



The synthesis of some organotin (IV) compounds in the melt- phase

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Abstract

The melt-phase synthesis of dioctyltin (IV) and triphenyltin (IV) benzoates were carried out using stoichiometric amounts of benzoic acids and the corresponding organotin (IV) compounds. The reagents were ground together in a mortar and fed into a boiling glass tube. A cannula tube was inserted into the boiling tube to discharge accumulated gaseous products. A syringe ensured a continuous flow of dry Nitrogen gas in the reaction vessel. The compounds are known using wet Chemistry. Their syntheses via the melt-phase were in good yields. The physical properties corresponded to those of the similar compounds prepared by wet chemistry. The IR, ¹H and ¹³C NMR data indicate that coordination to the tin atom is via carboxylate group.

Keywords: Organotin; Melt-phase; Carboxylate group; Benzoic acid.

1. Introduction

Organotin (IV) compounds have been variously applied both in agriculture and medicine [1-5]. This class of compounds has also been reported to be active as catalysts, antifouling agents and for wood preservation [6]. Because of this wide-spread application, there has been a continued interest in the study of organotin(IV) compounds. Apart from their wide biological and non biological applications, studies have also been carried out to explore the rich structural possibilities open to this class of compounds [7].

Environmental problems associated with disposal of wastes from most chemical reactions have led synthetic chemists to reconsider their research methods. The use of ionic liquids [8], supercritical CO₂ [9] and other procedures have been demonstrated [10]. The synthesis of compounds in the absence of solvents is another method being given prominent attention recently [11]. One major challenge associated with this method is that the role of diffusion and interaction between reactants is not yet clear [11]. Also it is not yet established that the reactions carried out in solid state will generate the same products as those performed using wet chemistry.

Synthesis of organotin(IV) complexes in the melt phase have not been reported, the present study is therefore undertaken to explore the possibility of preparing benzoic acid derivatives of dioctyltin(IV) and triphenyltin(IV) in the melt phase. The compounds were characterized using the IR, ¹H NMR and ¹³C NMR spectroscopic techniques. The compounds were obtained in good yield between 80-87% in most cases.

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2. Experimental

2.1. Materials

The dioctyltin oxide and triphenyltin chloride were obtained from BDH Chemicals, UK. All other chemicals were of AR grade and were used without further purification. Infrared spectra were performed at the Central Science Laboratory, Ladoko Akintola University of Technology, Ogbomoso, Nigeria. Proton and carbon -13 nuclear magnetic resonance studies of the compounds were run at the Central Science Laboratory, Obafemi Awolowo University, Ile-Ife, Nigeria.

2.2. Spectroscopic analyses

The infrared spectra of the organotin(IV) complexes were recorded in KBr discs on a Perkin Elmer 283B spectrophotometer in the range 4000 – 400 cm^{-1} . ^1H and ^{13}C NMR were recorded on JEOL GX 270 FT spectrometer. Samples were dissolved in CDCl_3 at $25 \pm 1^\circ\text{C}$. Coupling constants J are given in Hz. The multiplicities are given with chemical shifts (s = singlet, d = doublet, t = triplet, m = multiplet).

2.3. Synthesis of triphenyltin(IV) benzoate

A mixture of 0.55 g (4.5 mmol) of benzoic acid and 1.7262 g (4.5 mmol) of triphenyltin chloride were grounded together in agate mortar that had been previously acid washed and dried. The reaction is carried out in Pyrex boiling tubes immersed in a thermoregulated oil bath with the heated oil being stirred continuously throughout to maintain even temperature. A cannula tube was inserted into the boiling tube to discharge accumulated gaseous products and an inserted syringe ensured a continuous flow of dry Nitrogen gas in the reaction vessel. The progress of the reaction was monitored by Thin Layer Chromatography. The solid mixture melts at about 120°C and was allowed to remain in the melt for 15 minutes after which the product was extracted with spatula after cooling. White solid; m.p. $96\text{-}98^\circ\text{C}$; 71.4%; **IR cm^{-1}** : $\nu_{\text{Asym}}(\text{COO})$ 1553.69, $\nu_{\text{Sym}}(\text{COO})$ 1383.9, $\Delta\nu$ 199.7, $\nu(\text{Sn} - \text{C})$ 552.56, $\nu(\text{Sn} - \text{O})$ 448.23, $\nu(\text{C} - \text{O})$ 1128.19, $\nu(\text{C} - \text{H})$ str 3071.82, $\nu(\text{C} - \text{H})$ bend 667.66, $\nu(\text{C} = \text{C})$ 1602.73, **^1H NMR**: Sn- C_6H_5 (7.48-7.80 m), C_6H_5 (7.44-8.12 m), **^{13}C NMR**: COO(172 ppm), C_6H_5 (128.32 ppm).

