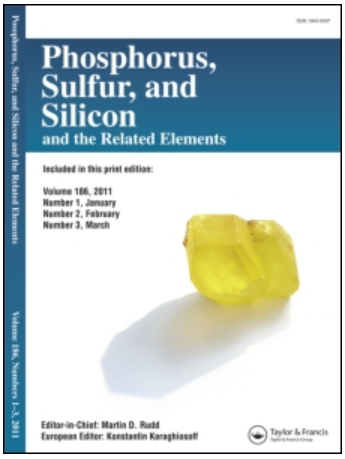

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Organotin(IV) Complexes of 2-[(2',4',6'- Trichlorophenylamido)]benzoic Acid: Synthesis, Coordination Chemistry, and Semi-Empirical Study

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ORGANOTIN(IV) COMPLEXES OF 2-[(2′,4′,6′-TRICHLOROPHENYLAMIDO)]BENZOIC ACID: SYNTHESIS, COORDINATION CHEMISTRY, AND SEMI-EMPIRICAL STUDY

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A new series of organotin(IV) complexes of aniline derivatives, R_2SnL_2 and R_3SnL [where R = Me,* n-*Bu,* n-*Oct, and Ph], have been synthesized by the reaction of ligand acid with respective organotin halides in the presence of triethylamine as base or dioctyltin oxide using a Dean–Stark trap for the removal of water under reflux conditions. Experimental details for the preparation and characterization, including elemental analysis, IR, semi-empirical study, multinuclear NMR (^1H, ^{13}C, and ^{119}Sn spectra and EI mass spectral studies) of all reported complexes are provided. The IR data indicate that in both di- and triorganotin(IV) carboxylates, the ligand moiety −COO acts as a bidentate group in the solid state. Multinuclear NMR data show that triorganotin complexes exhibits a four-coordinated geometry, while diorganotin(IV) complexes show a coordination number greater than four, probably five or six, in solution state.

Supplemental materials are available for this article. Go to the publisher's online edition of* Phosphorus, Sulfur, and Silicon and the Related Elements *to view the free supplemental file.

Keywords Organotin(IV) carboxylates; semi-empirical study; spectroscopic studies

INTRODUCTION

Organotin compounds show a diversity of applications. They are used as fungicides and bactericides. In addition, diorganotin compounds exhibit greater antitumor activity than the corresponding triorganotin compounds.[1] Organotin compounds are also interesting in view of the considerable structural diversity they possess; this aspect has attracted

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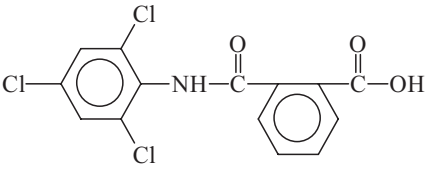


Figure 1 Structure of 2-[(2′,4′,6′-trichlorophenylamido)]benzoic acid (**HL**).

the attention of a number of researchers and, in recent years, a multitude of structural types have been discovered.[2] The increasing importance of organotin(IV) compounds are not only because of extensive commercial use[3] in industry as PVC stabilizing agents and anti-neoplastic agents, in agriculture as wood preservatives,[4] and as fungicide and pesticide, but also due to the environmental consequences of the widespread use of these complexes.[3] The organotin(IV) compounds are also used for pharmacological applications such as bactericides,[5] as an antitumor agent,[6] as an anti-inflammatory agent,[7] and as an antitubercular.[7]

We have investigated the reactions of di- and triorganotin chlorides/oxide with 2-[(2′,4′,6′-trichlorophenylamido)]benzoic acid. The generic structure of the ligand framework is shown in Figure 1. The characterization of the compounds is carried out by means of ^{1}H, ^{13}C, ^{119}Sn NMR, and FT-IR spectroscopy, as well as the elemental analyses, semi-empirical study, and mass spectrometric analyses.

RESULTS AND DISCUSSION

Reactions of di- and triorganotin chlorides/oxide with a stoichiometric amount of ligand acid were carried out at temperature of reflux in dry toulene. All the synthesized compounds are stable and soluble in common solvents. The physical data are summarized in Table I.

