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Novel Chelated Compounds of β-Carbobutoxyethyltin Trichloride

M. V. GARAD

Department of Chemistry, University of Poona, Pune 411 007, India

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This paper reports the synthesis and replacement reactions of β-carbobutoxyethyltin trichloride in continuation with our earlier work on β-carboalkoxyethyltin compounds [1–3]. The bidentate ligands used for replacement were acetylacetone, salicylaldehyde, dibenzoylmethane, 2-hydroxy-4-methoxybenzophenone, 8-hydroxyquinoline, benzoylphenylhydroxylamine and salazine. The stepwise replacement reactions of β-carbobutoxyethyltin trichloride were also carried out and products well characterized on the basis of their elemental analysis, infrared and PMR data. These compounds are monomeric in boiling benzene.

Introduction

The several organotin compounds have attained significant commercial importance for synthesis of intermediates to PVC stabilizers ($RSnCl_3$ and R_2SnCl_2 where R = Me, Bu, Oct) and biocides and fungicides (R_3SnCl, R = Bu, Ph) and several carry academic interest. Hutton and coworkers [4–6] have investigated a novel series of organotin compounds called β-substituted alkyltin halides. The crystal and molecular structures of $Cl_3SnCH_2CH_2CO_2Me$, $Cl_2Sn[CH_2CH_2CO_2Me]_2$ and $Cl_2Sn[CH_2CH_2CONH_2]_2$ are reported [7]. These compounds are synthesised by the hydrostannation route. The mechanism of hydrostannation is interesting, and according to Hutton *et al.* the first step is the formation of halogenostannane species as in eqn. 1.

$$SnCl_2 + HCl \xrightarrow[20\ ^\circ C]{\text{diethyl ether}} HSnCl_3 \qquad (1)$$

The halogenostannane species formed can be trapped between carbonyl activated olefin to give β-substituted products as in eqn. 2.

$$HSnCl_3 + ROCOCH{=}CH_2 \xrightarrow{\text{ether}} ROCOCH_2CH_2SnCl_3 \qquad (2)$$

R = β-carbobutoxyethyl group.

The tin atom in β-carbobutoxyethyltin trichloride has been observed to be penta-coordinated. The replacement reactions of β-carbobutoxyethyltin trichloride are carried out using sodio derivatives of different ligands. In the monosubstituted product both ester and ligand functional groups are coordinating to tin, while in the disubstituted product ester carbonyl coordination is broken off and both ligands are coordinating to tin. In trisubstituted product ester carbonyl coordination is broken off and at least two ligands may be coordinating to tin. All reactions gave well defined products.

Experimental

All experiments were carried out using dry, distilled solvents and N_2 atmosphere. IR spectra were recorded as a nujol mulls on a Perkin-Elmer 599B grating spectrophotometer. 60 MHz NMR spectra were recorded on a Varian T-60 spectrometer using $CDCl_3$ solutions of each compounds and TMS as internal standard.

Preparation of β-Carbobutoxyethyltin Trichloride

To 10 g (0.050 mol) of anhydrous stannous chloride suspended in 7.44 g (0.058 mol) of butylacrylate was added 2.95 g (0.081 mol) of anhydrous HCl during 2 hrs. The temperature was maintained at 20 °C or below. After the completion of the reaction the reaction mixture was kept at 150°/4 mm Hg to remove unreacted butylacrylate and $ClCH_2CH_2CO_2$-Bu. The warm residue was filtered to remove residual $SnCl_2$. The brown, low-melting solid was obtained, and was characterized by elemental analysis and spectroscopy, yield 17.1 g (90%).

Preparation of 8-Hydroxyquinolino-β-carbobutoxyethyltin Dichloride

β-Carbobutoxyethyltin trichloride (1.42 g, 0.004 mol) and sodio derivative of 8-hydroxyquinoline (0.668 g, 0.004 mol) were reacted in boiling benzene (50 ml) for 2 hrs. The contents were allowed to attain room temperature, were centrifuged, and for benzene solution containing compounds, concentrated to

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TABLE I. Analytical Data of Chelated β-Carbobutoxyethyltin Compounds.[a]

