Syntheses and Characterization of Dibutyltin(IV) dicarboxylate compounds Part 1: The preparation of \((C_4H_9)_2Sn(OOCR)_2\) (RCOO\(^-\) = Salicylic and Acetylsalicylic)

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Abstract

Two dibutyltin(IV) carboxylates, \((C_4H_9)_2Sn(OOCR)_2\) (RCOO\(^-\) = Salicylic and Acetyl salicylic), have been successfully prepared in our laboratory by the reaction of dibutyltin(IV) chloride, \((C_4H_9)_2SnCl_2\) with the respective carboxylic acid via dibutyltin(IV) oxide, \((C_4H_9)_2SnO\). The product in each reaction was afforded in very high yield (in average was more 80 \%). The product obtained in each step was mainly characterized by IR spectroscopy. These works were done as part of our on going work in the study of organotin(IV) carboxylate compounds and in attempts to find the possible biological activities of the organotin(IV).

Keywords: dibutyltin compound, synthesis, IR

Introduction

The organotin(IV) compounds are characterized by the presence of at least one covalent Sn – C bond. These compounds contain tetravalent Sn centers and can be classified as mono-, di-, tri-, and tetraorganotin(IV), depending on the number of alkyl (R) or aryl (Ar) moieties attached to the tin metal. The counter anion is usually chloride, oxide, fluoride, hydroxide, and thiolate\(^1\). Carboxylates has also been used successfully as counter anion\(^2\).

The chemistry of organotin compounds, nowadays, continues to be of interest on account of their interesting structural features and also because of their potentials as agricultural biocides, antitumor agents and other biological activities which are currently being investigated by many tin chemists\(^2\).

Previous investigations of the coordinating properties of carboxylates toward organotin compounds have led to the isolation of some new organotin(IV) carboxylates with antimicrobial\(^2\), antitumor\(^3\) or antifungal activity\(^4\).

In attempts to explore the possible biological activities of organotin(IV) compounds, we, here, reported the syntheses of two organotin(IV) dicarboxylates, \([(C_4H_9)_2Sn(OOCR)_2]\) with two different carboxylic acids, \(i.e.,\) salicylic and acetylsalicylic acids. The product obtained was characterized mainly by FT-IR spectroscopy by looking at the vibration change of Sn – Cl bond (in compound 1) to form Sn – O bond (compound 2) and followed by the disappearance of the characteristic Sn – O bond in compound 2 in the final product of organotin carboxylate compounds which showed several characteristic vibrations from carbonyl stretching. The
Materials and Methods

Materials

All reagents were of reagent grade. Dibutyltin dichloride \([\text{C}_4\text{H}_9\text{_2SnCl}_2]\) (1), Carboxylic acids, NaOH, \(\text{CH}_3\text{OH}\) were either Sigma or JT Baker products and were used without further purification.

Preparation of \([\text{C}_4\text{H}_9\text{_2SnO}]\) (2)

\([\text{C}_4\text{H}_9\text{_2SnO}]\) (2) was prepared by the hydrolysis of \([\text{C}_4\text{H}_9\text{_2SnCl}_2]\) (1) in alkaline media (NaOH), the procedure used was adapted from Szorcsik et al.\(^5\) and as follows:

To 3.0383 g (0.01 mol) \([\text{C}_4\text{H}_9\text{_2SnCl}_2]\) in 50 mL dry methanol was added with 0.8 g (0.02 mol) NaOH and the reaction mixtures were stirred for about 45 minutes. Compound 2 was precipitated out as white solid, filtered off and dried in vacuo till they are ready for IR and for further reaction. The yield in average was 2.3508 g (95 %).

Preparation of \([\text{C}_4\text{H}_9\text{_2Sn(OOCR)}_2]\) (3, 4)

To 0.37338 g (1.5 mmol) compound 2 in 50 mL dry methanol was added with 2 mol equivalents of carboxylic acids (3 = Salicylic acid; 4 = Acetylsalicylic acid) and was refluxed for 4 hours at 60 – 70°C. The product compounds 3 and 4 were obtained after removal of the solvent by rotary evaporator and dry in vacuo until they are ready for IR spectroscopy and used further for antifungal test (the experiment is on progress, and will be reported elsewhere). The average yield was more than ~ 90 %.