IR Spectra

The stretching frequencies of interest are those associated with COO, Sn—C, and Sn—O groups and are listed in Table II. The IR spectra of the ligand and the synthesized complexes have been recorded as KBr pellets or neat liquids in the range 4000–250 cm^{-1}. The assignment of the bands is based on comparison with the spectra of the free ligand (**HL**). The deprotonation of the carboxylic acid is evident from the disappearance of a broad band, owing to the COOH group in the region 3429 cm^{-1} of the ligand.[8] In the complexes, the carbonyl stretching frequencies are found to be shifted to lower wave numbers, which is ascribed to carboxylate coordination in accordance with earlier reports.[9,10]

The values of a difference $\Delta\nu = \nu_{asym}(COO) - \nu_{sym}(COO)$ in the spectra of the complexes are lower than the values for the ligand acid ($\Delta\nu = 218$ cm^{-1}). These observations suggest the anisobidentate nature of the carboxylate ligand[11,12] and supports the assessment that diorganotin(IV) carboxylates have hexa-coordinated, distorted, octahedral motifs, and triorganotin(IV) compounds may acquire polymeric geometries containing bridging COO groups in the solid state. This is totally consistent with the earlier reports.[13,14] Diorganotin(IV) carboxylates exhibit a hexa-coordinated geometry, while triorganotin(IV) show a trigonal bipyramidal geometry. Polymeric structure is supported by trigonal bipyramidal

Table I Physical data for organotin(IV) complexes of 2-[(2′,4′,6′-trichlorophenylamido)]benzoic acid

Compound No.	Quantity used: 1st Reactant	2nd Reactant	3rd Reactant	Mp (°C)	Yield (%)	Elemental analysis % Calculated (found): C	H	N
(**1**)	HL	Me_2SnCl_2	Et_3N	78–80	92	43.06	2.39	3.34
	1.0 g	0.31 g	0.40 mL			(43.26)	(2.48)	(3.27)
	(2.90 mmol)	(1.45 mmol)	(2.90 mmol)					
(**2**)	HL	Bu_2SnCl_2	Et_3N	105–106	90	46.95	3.47	3.04
	1.0 g	0.44 g	0.40 mL			(46.87)	(3.32)	(3.17)
	(2.90 mmol)	(1.45 mmol)	(2.90 mmol)					
(**3**)	HL	Oct_2SnO	–	158	85	51.16	4.65	2.71
	1.0 g	0.52 g				(51.02)	(4.55)	(2.63)
	(2.90 mmol)	(1.45 mmol)						
(**4**)	HL	Bu_3SnCl	Et_3N	172–173	75	49.28	5.37	2.21
	1.0 g	0.78 g	0.40 mL			(49.20)	(5.25)	(2.11)
	(2.90 mmol)	(2.90 mmol)	(2.90 mmol)					
(**5**)	HL	Ph_3SnCl	Et_3N	146–147	67	55.41	3.17	2.02
	1.0 g	1.12 g	0.40 mL			(55.32)	(3.10)	(2.19)
	(2.90 mmol)	(2.90 mmol)	(2.90 mmol)					

geometry. Absorption bands in the region 480–450 cm^{-1} are assigned to the stretching frequencies associated with the Sn−O bonds,[15] which substantiate further the formation of tin complexes.

Mass Spectrometric Data

The mass spectral data collected at 70 eV for both the di- and triorganotin(IV) derivatives are reported in Table S1 (Supplemental Materials, available online). The molecular ion peak is observed only for the methyl derivative (**1**) and is consistent with the literature.[16]

The fragment ions containing the Sn atom are quite intense. In triorganotin(IV) carboxylates, the primary fragmentation is due to the loss of the R group, and the same is true

Table II Assignment of characteristic FT-IR vibrations of 2-[(2′,4′,6′-trichlorophenylamido)]benzoic acid and their organotin(IV) complexes

Compound	IR peak (cm^{-1}): ν_{OH}	ν_{NH}	$\nu_{C=O}$	ν_{COO}		$\Delta\nu$	ν_{Sn-C}	ν_{Sn-O}
HL	3429b	3358s	1776s	1552m[a]	1334s[b]	218	–	–
(**1**)	–	3364s	1769s	1580m	1456m	124	550s	450m
(**2**)	–	3352m	1764s	1598m	1406s	192	510m	461m
(**3**)	–	3361m	1760s	1590s	1450s	140	570m	480w
(**4**)	–	3369s	1768s	1570s	1424m	146	560w	460m
(**5**)	–	3350s	1762s	1566m	1411m	155	252m	472m

[a]Antisymmetric

[b]Symmetric.

