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# New Drum and Ladder Organooxotin Carboxylates[1]

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The hexameric *n*-butyloxotin cyclopentanoate $[n\text{-BuSn(O)O}_2\text{CC}_5\text{H}_9]_6\cdot\text{C}_6\text{H}_6$ (**1**) and hexameric *n*-butyloxotin cyclohexanoate $[n\text{-BuSn(O)O}_2\text{CC}_6\text{H}_{11}]_6\cdot\text{C}_6\text{H}_6$ (**4**) were prepared by reacting *n*-butylstannanoic acid with the corresponding carboxylic acid. X-ray analysis showed these new substances to have "drum" structures. Reaction of *n*-butyltin trichloride with the silver salt of cyclohexanecarboxylic acid gave the dimeric composition $[(n\text{-BuSn(O)O}_2\text{CC}_6\text{H}_{11})_2(n\text{-BuSn(O}_2\text{CC}_6\text{H}_{11})_3)]_2$ (**3**). The synthesis of a novel chloro derivative, $[(n\text{-BuSn(O)O}_2\text{CPh})_2(n\text{-BuSn(Cl)(O}_2\text{CPh})_2)]_2$ (**2**), also is reported. Both **2** and **3** have "ladder" or "open-drum" structures. Interconversion of the drum and ladder structures is established in solution by $^{119}$Sn NMR, and a possible mechanism for the hydrolysis of a ladder to a drum formulation is presented. **1** crystallizes in the monoclinic space group $P2_1/n$ with $a$ = 14.452 (3) Å, $b$ = 18.424 (4) Å, $c$ = 15.150 (4) Å, $\beta$ = 102.53 (2)°, and $Z$ = 2. **2** crystallizes in the triclinic space group $P\bar{1}$ with $a$ = 12.900 (2) Å, $b$ = 14.416 (4) Å, $c$ = 14.420 (2) Å, $\alpha$ = 110.99 (2)°, $\beta$ = 96.89 (1)°, $\gamma$ = 112.55 (2)°, and $Z$ = 1. **3** crystallizes in the triclinic space group $P\bar{1}$ with $a$ = 13.877 (6) Å, $b$ = 15.126 (6) Å, $c$ = 15.148 (4) Å, $\alpha$ = 116.19 (2)°, $\beta$ = 103.31 (3)°, $\gamma$ = 93.26 (3)°, and $Z$ = 1. **4** crystallizes in the monoclinic space group $P2_1/n$ with $a$ = 14.592 (5) Å, $b$ = 19.342 (5) Å, $c$ = 15.526 (3) Å, $\beta$ = 97.85 (2)°, and $Z$ = 2. The final conventional unweighted residuals were 0.048 (**1**), 0.029 (**2**), 0.114 (**3**), and 0.076 (**4**).

## Introduction

In 1922, Lambourne[3] reported that reactions of methylstannanoic acid yielded compounds whose formulations corresponded to $[\text{MeSn(O)O}_2\text{CR}']_3$. Later Anderson[4] observed that *n*-butyltin and phenyltin tricarboxylates hydrolyze in moist ethanol to give polymeric oxo carboxylates formulated as $[\text{RSn(O)O}_2\text{CR}']_n$. From apparent hydrolysis products of triphenyltin stearate and triphenyltin undecenoate, the latter composition also has been suggested[5] where $n = 3$. In the latter two studies,[4,5] the degree of polymerization was not established. Both Lambourne[3] and Ford et al.[5] suggest cyclic structures for the trimers. In a subsequent paper, Lambourne[6] reported additional oxo carboxylates of methylstannanoic acid, $[\text{MeSn(O)O}_2\text{CR}]_6$ where (R = Et, *n*-Pr, *i*-Pr), having hexameric compositions established from cryoscopic molecular mass measurements in benzene. Both the trimer and hexamer derivatives were assigned cyclic structures containing tetracoordinated tin atoms.

Recently, we were able to isolate hexameric phenyloxotin cyclohexanecarboxylate, $[\text{PhSn(O)O}_2\text{CC}_6\text{H}_{11}]_6$,[7] as a minor hydrolysis product from the reaction of $\text{Ph}_3\text{SnOH}$ with cyclohexanecarboxylic acid. X-ray analysis showed it to possess a drum arrangement, thus providing the first example of this structural class for tin. It proved to be a remarkably stable material, which yielded crystals only in the reaction medium, at least for the variations we tried. Because of its insolubility, acquisition of solution properties was precluded.

