



# Microwave assisted solid-state synthesis of functional organotin carboxylates from sterically encumbered 3,5-di-*tert*-butylsalicylic acid

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## ABSTRACT

Microwave assisted solid-state reaction between equimolar quantities of sterically encumbered 3,5-di-*tert*-butylsalicylic acid (H<sub>2</sub>-DTBSA) and *n*-butylstannoic acid results in the formation of hexameric drum shaped stannoxane [<sup>119</sup>BuSn(O)(H-DTBSA)]<sub>6</sub> (**1**). Synthesis of **1** could not be achieved under normal thermal conditions or mechanical grinding. However, the azeotropic removal of water produced in the reaction of <sup>119</sup>Bu<sub>2</sub>SnO with 3,5-di-*tert*-butyl salicylic acid in benzene yielded the tetrameric ladder shaped stannoxane [{"<sup>119</sup>Bu<sub>2</sub>Sn(H-DTBSA)}<sub>2</sub>O]<sub>2</sub> (**2**), which could also be synthesized in better yields by microwave irradiation as in the case of **1**. Compounds **1** and **2** have been characterized by elemental analysis, IR, MALDI-MS and NMR (<sup>1</sup>H and <sup>13</sup>C) spectroscopy. The structures of compound **1** and **2** are determined by single crystal X-ray diffraction techniques. Compound **1** is hexameric with a Sn<sub>6</sub>O<sub>6</sub> drum core while compound **2** forms a ladder structure with three Sn<sub>2</sub>O<sub>2</sub> rings, both decorated with –OH functionalities on the exterior of the polyhedral structure. While the formation of **1** from *n*-butylstannoic acid is straightforward, the formation of **2** from *n*Bu<sub>2</sub>SnO (and not a cyclic structure similar to **3**, where the phenolic oxygen also coordinates to tin) can be understood in terms of the increased steric hindrance in DTBSA for the phenolic protons to react with tin.

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## 1. Introduction

Exploring newer and better experimental techniques to carry out chemical transformations has been an important premise of chemical synthesis. Irradiation of microwave on homogenous reaction mixtures and on solid surfaces has been one such technique, which has emerged as a useful method for achieving better yields of the products, significant reduction in reaction time, and reduction or elimination of environmentally detrimental solvents. For these reasons, microwave assisted synthesis has clearly become a rapidly growing field of study especially for various organic transformations [1].

Reactions of organotin oxides with carboxylic acids have been studied in detail because of the industrial [2] and biological [3] applications of the organotin carboxylates. In addition, a wide spectrum of interesting and exotic structural types can be obtained by changing either the stoichiometry of the reactants or changing the additional functionality on the carboxylate ligand [4–9]. Reaction of various carboxylic acids with RSn(O)(OH) has been extensively studied and in most of the cases a drum shaped [RSn(O<sub>2</sub>CR')]<sub>6</sub> stannoxane with a Sn<sub>6</sub>O<sub>6</sub> core has been isolated [4a,6]. The only exception where a mono-organotin carboxylate adopts linear chain structure, [SnPh(O<sub>2</sub>CCl<sub>3</sub>)O]<sub>6</sub>, was obtained

via dearylation reaction of Ph<sub>3</sub>Sn(OH) with Cl<sub>3</sub>CCOOH [7]. On the other hand, tetrameric tin carboxylates [{R<sub>2</sub>Sn(R'COO)<sub>2</sub>O]<sub>2</sub> (type A–D; Fig. 1) are obtained when the reaction between R<sub>2</sub>SnO and R'COOH is carried out in strictly 1:1 stoichiometry [8d,9d]. Recently we reported that the presence of other reaction centers on the carboxylate ligand (e.g. 3,5-di-isopropyl salicylic acid) leads to the formation of a hexameric cyclic tin carboxylate of formula [<sup>119</sup>Bu<sub>2</sub>Sn(3,5-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(O)(COO))]<sub>6</sub> [8a]. Later this reaction was generalized by Ma et al. with the synthesis of [<sup>119</sup>BuSn(*o*-SC<sub>6</sub>H<sub>4</sub>COO)]<sub>6</sub> [10].