2.4. Synthesis of triphenyltin(IV) 2-bromobenzoate

A mixture of 0.6533 g (3.25 mmol) of 2-bromobenzoic acid and 1.2467 g (3.25 mmol) of triphenyltin chloride were grounded together in an agate mortar. The synthetic procedure was then carried out in a manner analogous to that described above for triphenyltin(IV) dibenzoate. Brown solid; m.p. $106\text{-}108^\circ\text{C}$; 80%; **IR cm^{-1}** : $\nu_{\text{Asym}}(\text{COO})$ 1475.67, $\nu_{\text{Sym}}(\text{COO})$ 1310.95, $\Delta\nu$ 164.95, $\nu(\text{Sn} - \text{C})$ 554.68, $\nu(\text{Sn} - \text{O})$ 473.78, $\nu(\text{C} - \text{O})$ 1117.97, $\nu(\text{C} - \text{H})$ bend 686.56, $\nu(\text{C} - \text{O})$ 1688.66, $\nu(\text{C} = \text{C})$ 1583.44. **^1H NMR**: Sn- C_6H_5 (7.48-7.80 m), C_6H_5 (7.44-8.12 m), **^{13}C NMR**: COO(172 ppm), C_6H_5 (131.32 ppm).

2.5. Synthesis of dioctyltin(IV) dibenzoate

Benzoic acid, 0.5495 g (4.5 mmol) and 0.8125 g (2.25 mmol) of dioctyltin oxide were grounded together in an agate mortar. The procedure as described above for triphenyltin benzoate was then followed. The mixture melts completely at 108°C and was allowed to remain in the melt for 15 minutes before product extraction. Colourless sticky solid; 85.7%; **IR cm^{-1}** : $\nu_{\text{Asym}}(\text{COO})$ 1567.85, $\nu_{\text{Sym}}(\text{COO})$ 1361.06, $\Delta\nu$ 205.91, $\nu(\text{Sn} - \text{C})$ 549.93, $\nu(\text{Sn} - \text{O})$ 439.68, $\nu(\text{C} - \text{O})$ 1130.42, $\nu(\text{C} - \text{H})$ str 2853.90, $\nu(\text{C} - \text{H})$ bend 1493.79, $\nu(\text{C} = \text{C})$ 1605.89. **^1H NMR**: Sn-

C_8H_{17} (1.28-1.32 m) 1.29 s, Sn- CH_2 (2.54 s), C_6H_5 (7.44-8.12 m), ^{13}C NMR: COO(172 ppm), CH_3 (21.25 ppm), C_6H_5 (133.32 ppm)

2.6. Synthesis of dioctyltin(IV) bis(4-chlorobenzoate)

The synthesis of the compound of interest was accomplished by weighing out 0.5417 g (3.46 mmol) of 4-chlorobenzoic acid and 0.6247 g (1.73 mmol) of dioctyltin oxide into an agate mortar. After grinding together, the procedure described above for triphenyltin(IV) benzoate was then followed. At a temperature of 108°C the mixture melts completely and was allowed to remain in the melt for 15 minutes. The product was extracted with spatula after cooling to room temperature and stored in a desiccator over $CaCl_2$. white solid; m.p. 81-83°C; 87.5%; **IR cm^{-1}** : $\nu_{Asym}(COO)$ 1573.54, $\nu_{Sym}(COO)$ 1331.26, $\Delta\nu$ 242.05, $\nu(Sn - C)$ 551.27, $\nu(Sn - O)$ 475.48, $\nu(C - O)$ 1128.46, $\nu(C - H)$ str 2853.44, $\nu(C - H)$ bend 1487.28, $\nu(C = C)$ 1592.47., **1H NMR**: Sn- C_8H_{17} (1.28-1.32 m) 1.0 s, Sn- CH_2 (2.54 s), C_6H_5 (7.44-8.12 m), ^{13}C NMR: COO(172.9 ppm), CH_3 (16.25 ppm), C_6H_5 (132.32 ppm)