As outlined elsewhere,[8] we have employed a variation of the original reaction by Lambourne[3] in exploring condensation products leading to the drum composition as well as to a mixed oxo carboxylate–tricarboxylate formulation, $[(\text{R}'\text{Sn(O)O}_2\text{CR})_2\text{R}'\text{Sn(O}_2\text{CR})_3]_2$. The latter was identified as having an unfolded drum or ladder structure.[8] The reaction consists of a condensation of an organostannanoic acid with a carboxylic acid.

In this paper, we report the application of this reaction in forming a soluble drum compound, $[n\text{-BuSn(O)O}_2\text{CC}_5\text{H}_9]_6\cdot\text{C}_6\text{H}_6$ (**1**), containing cyclopentane units, and the formation of an unusual ladder compound, $[(n\text{-BuSn(O)O}_2\text{CPh})_2(n\text{-BuSn(Cl)(O}_2\text{CPh})_2)]_2$ (**2**). In addition the ladder compound $[(n\text{-BuSn(O)O}_2\text{CC}_6\text{H}_{11})_2(n\text{-BuSn(O}_2\text{CC}_6\text{H}_{11})_3)]_2$ (**3**) was prepared from the reaction of $n\text{-BuSnCl}_3$ with silver cyclohexanoate. The latter reaction was employed by Anderson[4] in synthesizing organotin tricarboxylates. Both the drum **1** and ladder **3** undergo structural changes in solution in interconversion processes as indicated by $^{119}$Sn NMR. A mechanism associated with this process is proposed.

## Experimental Section

The solvents used were of HPLC grade supplied by Fisher Scientific. These were further purified according to standard procedures.[9] *n*-Butyl stannanoic acid was a gift from Koriyama Kasei Co., Ltd. The organic acids were all used as received from Aldrich and Ventron.

$^1$H and proton-decoupled $^{119}$Sn NMR spectra were recorded on a Varian XL-300 FT NMR operating at 300 and 111.862 MHz, respectively. Chemical shifts are reported with reference to tetramethylsilane ($^1$H, internal standard) and tetramethyltin ($^{119}$Sn, external standard). Infrared spectra were recorded by using KBr windows on a Perkin-Elmer Model 180 spectrometer.

**Hexameric *n*-Butyloxotin Cyclopentanoate, $[n\text{-BuSn(O)O}_2\text{CC}_5\text{H}_9]_6\cdot\text{C}_6\text{H}_6$ (1).** To a suspension of *n*-butylstannanoic acid (2.29 g, 10.97 mmol) in benzene (200 mL) was added cyclopentanecarboxylic acid (1.25 g, 10.96 mmol), and the reaction mixture was refluxed for 6 h with a Dean–Stark apparatus used for the azeotropic removal of water. Removal of benzene from the reaction mixture yielded a solid. It was dissolved in a mixture of benzene (10 mL) and hexane (7 mL) and kept in a refrigerator for crystallization. Beautiful chunky crystals were isolated after 2 days; mp 252–260 °C (yield 2.50 g, 71.7%). $^1$H NMR ($\text{CDCl}_3$) (ppm): 7.30 (s), 1.70 (m), 1.00 (m), 0.60 (m). $^{119}$Sn NMR ($\text{CDCl}_3$) (ppm): −485.8. IR (Nujol) (cm$^{-1}$): 1580, 1530 ($\nu_{\text{COO}}$); 600 ($\nu_{\text{Sn–O}}$). Anal. Calcd for $\text{C}_{66}\text{H}_{114}\text{O}_{18}\text{Sn}_6$: C, 41.55; H, 6.02. Found: C, 41.54; H, 6.07. Addition of a 10-fold excess of cyclopentanecarboxylic acid to **1** causes the −485.8 ppm signal in the $^{119}$Sn NMR to disappear completely. Two minor peaks appear at −528.3 and −629.7 ppm, and two major peaks appear at −536.5 and −546.9 ppm.

**Isolation of Dimeric Bis(*n*-Butyloxotin benzoato)-*n*-butyltin Chloride Dibenzoate, $[(n\text{-BuSn(O)O}_2\text{CPh})_2(n\text{-BuSn(Cl)(O}_2\text{CPh})_2)]_2$ (2), from the Reaction of *n*-Butylstannanoic Acid and Benzoic Acid.** *n*-Butylstannanoic acid (2.15 g, 10.30 mmol) was taken in 250 mL of benzene, and benzoic acid (1.26 g, 10.32 mmol) was added to it. The reaction mixture was heated under reflux for 3$^1/_2$ h. Water formed in the reaction was removed azeotropically by the use of a Dean–Stark apparatus. Removal of solvent yielded a solid. It was redissolved in 30 mL of hot benzene and 5 mL of *n*-hexane and kept in the refrigerator at 5 °C for crystallization.