Abbreviations: s = strong; m = medium; w = weak; b = broad.

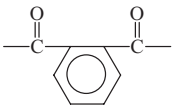
for diorganotin(IV) derivatives. However, the secondary and tertiary decomposition is also followed by the loss of the R group in triorganotin(IV) derivatives, while diorganotin(IV) derivatives manifest a slightly different pattern of fragmentation. All of the diorganotin(IV) derivatives exhibit almost the same behavior. In these compounds, the fragmentation proceeds via two pathways. In one case, the primary fragmentation may occur through loss of O_2CR', and the secondary fragmentation involves elimination of CO_2. The further fragmentations are due to release of the corresponding R and R′ groups generating $[RSn]^+$ and finally $[Sn]^+$. In the second pathway, primary fragmentation arises by loss of the R group, and removal of CO_2 provides the secondary fragmentation. Successive release of CO_2, R′, and R groups make the SnR, which ends at $[Sn]^+$. In conclusion, the fragmentation patterns of both di- and triorganotin(IV) carboxylates obey the established routes described in earlier reports.[16,17]

NMR Spectra

Tables III and IV show the ^1H, ^{13}C, and ^{119}Sn NMR chemical shifts of the ligand and its complexes in $CDCl_3$ solution. ^1H NMR spectra coincide with the expected integration and peak multiplicities. In ^1H NMR spectra of all the complexes studied, the CO(OH) resonance of the ligand is absent, which suggests the replacement of the carboxylic proton by the organotin(IV) moiety. The –NH signal remains unchanged, which indicates that this group is not involved in inter/intramolecular hydrogen bonding or in bonding to organotin moiety. The $^2J[^{119}Sn-^1H]$ coupling constant values for compound **1** is 81 Hz, which support hexa-coordinated environment around the tin atom.[15] In compound **4**, a tetrahedral geometry around tin is observed as indicated from $^2J[^{119}Sn-^1H]$ coupling constant value[15] in solution form.

In the case of diorganotin dicarboxylates, the geometry around tin in solution could not be determined with certainty due to the fluxional behavior of the carboxylate oxygens with coordination to tin atom; however, earlier reports suggest hexa-coordination around tin. The alkyl carbons attached to the tin occur at the normal values in the case of methyl and butyl tin compounds. The aromatic carbon resonances were assigned by the comparison of experimental chemical shift with those calculated from the incremental method.[18] The

Table III ^1H NMR data[a] of 2-[(2′,4′,6′-trichlorophenylamido)]benzoic acid and its organotin complexes

	Chemical shift (ppm)					
Proton	**HL**	**1**	**2**	**3**	**4**	**5**
$Cl_3-C_6H_2$	7.63s	7.45s	7.50s	7.68s	7.36s	7.30s
−NH	6.90s	6.90s	6.90s	6.90s	6.90s	6.90s
	7.50d (8.0)	7.08d (7.9)	7.78d (8.1)	7.20–7.24d,d (8.2)	7.55–7.59d,d (8.6)	7.27–7.31d,d (8.9)
	8.00–8.05d,d (8.0)	8.05–8.09d,d (7.9)	8.03–8.05d,d (8.1)	7.68–7.72d,d (8.2)	8.02–8.06d,d (8.6)	8.02–8.06d,d (8.9)
R	–	0.26s [81]	0.84t [81] 1.34–1.36m	0.88–1.52m	0.98t(7.7) 1.34–1.38m	7.65–7.82m

[a]Chemical shifts (δ) in ppm. $^2J[^{119}Sn, ^1H]$ and $^nJ(^1H, ^1H)$ in Hz are listed in square brackets and parenthesis, respectively. Multiplicity is given as: s = singlet, d = doublet, d,d = doublet of doublet, t = triplet, m = multiplet.