S. No.	Compound	Colour, melting or decomp. point 0 °C	Analytical data			
			Sn		Cl	
			Found	Calc.	Found	Calc.
1	$Cl_3Sn(Es)$	brown (A)	33.51	33.52	29.95	30.02
2	$Cl_2(Sa)Sn(Es)$	yellow (A)	27.10	27.00	16.00	16.13
3	$Cl_2(Dbm)Sn(Es)$	pale yellow (A)	21.66	21.90	12.99	13.08
4	$Cl_2(Acac)Sn(Es)$	pale yellow (A)	28.66	28.40	16.87	16.99
5	$Cl_2(Ombp)Sn(Es)$	pale green (A)	21.78	21.75	12.78	12.99
6	$Cl_2(Ox)Sn(Es)$	yellow 52	25.58	25.64	15.11	15.31
7	$Cl(Ox)_2Sn(Es)$	yellow (A)	20.58	20.77	6.19	6.20
8	$Cl(Sal)Sn(Es)$	yellow 235	22.84	22.74	6.73	6.79
9	$(Ox)_3Sn(Es)$	yellow 165	17.31	17.46		
10	$(Sa)_3Sn(Es)$	yellow (A)	19.27	19.44		
11	$Cl_2(Bpha)Sn(Es)$	red (A)	22.17	22.37	13.35	13.36

[a] Es = β-carbobutoxyethyl; other abbreviations: Sa = salicylaldehyde, Dbm = dibenzoylmethane, Acac = acetylacetone, Ombp = 2-hydroxy-4-methoxybenzophenone, Ox = 8-hydroxyquinoline, Sal = salicylaldazine, Bpha = benzoylphenylhydroxylamine. [b] A = semi solid.

obtain a yellow solid. The solid was washed with hexane and dried *in vacuo*. Yield 1.75 g (94.7% of theory). The yellow solid is soluble in benzene and chloroform, insoluble in hexane. *Anal.* Found: C, 41.42; H, 4.05; Sn, 25.63; Cl, 15.11%. Calc. for $[C_9H_6NO]Sn[C_7H_{13}O_2]Cl_2$: C, 41.50; H, 4.10; Sn, 25.65; Cl, 15.31%. Other chelated derivatives were prepared similarly using different metal to ligand ratio (Table I).

Results and Discussion

Vibrational Spectra

The infrared spectrum of butyl acrylate shows a carbonyl absorption at 1720 cm^{-1}. In β-carbobutoxyethyltin trichloride the carbonyl stretching frequency appears at 1650 cm^{-1}. This effect is consistent with strong intramolecular coordination of ester carbonyl to tin atom. The νC–O alcoholic in butyl acrylate is shifted to higher wave number in β-carbobutoxyethyltin trichloride. This shift is due to the participation of the lone pair of electrons of the butoxy group in the delocalization of carbonyl electron density on tin (Fig. 1) and the tin atom is penta coordinated.

8-Hydroxyquinolino-β-carbobutoxyethyltin Dichloride

In the IR spectrum of 8-hydroxyquinolino-β-carbobutoxyethyltin dichloride the νC=O (ester) appears at 1650 as in the parent trichloride, and νC=N is observed at 1605 and 1580 cm^{-1} indicating the coordination of the carbonyl group of the ester and the C=N of the 8-hydroxyquinoline to tin. Similarly in other monosubstituted products (Table II) the ester C=O as well as the ligand functional groups coordinate with tin as seen from their IR spectra.

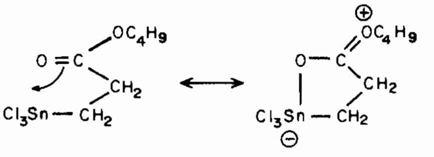


Fig. 1.

Bis-8-hydroxyquinolino-β-carbobutoxyethyltin Chloride

In bis-8-hydroxyquinolino-β-carbobutoxyethyltin chloride, the ester: νC=O appears at 1705 and νC=N of the ligand at 1600 and 1570 cm^{-1}. This observation indicates that coordination due to ester carbonyl is broken and C=N or C=O of the ligand coordination to give a hexa-coordinated structure to tin.