2.7. Synthesis of dioctyltin(IV)bis(2-bromobenzoate)

The titled compound was prepared by grinding together 0.5427 g (2.7 mmol) of 2-bromobenzoic acid and 0.4875 g (1.35 mmol) of dioctyltin oxide were grounded together in an agate mortar. The procedure as described above for triphenyltin benzoate was then followed. The mixture melts completely at 108°C and was allowed to remain in the melt for 15 minutes before being extracted with spatula on cooling to room temperature. Colourless liquid; **IR cm^{-1}** : $\nu_{Asym}(COO)$ 1584.54, $\nu_{Sym}(COO)$ 1343.02, $\Delta\nu$ 241.52, $\nu(Sn - C)$ 575.85, $\nu(Sn - O)$ 476.10, $\nu(C - O)$ 1130.36, $\nu(C - H)$ str 2853.20, $\nu(C - H)$ bend 1465.89, $\nu(C = C)$ 1605.89., **1H NMR**: Sn- C_8H_{17} (1.28-1.32 m) 1.4 s, Sn- CH_2 (2.54 s), C_6H_5 (7.44-8.12 m), ^{13}C NMR: COO(173.25 ppm), CH_3 (14.25 ppm), C_6H_5 (128.32 ppm)

2.8. Synthesis of dioctyltin(IV)bis(4-nitrobenzoate)

The compound of interest was synthesized by weighing out 0.7582 g (3.25 mmol) of 4-nitrobenzoic acid and 0.5868 g (1.625 mmol) of dioctyltin oxide into an agate mortar. After grinding together, the mixture was transferred into a Pyrex boiling tube and the procedure described above for triphenyltin benzoate was then followed. The mixture melts completely at 108°C and was allowed to remain in the melt for 15 minutes and the product was extracted on cooling to room temperature. Yellow powder; m.p. 111-112°C; 82.3%; **IR cm^{-1}** : $\nu_{Asym}(COO)$ 1583.48, $\nu_{Sym}(COO)$ 1393.17, $\Delta\nu$ 190, $\nu(Sn - C)$ 552.23, $\nu(Sn - O)$ 487.87, $\nu(C - O)$ 1148.85, $\nu(C - H)$ str 2853.14, $\nu(C - H)$ bend 1467.18, $\nu(C = C)$ 1583.48., **1H NMR**: Sn- C_8H_{17} (1.28-1.32 m) 0.89 s, Sn- CH_2 (2.54 s), C_6H_5 (7.44-8.12 m), ^{13}C NMR: COO(172.91 ppm), CH_3 (14.25 ppm), C_6H_5 (128.32 ppm)

3. Results and discussion

The complexes were obtained in good yields about 80% in most cases. This synthetic method apart from being environment friendly saves energy and cost due to non involvement of the use of solvents and sometimes the tedious reflux processes. The physical properties of the complexes closely resemble those of the known organotin(IV) compounds prepared using wet chemistry. For instance, synthesis of triphenyltin benzoate [12] and the chlorobenzoate [13] analogues prepared in solution phase has been reported. The 2- chlorobenzoate was obtained in 70% yield and has a melting point of 79-82°C, while the unsubstituted benzoate melts at 78-80°C with a 90% yield. The spectroscopic data (ir, 1H nmr) of these compounds are very similar to that of triphenyltin benzoate prepared in this study which was obtained in 71.4% yield with a melting

point of 96-98°C. The structure and the spectroscopic assignments of both complexes are in complete agreement. The complex was recrystallized in slightly wet ether/hexane mixtures and crystals of $[\text{Ph}_3\text{Sn}(o\text{-ClC}_6\text{H}_4\text{CO}_2)]_2 \cdot \text{H}_2\text{O} \cdot \text{Et}_2\text{O}$ with melting point of 96-98°C was obtained.

According to Holmes et al the significant increase in the melting point of the triphenyltin-2-chlorobenzoate after recrystallisation is due to dimerisation [13]. We therefore believe that dimerisation is also responsible for the comparatively higher (96-98°C) melting point observed for the triphenyltin benzoate prepared in this study at a temperature well above room temperature. Similar dimerisation process may not be completely ruled out for the dioctyltin derivatives of this study. The dimers are thought to occur via a weak Sn...Sn bonding. This phenomenon results in a quasi 6- and 5- coordinate geometry around the central Sn atoms of the triphenyltin and dioctyltin complexes respectively. This is because our infrared spectral analyses suggest a bidentate coordination mode for the triphenyltinbenzoates and a monodentate mode for the dioctyltin analogues. No product analysis has been done in this study; however the feasibility of melt phase syntheses of organotin compounds has been demonstrated.