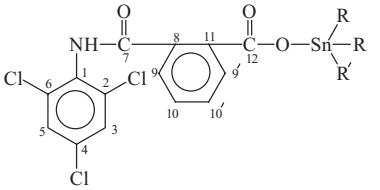
Table IV ^{13}C and ^{119}Sn NMR data[a–c] of 2-[(2′,4′,6′-trichlorophenylamido)]benzoic acid and its organotin(IV) complexes

Carbon	HL	1	2	3	4	5
1	136.0	136.7	136.4	136.2	136.8	136.5
2/6	128.1	128.4	128.0	128.7	128.6	128.5
4	127.8	127.5	127.2	127.7	127.4	127.1
3/5	136.0	136.7	136.6	136.5	136.2	136.4
7	167.4	167.6	167.5	167.3	167.9	167.2
8	129.1	129.2	129.9	129.3	129.3	129.7
9,9′	125.6	124.2	124.3	124.5	124.4	124.8
10,10′	114.2	114.0	114.3	114.1	114.4	114.7
11	127.7	127.5	127.3	127.6	127.7	127.2
12	174.7	175.8	175.2	175.5	175.7	175.9

[a]Compound **1**: Sn-CH_3, (C−α) 29.6. δ $^{119}Sn = -27.6$. Compound **2**: Sn-$CH_2CH_2CH_2CH_3$, (C−α) 29.6 [597], (C−β) 26.8, (C−γ) 26.3, (C−δ) 14.1. δ $^{119}Sn = -136.6$. Compound **3**: Sn-$CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$, (C−$\alpha$) 33.4 [583], (C−$\beta$) 32.7, (C−$\gamma$) 30.6 [92.1], (C−$\delta$) 29.6, (C−$\alpha^*$) 29.1, (C−$\beta^*$) 26.7, (C−$\gamma^*$) 22.4, (C−$\delta^*$) 14.0. δ $^{119}Sn = -139.3$. Compound **4**: Sn−$CH_2CH_2CH_2CH_3$, (C−α) 29.6 [358], (C−β) 27.8 [22.1], (C−γ) 26.8 ^3J[64.0], (C−δ) 14.1. δ $^{119}Sn = +80.0$. Compound **5**: Sn-C_6H_5, (C−α) 137.2, (C−β) 136.8, (C−γ) 135.7, (C−δ) 130.4. δ $^{119}Sn = -98.30$.

[b]Chemical shifts (δ) in ppm: ^nJ[^{119}Sn, ^{13}C] in Hz is listed in square brackets.

[c]



R′ = R for triorganotin, R′ = L for diorganotin.

resonances of the carboxylic carbons in organotin compounds showed downfield shift (175.9–175.2 ppm) as compared to ligand (174.7 ppm), suggesting the coordination of the ligand through the carboxylic oxygen, to the organotin(IV) moiety.

For the tri-*n*-butyltin(IV) derivative, with the ^1J[^{119}Sn−^{13}C] value being 350.6 Hz and by the use of the Holecek and Lycka equation,[19] a C−Sn−C value of 112.3° was calculated, which corresponds to a quasi-tetrahedral geometry in $CDCl_3$ solution (data are given in Table V). The geometric data calculated, as just described, are consistent with tetrahedral geometries for the triorganotin(IV) species, i.e., monomer in solution. In all complexes, ^{119}Sn NMR spectra show only a sharp singlet, indicating the formation of a single species.

Table V (C−Sn−C) angles (°) based on NMR parameters for organotin complexes of 2-[(2′,4′,6′-trichlorophenylamido)]benzoic acid

Compound No.	^1J[^{119}Sn, ^{13}C] (Hz)	^2J[^{119}Sn, ^1H] (Hz)	Angle (°)	
			^1J	^2J
1	—	81	—	132.1
2	597	81	134.6	132.1
3	583	—	133.3	—
4	358	—	112.3	—

The ^{119}Sn chemical shifts $\delta(^{119}Sn)$ of organotin compounds cover a range of over $\pm$600 ppm and are quoted relative to tetramethyltin as a reference. As the electron-releasing power of the alkyl group increases, the tin atom becomes progressively more shielded, and the $\delta(^{119}Sn)$ value moves to higher field. These values are also dependent on the nature of X in R_nSnX_{4-n} and generally move to lower field as the electronegativity of the latter increases. A very important property of the ^{119}Sn chemical shift is that an increase in the coordination number of tin from four to five, six, or seven usually produces a large upfield shift of $\delta(^{119}Sn)$.[20] In triorganotin(IV) complexes, ^{119}Sn chemical shift values lie in the tetrahedral region in non-coordinating solvents, whereas diorganotin(IV) compounds show a higher coordination, probably five. These values are strongly dependent on the nature and orientation of the organic groups bonded to tin. The shifts observed in complexes can be explained quantitatively in terms of an increase in electron density on the tin atom as the coordination number increases.[20]

