

Synthesis, Characterization and Thermal Analysis of Organotin(IV) Derivatives of 4-(N-Maleoyl)Butanoate

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Organotin(IV) derivatives of the type $R_{4-n}SnL_n$ where R = Me, *n*-Bu, Ph, L = 4-(N-maleoyl)butanoate and *n* = 1 or 2 were synthesized by refluxing R_3SnCl and R_2SnCl_2 with 4-(N-maleoyl)butanoate in the presence of triethylamine using dry toluene as solvent. These compounds were characterized by IR, multinuclear NMR and mass spectrometry. We also studied their thermal behavior and calculated the degradation pattern, energy of activation (E_a) and order of reaction (*n*).

Introduction

Organotin compounds play an important role in biology and the environment^{1,2} and are themselves powerful biocides³. Organotin compounds of oxygen and nitrogen donor ligands are well known for their biological activity⁴⁻⁶. We have been pursuing studies on the synthesis⁷ and structural characterization⁸ of organotin(IV) derivatives of various donor ligands.

In the present work, organotin(IV) derivatives of the type $R_{4-n}SnL_n$ (R = Me, *n*-Bu, Ph) where L = 4-(N-maleoyl)butanoate and *n* = 1 or 2 were synthesized. These compounds were characterized by IR, NMR (¹H, ¹³C, ¹¹⁹Sn) and mass spectroscopy. The IR data and '*J*' values from NMR were used to determine the nature of bonding and coordination numbers. The kinetic parameters such as order of reaction (*n*) and energies of activation (E_a) were calculated by thermal studies using the Redfern-Coats and Horowitz methods^{18,19}.

Experimental

Chemicals

Maleic anhydride and 4-aminobutyric acid were purchased from Fluka (Switzerland). Di- and triorganotin chlorides were obtained from Aldrich Chemicals (USA). The solvents used were dried and purified according to standard methods⁹. All the chemicals used during the synthesis were of analytical grade.

Synthesis

A solution of maleic anhydride (41.7 g, 0.425 mol in acetic acid, 175 ml) was added to a solution of 4-aminobutyric acid (43.7 g, 0.425 mol in acetic acid, 510 ml), and the mixture was stirred at room temperature for 3 h. The white precipitates were filtered, washed with cold water (50 ml), and dried in air at ambient temperature¹⁰. Maleamic acid (2.01g, 10 mmol) was suspended in dry toluene (100 ml), Et₃N (2.79 ml, 20 mmol) added and the mixture was refluxed for 3-4 h. Then diorganotin dichloride (5 mmol) or triorganotin chloride (10 mmol) was added as solid to the reaction flask with constant stirring, and the reaction mixture was refluxed for a further 3 h. in inert atmosphere using helium gas. The reaction mixture containing Et₃NHCl was filtered off, such that filtrate had the organotin(IV) derivatives. The solvent was removed by rotary apparatus and the mass left behind was crystallized from CH₂Cl₂.

Physical Measurements

Melting points were determined in a capillary tube by using an electrothermal melting point apparatus model MP-D Mitamura Riken Kogyo (Japan). The IR spectra were recorded using KBr discs on a Perkin Elmer 16FPC FT-IR. ¹H and ¹³C NMR were recorded on a Jeol JNM-LA 500 FT-NMR using CDCl₃ as internal reference. The mass spectral data were obtained on a MAT-1125 Mass Spectrometer whereas the thermal studies were carried out in air, on a NETZSCH STA 429, Simultaneous Thermal Analyzer, at the rate of 10 deg. min⁻¹ change in temperature.

Results and Discussion

Tri- and diorganotin complexes of 4-(N-maleoyl)butanoate were prepared by the reaction of triethyl ammonium salt of 4-(N-maleoyl)butanoate with triorganotin chloride/diorganotin dichloride in 1:1 and 2:1 molar ratios, respectively, in dry toluene. All the compounds are solid with definite melting points and are soluble in common organic solvents. Physical data for the compounds are reported in Table 1.