A low yield (5% based on butylstannanoic acid) of flat colorless crystals was isolated (200 mg); mp 308–312 °C. This compound was found to be the title compound by X-ray crystallography. The fact that a chlorine-containing derivative was isolated suggests the presence of an impurity such as $n\text{-BuSnCl(OH)}_2$ or $n\text{-BuSnCl}_2\text{OH}$ in the starting ma-

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(2) This work represents in part a portion of the Ph.D. Thesis of Charles G. Schmid, University of Massachusetts, Amherst, MA.

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terial albeit in a low percentage. We were not able accurately to determine the amount or nature of impurity present.

$^1$H NMR ($CDCl_3$) (ppm): multiplets centered around 8.1, 7.7, 7.4, 7.1, 6.9, 6.7, 6.4, 2.7, 2.1, 1.9, 1.5, 0.9, and 0.7. $^{119}$Sn NMR ($C_3D_6O$) (ppm): −516.0, −520.1, −521.0, −522.7, −549.8, −551.1; all singlets. IR (Nujol) (cm$^{-1}$): 1590, 1530 ($\nu_{COO}$); 600, 580 ($\nu_{Sn-O}$). Anal. Calcd for $C_{40}H_{47}O_{10}Sn_3Cl$: C, 44.51; H, 4.39; Cl, 3.29. Found: C, 44.69; H, 4.28; Cl, 3.30.

**Triclinic Dimeric Bis(*n*-Butyloxotin Cyclohexanoato)-*n*-butyltin Tricyclohexanoate, $[(n\text{-BuSn(O)O}_2\text{CC}_6\text{H}_{11})_2(n\text{-BuSn(O}_2\text{CC}_6\text{H}_{11})_3)]_2$ (3a).** To a stirred solution of *n*-butyltin trichloride (1.90 g, 6.75 mmol) in carbon tetrachloride (60 mL) was added silver cyclohexanoate (6.10 g, 25.96 mmol). A 2-h reflux of the reaction mixture followed by filtration of the silver chloride formed and removal of the solvent yielded a clear oil, assumed to be *n*-BuSn($O_2CC_6H_{11})_3$. When the oil was allowed to stand for 3 days in a stoppered flask at 25 °C, clear crystals formed. These were isolated and washed with 100% ethanol. More crystals were obtained by recrystallizing small portions of the oil in $CHCl_3$/hexane, $CH_2Cl_2$/hexane, and diethyl ether. Hydrolysis of the oil with 10 mL of 50% ethanol gave a white powder, which was filtered off under suction, washed with 100% ethanol, and dried. This white powder had a melting point and infrared spectrum identical with those of the crystals; mp 195–197 °C (total yield 2.44 g, 91%). IR (Nujol) (cm$^{-1}$): 1660 ($\nu_{COO}$); 1570, 1550 ($\nu_{COO}$); 615, 570 ($\nu_{Sn-O}$). Anal. Calcd for $C_{94}H_{164}O_{24}Sn_6$: C, 47.21; H, 6.92. Found: C, 47.25; H, 6.68.

**Monoclinic Dimeric Bis(*n*-Butyloxotin Cyclohexanoato)-*n*-butyltin Tricyclohexanoate, $[(n\text{-BuSn(O)O}_2\text{CC}_6\text{H}_{11})_2(n\text{-BuSn(OOCC}_6\text{H}_{11})_3)]_2$ (3b).** *n*-Butyltin trichloride (1.79 g, 6.35 mmol) was added to chloroform (60 mL). To this solution was added silver cyclohexanoate (4.50 g, 19.14 mmol), and the mixture was refluxed for 2 h. After refluxing, sodium sulfate was added as a drying agent. The sodium sulfate and silver chloride present were then filtered off. Solvent removal yielded a light tan oil. The oil was dissolved in hexane (20 mL), and *n*-butylamine (0.4 mL, 7.7 mmol) was added. After 1 week in the refrigerator, clear crystals had formed. These were isolated, washed in cold hexane, and dried; mp 181 °C (yield 2.28 g, 90%). IR (Nujol) (cm$^{-1}$): 1690 ($\nu_{COO}$); 615, 580 ($\nu_{Sn-O}$). Both **3a** and **3b** had the same $^{119}$Sn NMR spectrum consisting of singlets with some fine structure. $^{119}$Sn NMR ($CDCl_3$) (ppm): −479, −486, −492, −503, −524, −532, −552, −630. Anal. Calcd for $C_{94}H_{164}O_{24}Sn_6$: C, 47.21; H, 6.92. Found: C, 47.08; H, 6.73.