Semi-Empirical Study

In all five structures **1**–**5**, the carboxylate group binds in an anisobidentate mode to the Sn atom. The bond lengths and angles are similar to those in the literature.[21] In **1**, the Sn atom is 2.012 and 2.709 Å away from the oxygens of one of the carboxylic group, while the other oxygens of the carboxylic group are 2.011 and 2.712 Å away. The long and the short bonds are *trans* to each other. The C—O bond are also unequal (1.316, 1.239 Å and 1.314, 1.238 Å), the shorter C—O bond corresponding to the weakly coordinating oxygens. The two methyl groups are equidistant from Sn (2.079, 2.079 Å) and are in *trans* position. The optimized structure is shown in Figure S1 (Supplemental Materials).

Similarly in compound **2**, the displacement of the Sn atom from the O atoms of the carboxylic acid groups are 2.014 and 2.710 Å away from one of the carboxylic groups, while the other carboxylic group is 2.014 and 2.720 Å. The long and the short bonds are *trans* to each other. The C—O bonds are also unequal, being 1.239 and 1.316 Å for both the ligands, with the longer Sn—O bond associated with the shorter C—O bond. The two butyl groups are equidistant from Sn (2.108, 2.107 Å) and complete the coordination sphere of Sn. The optimized structure is shown in Figure S2 (Supplemental Materials). In **3**, again the Sn atom is asymmetrically attached to the carboxylic acid with displacement of the Sn atom from the O atoms being 2.015, 2.701 Å and 2.014, 2.717 Å. The long and the short bonds are *cis* to each other. The C—O bonds are also unequal, being 1.239 and 1.316 Å and 1.239 and 1.315 Å, with the shorter C—O bond for the weakly coordinated longer Sn—O. The two octyl groups are equidistant from Sn (2.111 Å, 2.113 Å) and complete the coordination sphere of Sn. The optimized structure is shown in Figure S3 (Supplemental Materials). In **4**, the Sn atom is asymmetrically attached to the carboxylic acid with displacement of the Sn atom from the O atoms being 2.028, 2.737 Å. The C—O bonds are also unequal, being 1.237 and 1.317 Å, with the shorter C—O bond for the weakly coordinated longer Sn—O. The three butyl groups are equidistant from Sn (2.133, 2.135, 2.138 Å) and complete the coordination. The optimized structure is shown in Figure S4 (Supplemental Materials). In **5**, the Sn atom is asymmetrically attached to the carboxylic acid with displacement of Sn atom from the O atoms being 2.11, 2.793 Å. The C—O bonds are also unequal, being 1.235 and 1.316 Å with the shorter C—O bond for the weakly coordinated longer Sn—O. The three phenyl groups are nearly equidistant from Sn (2.064, 2.065, 2.071 Å) and complete the coordination. The selected bond lengths and angles of the optimized structure are shown in Table S2 (Supplemental Materials). The optimized structure is shown in Figure S5.

CONCLUSION

Organotin(IV) complexes of 2-[(2′,4′,6′-trichlorophenylamido)]benzoic acid have been synthesized in anhydrous toluene and characterized by various analytical and spectroscopic techniques. The IR data indicate that in both di- and triorganotin(IV) carboxylates, the ligand moiety −COO acts as a bidentate group in solid state, which is also confirmed by semi-empirical study. Semi-empirical study shows that in the compounds **1**–**5**, the carboxylate group binds in an anisobidentate mode to the Sn atom. Spectral studies of reported complexes in solution state indicate that their structures are tetrahedral for triorganotin(IV) complexes, while the polymeric structure was exhibited by the diorganotin(IV) complex, which has a penta-coordinated geometry around the tin atom.