Trial runs indicate 108°C as the lowest temperature that maintains the integrity of reactant mixtures in the melt. Differential Scanning Calorimetric (DSC) studies of ref. 14 and 15 also reveal such melting activities at threshold temperatures close to the actual melting points of substances without extensive decomposition. Attempts to prepare these compounds from the sodium salts did not succeed because the sodium salts of the acids do not melt below 300°C. We therefore, suspect that these are most probably not solid-state reactions, but perhaps strictly melt-phase processes. The synthesized organotin(IV) compounds have sharp melting points as recorded in Table 1. They were characterized by both the IR and NMR spectroscopic analyses and the results are discussed below.

Table 1

Summary of the physical properties of the complexes.

Complex	Mol. formula	Mol. Wt. (g mol ⁻¹)	M.P. (°C)	Yield (%)	Appearance
Triphenyltin(IV) benzoate	C ₂₅ H ₂₀ O ₂ Sn	471	96-98	71.4	White solid
Triphenyltin(IV) 2-bromobenzoate	C ₂₅ H ₁₉ Br ₂ Sn	516	106-108	80	Brown solid
Dioctyltin(IV) dibenzoate	C ₃₀ H ₄₄ O ₄ Sn	587	-	85.7	Colourless sticky solid
Dioctyltin(IV)bis(4-chlorobenzoate)	C ₃₀ H ₄₂ Cl ₂ O ₄ Sn	656	81-83	87.5	White solid
Dioctyltin(IV)bis(2-bromobenzoate)	C ₃₀ H ₄₂ Br ₂ O ₄ Sn	745	-	81.2	Colourless liquid
Dioctyltin(IV)bis(4-nitrobenzoate)	C ₂₃ H ₃₈ NO ₄ Sn	511	111-112	82.3	Yellow powder

3.1. Infrared spectral studies

In the IR spectra of all the synthesized complexes, the absence of a broad band in the range 3500 – 2500 cm⁻¹ indicates the deprotonation of the COOH group on the ligands on complexation [16]. Also the presence of bands between 487 – 440 cm⁻¹ suggests that the coordination was through the oxygen atom of the carboxylate group on the ligands [16]. The bands occurring between 1584 – 1475 cm⁻¹ in all the complexes and those occurring in the region 1393 – 1310 cm⁻¹ are assigned to the $\nu_{\text{Asym}}(\text{COO})$ and $\nu_{\text{Sym}}(\text{COO})$ carboxylate groups respectively [17]. The $\nu(\text{Sn} - \text{O})$ and $\nu(\text{Sn} - \text{C})$ band signals are visible in all the complexes between 487 – 439 cm⁻¹ and 575 – 549 cm⁻¹ respectively [18]. These low values of the asymmetric acido groups are an indication that coordination to the Sn center was through the carboxylate oxygen [19]. Three of

the complexes (Dioctyltin benzoate, Dioctyltin-4-chlorobenzoate and Dioctyltin-2-bromobenzoate) have their $\nu_{\text{Asym}}(\text{COO})$ shifted to a higher frequencies than the $\nu_{\text{Sym}}(\text{COO})$ leading to a decrease in $\Delta\nu$ and the difference is more than 200 cm^{-1} in each case indicating that the nature of the Sn – O bond is covalent and that the mode of the coordination (Figure 1a) is monodentate [20]. The $\Delta\nu$ value of 190 cm^{-1} observed for the dioctyltin bis(4-nitrobenzoate) is close enough to 200 cm^{-1} . As a result, the 4-nitrobenzoate of dioctyltin is thought to adopt geometry, similar to the other dioctyltin analogues. Similar structure exists in the literature [21]. But in the other three complexes (Triphenyltin (IV) benzoate and Triphenyltin bromobenzoate, the frequencies of $\nu_{\text{Sym}}(\text{COO})$ are shifted to higher wave numbers compared to those of the free acids as observed from their IR spectra. The $\Delta\nu$ values in this case were found to be less than 200 cm^{-1} which indicates that the carboxylate groups (Figure 2a) are chelated and the bonding to the Sn metal is bidentate [22].