**Hexameric *n*-Butyloxotin Cyclohexanoate, $[n\text{-BuSn(O)O}_2\text{CC}_6\text{H}_{11}]_6\cdot\text{C}_6\text{H}_6$ (4).** *n*-Butylstannanoic acid (4.23 g, 20.2 mmol) and cyclohexanecarboxylic acid (2.59 g, 20.2 mmol) were reacted in benzene under reflux for 4 h. Water formed in the reaction was removed by azeotropic distillation using a Dean–Stark apparatus. Removal of solvent by rotary evaporation yielded a solid. The solid was dissolved in hot benzene and placed in a refrigerator Very large clear crystals formed. The solid was dried before analysis; mp 219 °C (yield 4.51 g, 70.0%). $^1$H NMR ($CDCl_3$) (ppm): multiplets centered at 2.2, 1.6, 1.2, and 0.9. $^{119}$Sn ($CDCl_3$) (ppm): −486.2 (s). IR (Nujol) (cm$^{-1}$): 1590, 1530 ($\nu_{COO}$); 590 ($\nu_{Sn-O}$). Anal. Calcd for $C_{11}H_{20}O_3Sn$: C, 41.42; H, 6.32. Found: C, 41.50; H, 6.34.

**X-ray Studies.** All X-ray crystallographic studies were performed by using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation ($\lambda(K\alpha_1)$ = 0.709 30 Å ($K\alpha_2$) = 0.713 59 Å) at an ambient temperature of 23 ± 2 °C. Details of the experimental and computational procedures have been described previously.[10]

Crystals were mounted inside thin-walled glass capillaries, which were sealed as a precaution against moisture. The structures were solved by using standard Patterson and difference-Fourier techniques and were refined by using full-matirx least-squares.[11]

**Crystallographic X-ray Study of $[n\text{-BuSn(O)O}_2\text{CC}_5\text{H}_9]_6\cdot\text{C}_6\text{H}_6$ (1).** A colorless crystal of **1**, which was cut from a fused mass of chunky crystals and which had dimensions of 0.30 × 0.30 × 0.38 mm, was used for the X-ray study.

Crystal data: $(C_{10}H_{18}O_3Sn)_6\cdot C_6H_6$ (**1**), monoclinic space group $P2_1/n$ (alternate setting of $P2_1/c$ [$C_{2h}^5$-No. 14][12]), $a$ = 14.452 (3) Å, $b$ = 18.424 (4) Å, $c$ = 15.150 (4) Å, $\beta$ = 102.53 (2)°, $Z$ = 2, $\mu_{MoK\alpha}$ = 1.946 mm$^{-1}$. A total of 4487 independent reflections ($+h,+k,\pm l$) were measured by using the $\theta$–$2\theta$ scan mode for 3° ≤ $2\theta_{MoK\bar{\alpha}}$ ≤ 43°. No corrections were made for absorption.

The refinement was based only on the 45 independent non-hydrogen atoms, 24 of which were refined anisotropically. The remaining 21 atoms outermost C atoms of the *n*-Bu groups, 12 methylene C atoms of the cyclopentane rings), which were poorly defined, were treated as isotropic scatterers. The quality of the data did not support inclusion of hydrogen atoms in calculated positions. The final agreement factors[13] were $R$ = 0.048 and $R_w$ = 0.069 for the 3659 reflections having $I \geq 2\sigma(I)$.

**Crystallographic X-ray Study of $[(n\text{-BuSn(O)O}_2\text{CPh})_2(n\text{-BuSn(Cl)(O}_2\text{CPh)}_2)]_2$ (2).** A colorless crystal of **2**, which was cut from a polycrystalline mass and which had dimensions of 0.24 × 0.33 × 0.35 mm, was used for the X-ray study.