The reaction between an organotin oxide or acid and a carboxylic acid proceeds through the elimination of water to produce oligomeric organotin carboxylate clusters. Traditionally, the water produced in the above reaction is removed from the reaction mixture via simultaneous azeotropic distillation from a benzene or toluene medium, depending on the temperature required for the reaction. Not only these reactions are very slow but often require high temperatures in environmentally detrimental solvents. Considering the industrial and biological utilization of organotin carboxylates, a much faster and environmentally benign method for their synthesis is desired. Chandrasekhar et al. have recently reported the synthesis of organotin carboxylates having most commonly observed structure using a solventless methodology where the starting materials are ground together [11]. The only limitations of this very useful method are the relatively slower rates and the hazards associated with prolonged grinding of the reaction

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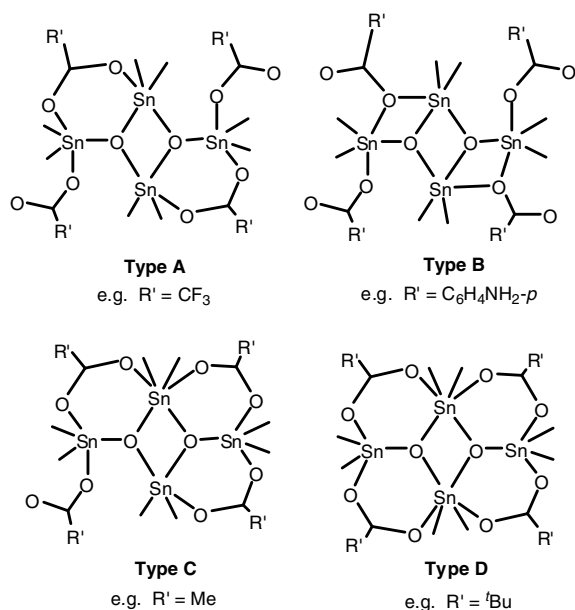


Fig. 1. Four different structural types of  $[(\text{R}_2\text{Sn}(\text{R}'\text{COO})_2)_2\text{O}]_2$ .

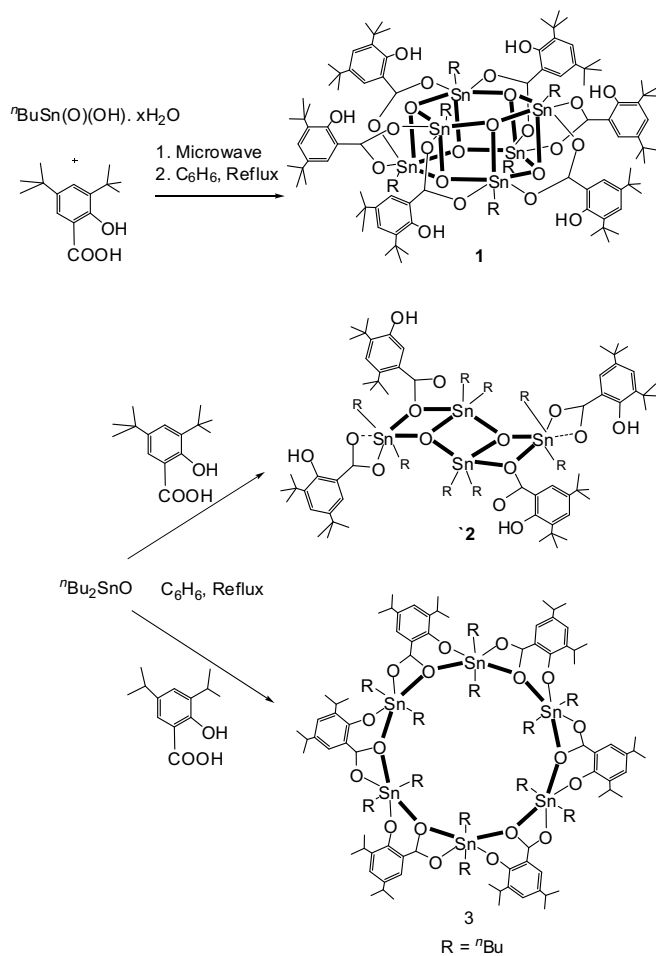
mixture (organotin carboxylates are known to have anti-neoplastic properties) [12]. Continuing our earlier studies on tin carboxylates derived from bulkier carboxylic acids [8a] we wish to report in this contribution a synthetic strategy that utilizes both grinding and microwave irradiation to efficiently remove the water produced in the condensation reaction between an organotin acid/oxide and 3,5-di-*tert*-butylsalicylic acid.