Results and Discussion

The syntheses of the dibutyltin(IV) dicarboxylates, \([\text{C}_4\text{H}_9\text{_2Sn(OOCR)}_2]\) (3, 4), was successfully afforded from compound 1 via \([\text{C}_4\text{H}_9\text{_2SnO}]\) (2). The reaction occurred in each step is shown in Scheme 1.

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\begin{align*}
\text{[C}_4\text{H}_9\text{_2SnCl}_2] & \xrightarrow{\text{NaOH in MeOH, Stirred 45 mins}} \text{[C}_4\text{H}_9\text{_2SnO]} & & \xrightarrow{2\text{RCOOH in MeOH, 60°C}} \text{[C}_4\text{H}_9\text{_2Sn(OOCR)}_2] \\
1 & & 2 & & 3, 4
\end{align*}
\]

\(3 = \text{Salicylic} [\text{o-C}_6\text{H}_4(\text{OH})\text{COO}^-] \)

\(4 = \text{Acetylsalicylic} [\text{o-C}_6\text{H}_4(\text{OOCCH}_3)\text{COO}^-] \)

Scheme 1. The preparative route of \([\text{C}_4\text{H}_9\text{_2Sn(OOCR)}_2]\)

The identity of the products obtained was confirmed mainly by analyzing them with FT-IR spectroscopy in the frequency range of 4000 – 250 cm\(^{-1}\). The infrared spectrum of compound 1 is shown in Figure 1, the characteristic band of this compound is the appearance of strong stretching band of Sn - Cl bond at 390 – 310 cm\(^{-1}\), and in this spectrum, this bond appeared at frequency of 334.2 cm\(^{-1}\). The other characteristic bands of this compound appear as stretching band from butyl ligands at 2956 – 2861 cm\(^{-1}\), and bending vibration of C – H of the butyl at frequency of 1458 – 1399 cm\(^{-1}\).
When compound 1 is converted to compound 2, the main stretching band of Sn – Cl disappeared and a strong new band at frequency of 417.4 cm\(^{-1}\) appeared as the main stretching band. This band is characteristic for Sn – O bond in compound 2. The stretching band due to the butyls and their bending vibrations are still appeared as expected. The infrared spectrum of 2 is shown in Figure 2.

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**Figure 1. The infrared spectrum of compound 1**

**Figure 2. The infrared spectrum of compound 2**
The syntheses of the target compound (the organotin carboxylate compounds) was performed by reacting 2 and the respective carboxylic acids desired by refluxing the mixtures of the reaction. The white solid of the compounds was obtained after the removal of the solvent by rotary evaporator. Two different acids were used to get higher possibility of the antifungal activities of the target compounds. Figure 3 is the example of the infrared spectrum of the final product obtained from the reaction of 2 with salicylic acid.

The important of infrared band of all the compounds both starting material and the final products obtained is tabulated in Table 1.

**Table 1. Important IR bands of the compounds (cm⁻¹)**

<table>
<thead>
<tr>
<th>Compound</th>
<th>V(Sn – Cl)</th>
<th>V(Sn – O)</th>
<th>V(C=O)</th>
<th>V(CO₂)</th>
<th>V(Sn-O-C)</th>
<th>Sn - Bu</th>
<th>Butyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>334.2s</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>564.7,</td>
<td>2956 –</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>595.3s</td>
<td>2861s</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>417.4s</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>564.7,</td>
<td>2947 –</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>595.3s</td>
<td>2860s</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>434.5m</td>
<td>1629s</td>
<td>1589s</td>
<td>1085w</td>
<td>567w,</td>
<td>2955 –</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>529m</td>
<td>2862s</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>435.7m</td>
<td>1626s</td>
<td>1589m</td>
<td>1080w, 1029m</td>
<td>567w,</td>
<td>2955 –</td>
</tr>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>528w</td>
<td>2866b,w</td>
</tr>
</tbody>
</table>

s=strong, m=medium, w=weak, b=broad

**Conclusions and Future Work**

The syntheses of the dibutyltin(IV) dicarboxylate compounds were successfully achieved in very high yield and the procedure we have utilized will be used and applied for other similar works in our laboratory. A manuscript of another paper
in a similar work with different carboxylate ligands is being written and will be presented in a seminar held by Universitas Lampung in its 39th Dies Natalis. The antifungal activity of the compounds obtained and related compounds against some fungus are in progress and will be reported elsewhere soon.

References