IR Spectroscopy

IR spectra were recorded in the range 4000-400 cm⁻¹ by using KBr discs, and important bands for structural assignments are given in Table 1. The important frequencies are $\nu_{asym}(\text{COO})$, $\nu_{sym}(\text{COO})$, $\nu(\text{Sn-C})$ and $\nu(\text{Sn-O})$. The complexation of tin with ligand is confirmed by the absence of a band in the range 2900-2600 cm⁻¹ due to $\nu(\text{OH})$ of the COOH group. The band in the range 1696 - 1714 cm⁻¹ for imide (CO) remains unchanged showing no interactions of Sn with imide CO¹⁰. The difference between $\nu_{asym}(\text{COO})$ and $\nu_{sym}(\text{COO})$ is important in the prediction of the nature of the ligand. In all compounds the difference $\Delta\nu$ is less than 200 cm⁻¹, which indicates that the ligand acts as bidentate in all compounds¹¹⁻¹³.

Bands in the ranges 560-520 cm⁻¹ and 480-450 cm⁻¹ indicate the presence of Sn-C and Sn-O in these compounds, respectively.

Table 1. Physical and Infrared Data (cm^{-1}) for R_3SnL and R_2SnL_2 .

S. No.	Complex	Empirical formula	%C Calcd./expl.	%H Calcd./expl.	mp ($^{\circ}\text{C}$)	(%) Yield	ν (Sn-O)	ν (Sn-C)	ν (CO) (imide)	ν (COO) (asym)	ν (COO) (sym)	$\Delta\nu$
1	Me_3SnL	$\text{C}_{11}\text{H}_{17}\text{NO}_4\text{Sn}$	38.15/38.35	4.91/5.05	135-136	52	460	546	1714	1570	1408	162
2	Ph_3SnL	$\text{C}_{26}\text{H}_{23}\text{NO}_4\text{Sn}$	58.65/58.25	4.32/4.52	72-73	42	454	548	1706	1574	1406	168
3	Bu_3SnL	$\text{C}_{20}\text{H}_{35}\text{NO}_4\text{Sn}$	50.85/51.12	7.42/7.59	59-60	45	456	502	1710	1572	1420	152
4	Me_2SnL_2	$\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_8\text{Sn}$	42.11/41.95	4.29/4.25	123-125	50	462	586	1710	1570	1406	164
5	Ph_2SnL_2	$\text{C}_{28}\text{H}_{26}\text{N}_2\text{O}_8\text{Sn}$	52.75/52.92	4.08/3.98	62-65	40	462	546	1696	1572	1412	160
6	Bu_2SnL_2	$\text{C}_{24}\text{H}_{34}\text{N}_2\text{O}_8\text{Sn}$	48.24/48.70	5.70/5.35	69-71	52	454	500	1710	1570	1412	158

NMR Spectroscopy

^1H , ^{13}C and ^{119}Sn NMR of the investigated compounds are given in Tables 2 and 3. The expected resonances are assigned by their multiplicity and intensity pattern as well as by coupling constants. In ^1H NMR different signals in the range 1.90-3.60 ppm appear due to the presence of different methylene protons present in the ligand. Similarly the signal at 6.55-6.75 ppm is due to H-C=C-H protons present in the ring¹¹. The different R groups attached to the Sn atom give signals in the expected range.

The spin-spin coupling constants involving ^{119}Sn and a number of other nuclei are often informative. The most detailed studies have been carried out on couplings involving tin and hydrogen, $^2J[^{119}\text{Sn}, ^1\text{H}]$, and correlations of their magnitude with stereochemistry are always important. For example, $^2J[^{119}\text{Sn}, ^1\text{H}]$ for tetrahedral trimethyltin compounds are lower than for pentacoordinate trimethyltin compounds^{14a}. Wrackmeyer reported that generally the value of $^2J[^{119}\text{Sn}, ^1\text{H}]$ in methyltin compounds increases with the coordination number of tin and with an increasing number of electronegative ligands at the tin atom^{14b}.

The coupling constant values observed for the $(\text{CH}_3)_3\text{SnL}$ and $(\text{CH}_3)_2\text{SnL}_2$ are given in Table 2. For the trimethyltin compound the 2J value falls in the tetrahedral environment, whereas the value of 2J for the dimethyltin compound confirms the higher coordination number for tin, probably five or six^{7,14}.