Crystal data: $(C_{40}H_{47}O_{10}ClSn_3)_2$ (**2**), triclinic space group $P\bar{1}$ $C_i^1$-No. 2][14], $a$ = 12.900 (2) Å, $b$ = 14.416 (4) Å, $c$ = 14.420 (2) Å, $\alpha$ = 110.99 (2)°, $\beta$ = 96.89 (1)°, $\gamma$ = 112.55 (2), $Z$ = 1, $\mu_{MoK\alpha}$ = 1.807 mm$^{-1}$. A total of 6897 independent reflections ($+h,\pm k,\pm l$) were measured by using the $\theta$–$2\theta$ scan mode for 3.0° ≤ $2\theta_{MoK\bar{\alpha}}$ ≤ 48°. No corrections were made for absorption.

The 54 independent non-hydrogen atoms were refined anisotropically. The 38 independent H atoms with positions that could be inferred from the molecular geometry were included in the refinement as fixed isotropic scatterers whose coordinates were updated as refinement converged so that the final C–H bond lengths were 0.98 Å. The nine independent methyl hydrogen atoms were omitted from the refinement. The final agreement factors[13] were $R$ = 0.029 and $R_w$ = 0.041 for the 5883 reflections having $I \geq 2\sigma(I)$.

**X-ray Crystallographic Study of $[(n\text{-BuSn(O)O}_2\text{CC}_6\text{H}_{11})_2(n\text{-BuSn(O}_2\text{CC}_6\text{H}_{11})_3)]_2$ (3).** The crystal used for data collection was cut from a colorless polycrystalline mass and had dimensions of 0.23 × 0.35 × 0.38 mm.

Crystal data: $[(n\text{-BuSn(O)O}_2\text{CC}_6\text{H}_{11})_2(n\text{-BuSn(O}_2\text{CC}_6\text{H}_{11})_3)]_2$ (**3**), triclinic space group $P\bar{1}$, $a$ = 13.877 (6) Å, $b$ = 15.126 (6) Å, $c$ = 15.148 (4) Å, $\alpha$ = 116.19 (2)°, $\beta$ = 103.31 (3)°, $\gamma$ = 93.26 (3)°, $Z$ = 1. A total of 6286 independent reflections ($+h,\pm k,\pm l$) were measured for 3° ≤ $2\theta_{MoK\alpha}$ ≤ 43°. No corrections for absorption. Three of the independent cyclohexyl groups are badly disordered, and it was not possible to obtain reasonable initial coordinates for 13 of the carbon atoms of these groups. Isotropic refinement of the remaining 49 independent non-hydrogen atoms led to $R$ = 0.114 and $R_w$ = 0.142[13] for the 4462 independent reflections having $I \geq 2\sigma(I)$.

**X-ray Crystallographic Study of $[n\text{-BuSn(O)O}_2\text{CC}_6\text{H}_{11}]_6\cdot\text{C}_6\text{H}_6$ (4).** The crystal used for data collection was cut from a large polyfaceted chunky colorless crystal and had dimensions of 0.35 × 0.40 × 0.45 mm.

Crystal data: $[n\text{-BuSn(O)O}_2\text{CC}_6\text{H}_{11}]_6\cdot\text{C}_6\text{H}_6$ (**4**), monoclinic space group $P2_1/n$, $a$ = 14.592 (5) Å, $b$ = 19.342 (5) Å, $c$ = 15.526 (3) Å, $\beta$ = 97.85 (2)°, $Z$ = 2, $\mu_{MoK\alpha}$ = 1.769 mm$^{-1}$. A total of 4957 independent reflections ($+h,+k,\pm l$) were measured by using the $\theta$–$2\theta$ scan mode for 3.0° ≤ $2\theta$ ≤ 43°. No corrections were made for absorption.

The three independent cyclohexyl groups showed signs of disorder, and it was not possible to obtain reasonable initial coordinates for three of the carbon atoms of one of these groups; these three atoms were, therefore, omitted from the refinement. The three independent tin atoms and the three independent oxygen atoms defining the core of the "drum" were refined anisotropically, and the remainder of the non-hydrogen atoms were refined isotropically. The agreement factors[13] converged to $R$ = 0.076 and $R_w$ = 0.091, but convergence of the parameters for several of the cyclohexyl group carbon atoms could not be achieved.

## Results

The molecular geometry and atom-labeling scheme for **1** are shown in the ORTEP plots of Figures 1 and 2. Atomic coordinates are given in Table I while selected bond lengths and angles are given in Table II. The corresponding information for **2** is given in Figure 3 and in Tables III and IV. Although it was not possible to obtain fully refined X-ray structures due to disorder in the cyclohexyl groups, the general structural features of **3** and **4** have been established. These are displayed in Figures 4 and 5, respectively.