## 2. Results and discussion

### 2.1. Synthesis and characterization of $[\text{n-BuSn}(\text{O})(\text{H-DTBSA})]_6$ (**1**)

The reaction between *n*-butylstannic acid and  $\text{H}_2\text{-DTBSA}$  in refluxing benzene or toluene did not yield **1**, but an insoluble powder which could not be characterized. Similarly, the use of grinding methodology described by Chandrasekhar et al. [11] also did not lead to product formation in this case. Hence this reaction was attempted using microwave irradiation. Initially the solid reactants were ground together in a mortar to obtain a homogeneous mixture and transferred to a Petri dish. The homogeneous mixture was covered with another Petri dish and placed inside a microwave oven and irradiated for 2 min at 400 W. The irradiation was repeated three times during which time water produced from the reaction condensed on the lid. In order to completely remove the water from the product formed, the contents of the Petri dish were dissolved in benzene and heated under reflux using a Dean–Stark apparatus. After all the water has been removed as azeotrope, the clear benzene solution was left for crystallization to obtain single crystals of  $[\text{n-BuSn}(\text{O})(\text{H-DTBSA})]_6$  (**1**) in good yield (Scheme 1). Compound **1** is a stable colorless solid that melts at 200–203 °C.

The IR spectrum of compound **1** shows a broad band centered at  $3239\text{ cm}^{-1}$ , indicating the presence of unreacted phenolic –OH group on the carboxylate ligand. The symmetrical double absorption observed for **1** at  $1566$  and  $1531\text{ cm}^{-1}$  is due to the antisymmetric stretching vibrations of the carboxylate ligands, which bridge the tin centers in the drum structure. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR data obtained are consistent with the formulation of compound **1**. In particular, the presence of a broad resonance at 10.62 ppm is indicative of the non-participation of the phenolic group of the ligand in the reaction with the tin acid.



Scheme 1. Synthesis of **1–3**.

### 2.2. Molecular structure of **1**

Colorless rectangular crystals of **1** obtained directly from the reaction mixture were found to be suitable for single crystal X-ray diffraction measurements. The compound crystallizes in the centrosymmetric triclinic  $\text{P}\bar{1}$  space group with four molecules of benzene. The final refined molecular structure of compound **1** is shown in Fig. 2 while important bond lengths and bond angles are listed in Table 2. The centrosymmetric structure of **1** is built around a drum shaped  $\text{Sn}_6\text{O}_6$  central stannoxane core that is made up of two hexameric  $\text{Sn}_3\text{O}_3$  rings. These hexameric  $\text{Sn}_3\text{O}_3$  rings exist in a puckered chair conformation and form the upper and lower lids of the drum polyhedron. The two  $\text{Sn}_3\text{O}_3$  rings are connected further by six Sn–O bonds containing tri-coordinate O atoms and thus the side faces of the drum are characterized by six four-membered  $\text{Sn}_2\text{O}_2$  rings. It can be seen from Fig. 2 that the four-membered  $\text{Sn}_2\text{O}_2$  rings are not planar; the oxygen atoms are tilted toward the cavity of the drum. Thus the interior of the drum can be considered as a crown made of six oxygen atoms in a trigonal antiprismatic arrangement. The two tin atoms in each of the six  $\text{Sn}_2\text{O}_2$  rings are bridged by a carboxylate ligand to form a symmetrical bridge between two carboxylate ligands. The Sn–O bond lengths inside the core range between 2.072(3) and 2.157(4) Å. These distances are comparatively shorter than the Sn–O bonds to the bridging carboxylate ligands (2.145(3)–2.197(4) Å). All the six tin atoms are chemically equivalent and are six coordinate with three of the coordination sites occupied by bridging tri-coordinate oxygen atoms. While oxygen atoms from the bridging carboxylate

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