Table 2. $^1\text{HNMR}$ Data for R_3SnL and R_2SnL_2 ^{a,b,c,d}

Proton No.	(I) $\text{R}_3=\text{Me}$	(II) $\text{R}_3=\text{Ph}$	(III) $\text{R}_3=\text{Bu}$	(IV) $\text{R}_2=\text{Me}$	(V) $\text{R}_2=\text{Ph}$	(VI) $\text{R}_2=\text{Bu}$
1	-	-	-	-	-	-
2	2. 35(t)	2. 42(t)	2. 30(t)	2. 38(t)	2. 38(t)	2. 38(t)
3.	1. 91(m)	1. 94(m)	1. 90(m)	1. 93(m)	1. 93(m)	1. 93(m)
4.	3. 60(t)	3. 55(t)	3. 57(t)	3. 60(t)	3. 60(t)	3. 60(t)
5,5'	-	-	-	-	-	-
6,6'	6. 7	6. 55	6. 68	6. 72	6. 71	6. 71
α	0. 63 [50]	-	1. 35 [n. o]	1. 126 [76. 1]	-	1. 75 [n. o]
β	-	7. 71(m) [n. o]	1. 60(m) [n. o]	-	7. 53(m) [n. o]	1. 40(m) [n. o]
γ	-	7. 45(m) [6. 2]	1. 25(m) [n. o]	-	7. 36(m) [n. o]	-
δ	-	7. 40(t) [n. o]	0. 91(t) [n. o]	-	7. 26(t) [n. o]	0. 94(t) [7. 1]

(a) in CDCl_3 at 295K

(b) chemical shift (δ) in ppm, $^nJ[^{119}\text{Sn}-^1\text{H}]$ in Hz.

(c) t = triplet, m = multiplet, n. o = not observed

(d) numbering scheme for L and R groups:

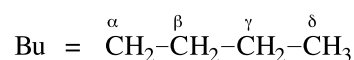
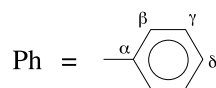
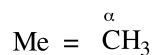
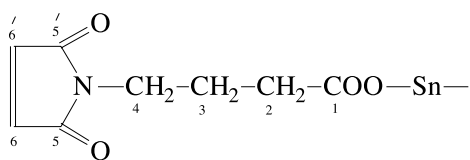


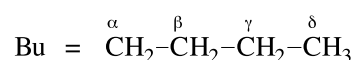
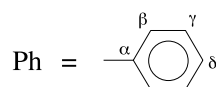
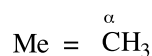
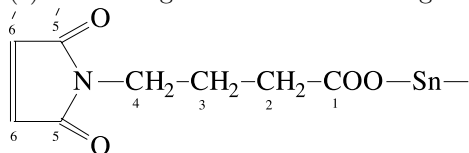
Table 3. ^{13}C and ^{119}Sn NMR Data for R_3SnL and $\text{R}_2\text{SnL}_2^{\text{a,b,c}}$

Carbon No.	(I) $\text{R}_3=\text{Me}$	(II) $\text{R}_3=\text{Ph}$	(III) $\text{R}_3=\text{Bu}$	(IV) $\text{R}_2=\text{Me}$	(V) $\text{R}_2=\text{Ph}$	(VI) $\text{R}_2=\text{Bu}$
1	177. 0	177. 0	179. 9	180. 7	178. 4	179. 9
2	24. 1	24. 6	24. 8	23. 9	23. 6	23. 9
3.	31. 5	31. 4	32. 0	30. 9	29. 7	30. 9
4.	37. 1	37. 3	37. 4	36. 9	37. 0	37. 0
5,5'	170. 9	170. 9	170. 9	170. 9	170. 9	170. 9
6,6'	134. 2	134. 2	134. 2	134. 2	134. 3	134. 3
α	8. 5	136. 8	16. 5	8. 6	145. 6	26. 3
β	-	135. 6	27. 9	-	137. 6	27. 2
γ	-	133. 9	24. 8	-	131. 0	26. 9
δ	-	128. 9	13. 7	-	128. 8	13. 5
^{119}Sn	136. 7	-111. 5	110. 4	-	-	-

(a) in CDCl_3 at 295K

(b) chemical shift(δ) in ppm

(c) numbering scheme for L and R groups:



^{13}C NMR data also reveals expected signals within the specified range. The presence of two types of $-\text{C}=\text{O}$ groups in the ligand are well separated by two signals in the range 170-180 ppm. The $-\text{C}=\text{C}-$ signal in the ring appeared at 134 ppm. The R groups attached to the tin atom have their signals in various ranges according to the nature of the R group.