The basic structures of **1** and **4**, descriptively, is that of a "drum" whereas **2** and **3** may be considered to result from unfolding the drum to give a "ladder" arrangement.

Thermal parameters and additional bond lengths and angles for **1** and **2** and hydrogen atom parameters for **2** are provided as supplementary material.

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(10) Sau, A. C.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3076.

(11) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oLp/\sigma_I$. Mean atomic scattering factors were taken from: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 72–98. Real and imaginary dispersion corrections for Cl, Sn and O were taken from: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 149–150.

(12) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1969; Vol. I, p 99.

(13) $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$.

(14) Reference 12; p 75.

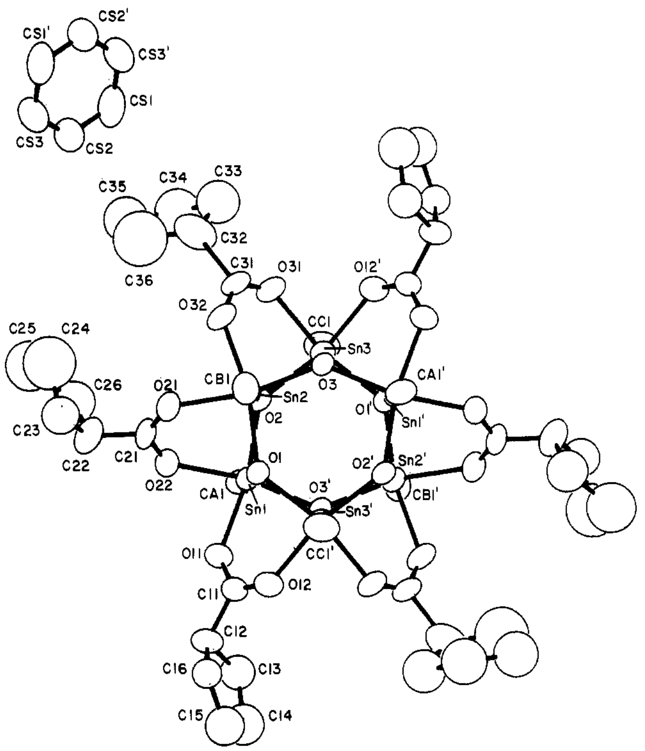

**Figure 1.** ORTEP plot of $[n\text{-BuSn(O)O}_2\text{CC}_5\text{H}_9]_6\cdot\text{C}_6\text{H}_6$ (**1**) with thermal ellipsoids shown at the 30% probability level. Primed atoms are related to unprimed ones by the inversion operation. The view is down the pseudo $S_6$ axis. The terminal carbon atoms of the *n*-Bu groups are omitted for purposes of clarity.

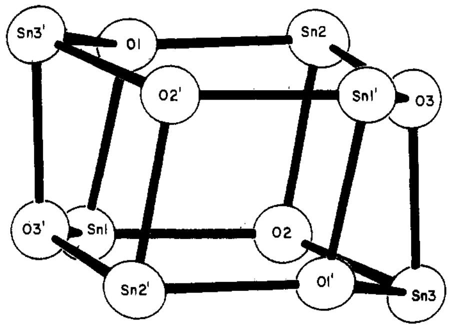

**Figure 2.** ORTEP plot of the stannoxane "drum" in $[(n\text{-BuSn(O)O}_2\text{C}_5\text{H}_9]_6\cdot\text{C}_6\text{H}_6$ (**1**).

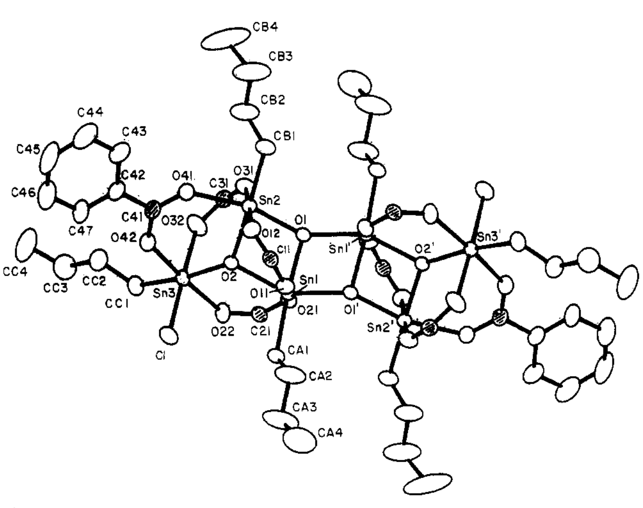

**Figure 3.** ORTEP plot of $[(n\text{-BuSn(O)O}_2\text{CPh})_2(n\text{-BuSn(Cl)(O}_2\text{CPh)}_2)]_2$ (**2**) with thermal ellipsoids at the 30% probability level. Six of the eight phenyl groups and all hydrogen atoms have been omitted for purposes of clarity. The eight carboxylate carbon atoms are shaded. Primed atoms are related to unprimed ones by the inversion operation.