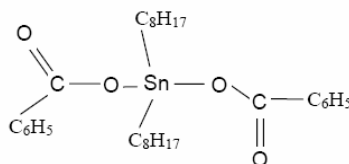


Fig. 1a. Dioctyltin(IV) dibenzoate (Representing the monodentate structures).

At the operating temperatures of this study, the geometries in figures 1a and 2a are believed to dimerise to figures 1b and 2b respectively. Based on this the following structures (Figure 1a, 1b and 2a, 2b) were proposed for the complexes:

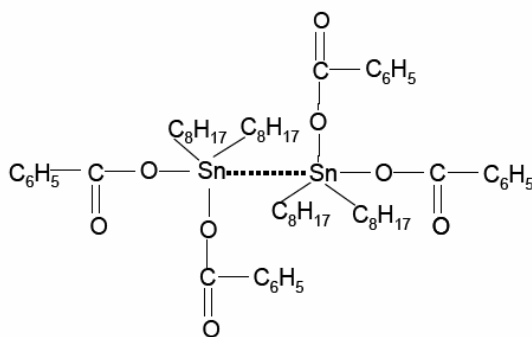


Fig. 1b. Dioctyltin(IV) dibenzoate (Dimerised products).

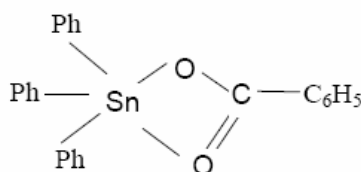


Fig. 2a. Triphenyltin (IV) benzoate (Representing the bidentate structures).

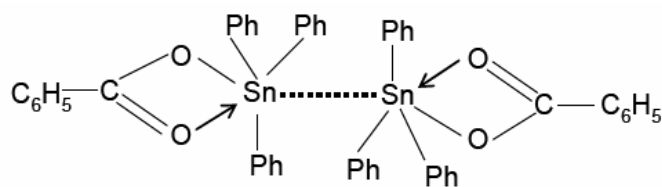


Fig. 2b. Triphenyltin (IV) benzoate (Dimerised products).

Similar structures for various triphenyltin esters of salicylic acid, *o*-anisic acid, *p*-methylthiobenzoic acid, anthralinic acid, *o*-(dimethylamino)benzoic acid and *p*-aminobenzoic acid synthesized in solution phase have been reported [23, 24].

3.2. ^1H NMR spectral studies

The absence of signals between 10 and 13.0 ppm in the NMR spectra of these complexes confirms the deprotonation of the COOH group on complexation [16]. The phenyl proton signals of the acids were visible in all the complexes between 7.44 – 8.12 ppm downfield while the aromatic proton signals of the organotins were observed between 6.0 – 8.5 ppm [24]. In some of the complexes, the appearance of aromatic proton signals between 8.12 – 8.20 ppm support that the coordination to the Sn center was through the carboxylate moiety [24]. The conclusions drawn from the ^1H NMR spectra of the complexes gives further support to the mode of bonding ascribed under the IR signals above. Also the number of protons calculated from the integration curves on the spectra when compared with those calculated from the proposed molecular formula of the corresponding complexes is in complete agreement. This further supports the proposed structures for the complexes.

3.3. ^{13}C NMR spectral studies

There is no visible difference between the carbon signals in the ligands and their corresponding organotin(IV) complexes except the carboxylate carbon signal that appeared at lower δ values. This further supports the participation of the carboxylate group in the bonding to Sn center [26]. The ^{13}C chemical shifts of the methyl and phenyl groups in the complexes were observed between 14.29-33.02 and 128-133 ppm respectively and are in agreement with the literature values [25]. The chemical shift signal of the COO⁻ group of the acid are observed in the complexes between 172.92 - 173.47.

4. Conclusions

The complexes were obtained in good yields. The physical properties of the complexes closely resemble those of the organotin(IV) compounds prepared using wet chemistry. Also the IR, ^1H and ^{13}C -NMR spectra of these complexes compare very well with those prepared using solvents. The sodium salts of the acids do not melt below 300°C. Attempts to prepare these compounds from the sodium salts did not succeed. We therefore, suspect that these are most probably not solid-state reactions, but perhaps strictly melt-phase processes.

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