EXPERIMENTAL

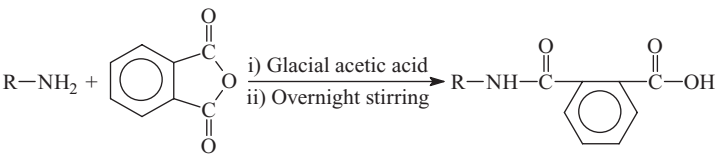
Glass apparatus with standard quick-fit joints were used throughout the work after cleaning and drying at 120 °C. Phthalic anhydride and organotin(IV) chlorides were purchased from Aldrich Chemical Company (USA), while dioctyltin oxide was procured from Alfa Aesar (USA) and used as such. Glacial acetic acid, toluene, acetone, dichloromethane, diethyl ether, methanol, and chloroform were obtained from Merck Chemicals (Germany). All solvents were purified and dried by the reported methods.[22] Melting points were determined on an electrothermal melting point apparatus, model MP-D Mitamura Riken Kogyo (Japan) by using capillary tubes and are uncorrected. Elemental analysis was carried out on a Perkin-Elmer 2400 analyzer (USA). Infrared spectra were recorded as KBr pellets on a 1000 Perkin Elmer instrument in the range 4000–250 cm^{-1}. Mass spectra were recorded on a MAT 8500 Finnigan (Germany). The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-250 using $CDCl_3$ as an internal reference. ^{119}Sn NMR spectra were obtained on a Bruker 250 ARX instrument with Me_4Sn as an external reference.

The structure of complexes **1–5** were modeled by the MOPAC 2007[23] program using the PM6 method.[24] Selected parts of the molecule not containing the metal ion were preoptimized using the molecular mechanics method before subjecting the whole molecule to geometry optimization.

General Procedure for the Synthesis of Carboxylic Acid

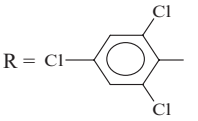
Carboxylic acid has been synthesized by the method in the literature.[25] Detail of the procedure is as follows:

A solution of phthalic anhydride (1 mmol) in a HOAc (300 mL) was added to a solution of substituted aniline (1 mmol) in a HOAc (150 mL) in a 1 L round bottom flask, and the mixture was stirred at room temperature overnight. The precipitates formed were filtered, washed with cold distilled water (200 mL), and air dried [Equation (1)]. Yield = 95%.



(1)

Where



General Procedure for the Synthesis of Organotin(IV) Complexes from Organotin(IV) Chloride

The synthesized carboxylic acid (10 mmol) was suspended in dry toluene (100 mL) and treated with triethylamine in a 1:1 molar ratio. The mixture was refluxed for 2–3 h. To a solution of triethylammonium salt of the ligand in dry toluene (100 mL), diorganotin dichloride (5 mmol) or triorganotin chloride (10 mmol) was added as a solid to a reaction flask with constant stirring, and the reaction mixture was refluxed for 8–10 h. The reaction mixture was contained Et_3NHCl and was filtered. The filtrate contained the organotin(IV) derivative. The solvent was removed in a rotary apparatus under reduced pressure. The residue was recrystallized from $CHCl_3$ and ether (1:1) [Equations (2) and (3)].

$$R_2SnCl_2 + 2Et_3NHL \xrightarrow[\text{ii) Reflux for 8}-\text{10 hrs}]{\text{i) Toluene}} R_2SnL_2 + 2Et_3NHCl \quad (2)$$

$$R_3SnCl + Et_3NHL \xrightarrow[\text{ii) Reflux for 8}-\text{10 hrs}]{\text{i) Toluene}} R_3SnL + Et_3NHCl \quad (3)$$

From Organotin(IV) Oxide

The synthesized carboxylic acid (10 mmol) was suspended in dry toluene (100 mL) and treated with organotin oxide (5 mmol) in a reaction flask with constant stirring. Then the mixture was refluxed for 8–10 h. Water formed was removed via a Dean–Stark trap. After completion and cooling the reaction mixture to room temperature, the solvent was removed in a rotary apparatus under reduced pressured. The residue was recrystallized from $CHCl_3$ and ether (1:1) [Equation (4)].

$$R_2SnO + 2HL \xrightarrow[\text{ii) Reflux for 8}-\text{10 hrs}]{\text{i) Toluene}} R_2SnL_2 + H_2O \quad (4)$$

Where

R_2	Me_2	Bu_2	Oct_2
	(**1**)	(**2**)	(**3**)
R_3	–	Bu_3	Ph_3
	–	(**4**)	(**5**)

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