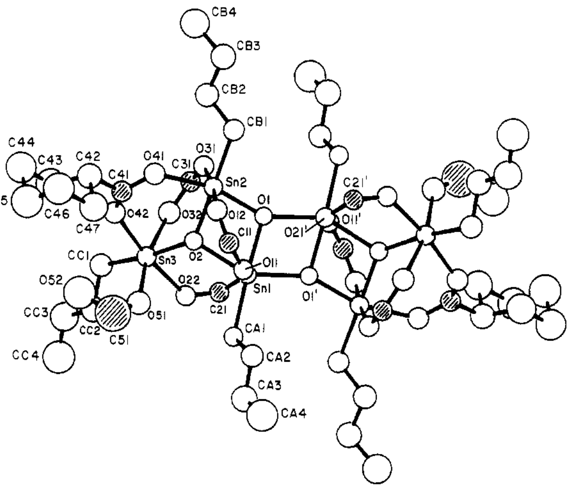

**Figure 4.** ORTEP plot of $[(n\text{-BuSn(O)O}_2\text{CC}_6\text{H}_{11})_2(n\text{-BuSn(O}_2\text{CC}_6\text{H}_{11})_3)]_2$ (**3**) from isotropic refinement of 49 of the 62 independent non-hydrogen atoms. Carbon atoms of only two of the cyclohexyl groups are shown. The 10 carboxylate carbon atoms are shaded. Primed atoms are related to unprimed ones by the inversion operation.

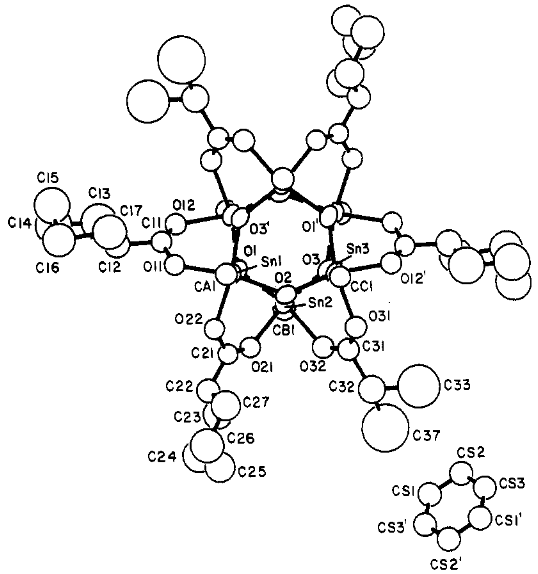

**Figure 5.** ORTEP plot of $[n\text{-BuSn(O)O}_2\text{CC}_6\text{H}_{11}]_6\cdot\text{C}_6\text{H}_6$ (**4**) based on refinement of 45 of the 48 independent non-hydrogen atoms. The terminal carbon atoms of the *n*-Bu groups have been omitted for purposes of clarity.

## Discussion

**Synthesis.** Both the cyclopentanoate drum composition **1** and the cyclohexanoate drum **4** were prepared by a condensation reaction of *n*-butylstannanoic acid with the corresponding carboxylic acid, eq 1. When this reaction was employed with *n*-butylstannanoic acid and benzoic acid in an attempt to obtain the benzoate drum or ladder, the unfolded drum composition **2** resulted instead, containing a Sn–Cl bond. Obviously, the starting material had a chloro precursor such as $n\text{-BuSn(OH)}_2\text{Cl}$ or $n\text{-BuSn(OH)Cl}_2$. The latter has been isolated in a dimeric hydrated form, $[n\text{-BuSn(OH)Cl}_2\cdot\text{H}_2\text{O}]_2$, from the initial hydrolysis of $n\text{-BuSnCl}_3$.[15] In alkali, $n\text{-BuSnCl}_3$ forms the former compound.[15] A possible synthetic route for **2** is shown in eq 2.