^{119}Sn NMR plays a significant role in determining the geometry around the tin atom. The ^{119}Sn chemical shifts are comparable with earlier reports describing tetrahedral monomeric geometry in non-coordinating solvent¹³⁻¹⁶.

Mass Spectroscopy

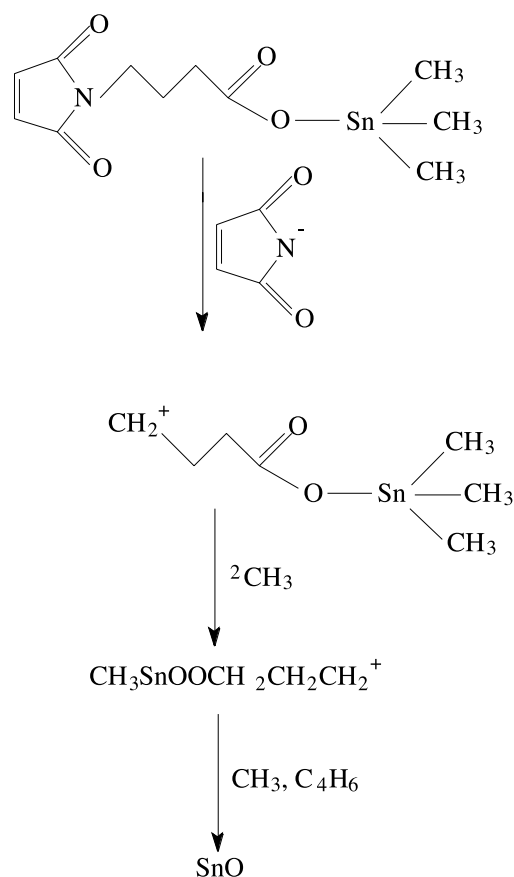
Mass spectral fragmentation for the three compounds are described in Table 4. The molecular ion peak in all cases is not observed^{15,17}. In The trimethyltin compound the first loss is of methyl radical that gives m/z at 332. The fragments at m/z 302 and 288 are due to the loss of C_2H_6 and CO_2 molecules, respectively. The further fragments of SnH^+/Sn^+ (121/120), $\text{CH}_2\text{NCOCHCHCO}^+$ (110) COCHCHCO^+ (82), C_3H_9^+ (45), CHCHCO^+ (54) and C_2H_2^+ (26) are obtained. Similarly, in the triphenyl compound no molecular ion peak is obtained but again it shows a pattern similar to that obtained in the trimethyltin compound. In tributyltin the loss of the butyl group gives m/z 416, which on loss of CO_2 and butyl group yields m/z 372 and 359, respectively. The other fragments are reported in Table 4.

Thermal Analysis

TG results of the compounds are given in Tables 5 and 6. Thermogravimetric (TG) analysis of di- and triorganotin (IV) derivatives of 4-(N-maleoyl)butanoate reveals that decomposition of these compounds occurs as the temperature increases. The degradation pattern for the triorganotin derivatives is different from those of the diorganotin derivatives. Furthermore, it is found that the weight losses observed due to thermal decomposition of these derivatives are much closer to the calculated values. The slight difference in the values indicates the error, which is in the acceptable range of $\pm 3\%$. The decomposition process for compound 1 is proposed in Scheme 1. In the 1st step, part of the ligand is evolved while in the 2nd step two methyl groups bonded to tin are detached. In the 3rd step the remaining part of the ligand and the methyl group evolved leaving SnO as residue. The residue in all compounds were characterized by infrared while the species evolved were proposed from the weight loss observed and calculated.

The TG data is interpreted to calculate the kinetic parameters such as order of reaction and energies of activation. Tri- and diorganotin derivatives show a 1.25 order of reaction for their 1st step decomposition. However, the observed values for order of reaction of the 2nd and 3rd steps are sometimes different.

The energies of activation at different steps were calculated by Redfern's method¹⁸ and the results were compared by Horowitz's method¹⁹. The energies of activation were comparable.



