH)$_2$ and Bu$_2$Sn(L'H)$_2$ [X–XIII], respectively exhibits hexa-coordination in each case as



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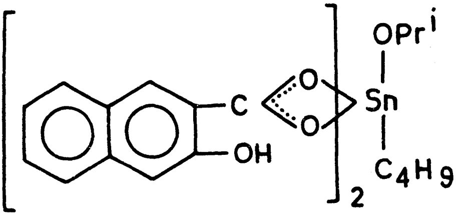

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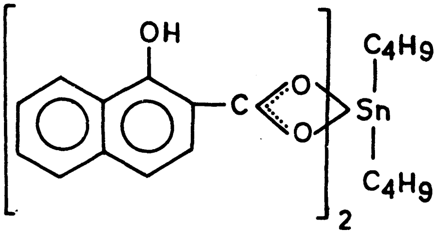

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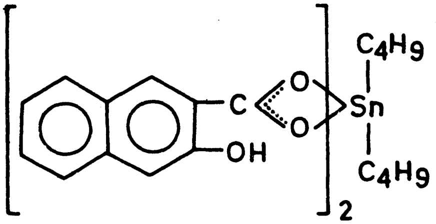
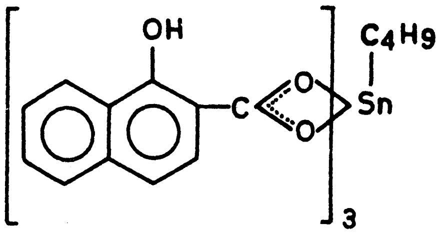


(XIII)

a result of bonding with both the oxygens from each of the two carboxylate groups available from two moles of LH_2 or $L'H_2$, along with a butyl and an *iso*propoxy group or two butyl groups, as the case may be.

$BuSn(LH)_3$ and $BuSn(L'H)_3$ [**XIV and XV**], contain a hepta-coordinated tin atom in each case by way of bonding with both the oxygens from each of the



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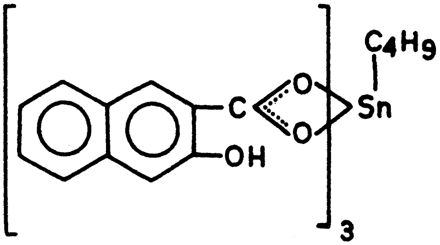
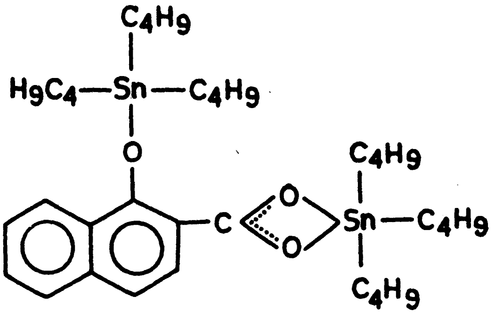


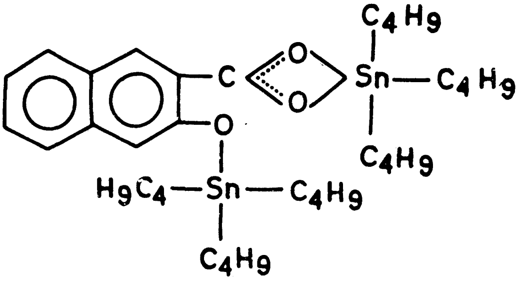
(XV)

three carboxylate groups available from three moles of LH_2 or $L'H_2$ along with a butyl group.

In the derivatives, $(Bu_3Sn)_2L$ and $(Bu_3Sn)_2(L')$ [**XVI and XVII**], one of the tin atoms is observed to be penta-coordinated as a result of bonding with both the oxygens from the carboxylate group, along with three substituted butyl groups, while the other shows tetra-coordination, as a consequence of bonding with the oxygen from the hydroxy group, along with three substituted butyl groups.



(XVI)



(XVII)

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