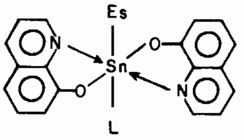
Tris-8-hydroxyquinolino-β-carbobutoxyethyltin Compound

The carbonyl absorption in β-carbobutoxyethyltin trichloride appears at 1650 cm^{-1}. This absorption has been shifted to 1705 cm^{-1}, in tris-8-hydroxyquinolino-β-carbobutoxyethyltin, which indicates the non-coordinating nature of ester carbonyl and coordination due to 8-hydroxyquinoline. The evidence of coordination of 8-hydroxyquinoline is also obtained from splitting of νC=N frequency. The νSn–C in β-carbobutoxyethyltin trichloride has also been shifted to longer wave number. Above finding suggests at least two of the three ligand molecules coordinates to tin resulting stable hexa-coordinated structure shown in (Fig. 2).

TABLE II. IR and PMR Spectral Data of Chelated β-Carbobutoxyethyltin Compounds.

S. No.	Compound	IR spectral frequencies in the range 1500–1750 cm^{-1}	Chemical shifts (δ ppm in $CDCl_3$)^a			
			α-CH_2	β-CH_2	-OCH_2	Butoxy residue
1	$Cl_3Sn(Es)$	1650s	2.20	2.96	4.40	0.80–1.96
2	$Cl_2(Sa)Sn(Es)$	1525s, 1590s, 1625s, 1640s	1.86	2.96	4.40	0.73–1.73
3	$Cl_2(Dbm)Sn(Es)$	1525s, 1575s, 1625s	1.80	2.90	4.13	0.66–1.66
4	$Cl_2(Acac)Sn(Es)$	1525s, 1575s, 1650s	1.76	2.86	4.30	0.90–1.60
5	$Cl_2(Ombp)Sn(Es)$	1500s, 1550s, 1575s, 1600s, 1640s	1.80	2.86	4.23	0.73–1.63
6	$Cl_2(Ox)Sn(Es)$	1500s, 1580s, 1605m, 1650s	1.73	2.93	3.96	0.56–1.56
7	$Cl(Ox)_2Sn(Es)$	1500s, 1570s, 1600m, 1650s, 1705s	B	B	B	B
8	$Cl(Sal)Sn(Es)$	1560s, 1600s, 1700s	B	B	B	B
9	$(Ox)_3Sn(Es)$	1560s, 1590m, 1705s	1.73	2.23	3.36	0.70–1.63
10	$(Sa)_3Sn(Es)$	1590s, 1610s, 1640s, 1650s, 1705s	B	B	B	B
11	$Cl_2(Bpha)Sn(Es)$	1525s, 1590m, 1625s	1.93	2.90	4.13	0.60–1.70

^{a}B = data are not available due to low solubility.



Es = β – Carbobutoxyethyl group
L = 8 – Oxyquinilino group

Fig. 2.

PMR Data

The PMR data of β-carbobutoxyethyltin trichloride exhibits three triplets centered at (chemical shifts δ ppm) 2.20, 2.96, and 4.40 attributable to α-CH_2, β-CH_2 and -OCH_2 protons respectively; remaining protons of the butyl group resonate between 0.8 and 1.96 when all the chlorine atoms are replaced by bidentate chelating ligand, the ester coordination is broken off as seen from IR spectra. Further evidence of the non-coordinating nature of the ester carbonyl group in tri-substituted complexes is obtained from the values of chemical shifts of methylenic and butyl protons. Both the β-methylenic and butyl protons of the ester part in the ester tin chelates also suffer shielding and revert to the positions characteristic of ester group as in butyl propionates. The α-methyleneic protons in all the chelated compounds resonate upfield compared to those in the trichloride. This upfield shift is due to higher electron density on tin atom when chlorine atom is replaced by chelate.

The PMR spectrum of β-carbobutoxyethyltin trichloride in benzene exhibits the three triplets centered at 1.70, 2.09 and 3.73 attributable to α-CH_2, β-CH_2 and -OCH_2 proton respectively, remaining protons of butyl group resonate between 0.6 and 1.80. This behaviour is expected in benzene solution as the result of stereospecific interaction between solvent and ester grouping so as to avoid δ^- on oxygen atom as shown in (Fig. 3).

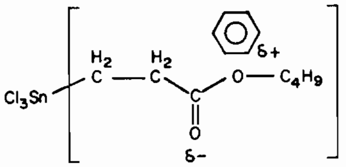


Fig. 3.

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