Scheme 1. Proposed Thermal Degradation for Compound 1

Table 4. Relative Abundance (%) of Common Ions Observed for the Investigated Compounds*

Fragment ion	R ₃ =Me	R ₃ =Ph	R ₃ =Bu
R ₃ SnCO ₂ (CH ₂) ₃ NCOCHCHCO ⁺	n. o.	n. o.	n. o.
R ₂ SnCO ₂ (CH ₂) ₃ NCOCHCHCO ⁺	48	2	83
R ₂ Sn(CH ₂) ₃ NCOCHCHCO ⁺	6	4	2
SnCO ₂ (CH ₂) ₃ NCOCHCHCO	8	4	16
CH ₂ NCOCHCHCO ⁺	89	6	14
SnH ⁺ /Sn ⁺	6	4	9
COCHCHCO ⁺	100	4	10
C ₆ H ₆ ⁺	-	100	-
C ₆ H ₅ ⁺	-	29	-
C ₄ H ₉ ⁺	-	-	43
C ₂ H ₅ ⁺	-	-	100
C ₂ H ₂ ⁺	60	29	26

*n. o. = not observed

Table 5. Kinetic Parameters of Tri- and Diorganotin [4-(N-maleoyl)butanoate]

Compound	Ts (K)	Reaction order (n)	Ea (kcal/mol)	
			I	II
Me ₃ SnL*	453	1.25	14.06	13.60
	633	1.25	7.7	8.9
	713	0.75	6.09	7.8
Bu ₃ SnL	513	1.25	20.29	20.23
	613	1.25	7.12	7.33
	633	1.25	16.64	15.34
Ph ₃ SnL	593	1.25	14.40	12.60
	773	1.25	5.3	6.03
Me ₂ SnL ₂	503	1.25	19.92	19.70
	583	0.75	13.5	15.97
	753	1.25	10.97	11.01
Bu ₂ SnL ₂	513	1.25	19.90	18.80
	953	0.90	13.2	13.07
Ph ₂ SnL ₂	453	1.25	10.20	11.08
	563	1.25	15.23	15.0
	893	1.0	9.87	9.95

*L = 4-(N-maleoyl)butanoate

Table 6. Thermal Degradation Pattern of Tri- and Diorganotin [4-(N-maleoyl)butanoate]

Compound	Ts (°C)	Evolved species (mole)	Wt. loss% Calcd.	Wt. loss% Obs.	Error
Me ₃ SnL*	180	0.5 C ₄ H ₂ NO ₂	22.45	22.0	0.45
	320	1.0 C ₄ H ₂ NO ₂			
	440	3.0 CH ₃ 0.4 Sn 3.0 CH ₃ 1.0 L	40.7 79.4	42.0 80.0	1.3 0.6
Bu ₃ SnL	240	0.5 C ₄ H ₂ NO ₂ 1.0 C ₄ H ₉	22.7	20.0	2.7
	340	1.0 C ₄ H ₂ NO ₂ 3.0 C ₄ H ₉	56.5	55.0	1.5
	460	0.4 Sn 3.0 C ₄ H ₉ 1.0 L	76.9	75.0	1.9
Ph ₃ SnL	320	1.0 C ₄ H ₂ NO ₂ 2.0 C ₆ H ₅	47.0	50.0	3.0
	500	0.1 Sn 1.0 L 3.0 C ₆ H ₅	70.0	68.0	2.0
Me ₂ SnL ₂	230	1.0 C ₇ H ₈ NO ₂ 2.0 CH ₃	24.5	27.0	2.5
	310	0.5 C ₄ H ₂ NO ₂ 1.0 L 2.0 CH ₃	51.5	49.0	2.5
	480	0.3 Sn 2.0 L 2.0 CH ₃	83.7	84.0	1.7
Bu ₂ SnL ₂	240	1.0 C ₇ H ₈ NO ₂ 2.0 C ₄ H ₉	66.5	69.6	3.1
	680	0.5 Sn 2.0 L 2.0 C ₄ H ₉	92.0	90.0	2.0
Ph ₂ SnL ₂	180	0.5 C ₄ H ₂ NO ₂	15.1	15.0	0.1
	290	0.5 C ₇ H ₈ NO ₂ 1.0 L	49.8	50.0	0.2
	620	2.0 C ₆ H ₅ 2.0 L	81.3	80.0	1.3

*L = 4-(N-maleoyl)butanoate

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