$$6n\text{-BuSn(O)OH} + 6\text{RCO}_2\text{H} \rightarrow [n\text{-BuSn(O)O}_2\text{CR}]_6 + 6\text{H}_2\text{O} \qquad (1)$$

$$5n\text{-BuSn(O)OH} + n\text{-BuSn(OH)Cl}_2 + 8\text{PhCO}_2\text{H} \rightarrow [(n\text{-BuSn(O)O}_2\text{CPh})_2(n\text{-BuSn(Cl)(O}_2\text{CPh)}_2)]_2 + 7\text{H}_2\text{O} \qquad (2)$$

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(15) Luijten, J. G. A. *Recl. Trav. Chim. Pays-Bas* **1966**, *85*, 873.

**Table I.** Atomic Coordinates in Crystalline $[n\text{-BuSn(O)O}_2\text{CC}_5\text{H}_9]_6\cdot\text{C}_6\text{H}_6$ (**1**)[a]

| atom type[b] | $10^4x$ | $10^4y$ | $10^4z$ |
|---|---|---|---|
| Sn1 | −1379.1 (5) | 459.8 (4) | −1162.9 (5) |
| Sn2 | −687.1 (6) | 879.3 (4) | 928.7 (5) |
| Sn3 | 1123.4 (6) | 1028.0 (4) | 49.8 (5) |
| O1 | −1434 (5) | 59 (4) | 118 (4) |
| O2 | −353 (5) | 1087 (4) | −317 (4) |
| O3 | 730 (5) | 550 (4) | 1153 (4) |
| O11 | −2706 (5) | −92 (4) | −1702 (5) |
| O12 | −2535 (5) | −1119 (4) | −903 (6) |
| O21 | −1931 (6) | 1550 (4) | 476 (6) |
| O22 | −2389 (5) | 1289 (4) | −977 (5) |
| O31 | 1068 (7) | 2072 (4) | 678 (6) |
| O32 | −161 (7) | 1947 (5) | 1367 (6) |
| CA1 | −1218 (9) | 864 (6) | −2454 (8) |
| CA2 | −1545 (11) | 311 (9) | −3241 (10) |
| CA3 | −1473 (17) | 688 (14) | −4181 (15) |
| CA4 | −600 (20) | 719 (16) | −4206 (18) |
| CB1 | −955 (9) | 585 (8) | 2231 (7) |
| CB2 | −2007 (10) | 613 (9) | 2254 (10) |
| CB3 | −2114 (12) | 350 (9) | 3180 (11) |
| CB4 | −3158 (16) | 399 (12) | 3305 (15) |
| CC1 | 1458 (10) | 1470 (8) | −1122 (9) |
| CC2 | 2420 (12) | 1879 (10) | −925 (12) |
| CC3 | 2705 (14) | 2154 (12) | −1823 (12) |
| CC4 | 3708 (16) | 2488 (13) | −1520 (14) |
| C11 | −2965 (8) | −706 (8) | −1506 (9) |
| C12 | −3927 (9) | −949 (8) | −2062 (9) |
| C13 | −3721 (12) | −1350 (11) | −2892 (12) |
| C14 | −4310 (17) | −2023 (14) | −2992 (17) |
| C15 | −4772 (15) | −2117 (13) | −2202 (16) |
| C16 | −4465 (10) | −1495 (8) | −1586 (10) |
| C21 | −2462 (9) | 1633 (7) | −283 (10) |
| C22 | −3290 (12) | 2143 (8) | −428 (11) |
| C23 | −3624 (15) | 2367 (13) | 464 (14) |
| C24 | −3135 (27) | 3062 (25) | 662 (29) |
| C25 | −3261 (24) | 3448 (21) | −201 (26) |
| C26 | −2966 (17) | 2801 (15) | −819 (17) |
| C31 | 538 (13) | 2310 (7) | 1125 (11) |
| C32 | 520 (17) | 3129 (11) | 1675 (19) |
| C33 | 1291 (20) | 3367 (17) | 1477 (19) |
| C34 | 758 (24) | 3846 (18) | 630 (22) |
| C35 | −149 (23) | 4134 (17) | 856 (21) |
| C36 | −332 (29) | 3579 (26) | 1487 (30) |
| CS1 | 374 (13) | 4617 (9) | 4366 (12) |
| CS2 | −599 (11) | 4661 (9) | 4235 (11) |
| CS3 | −988 (10) | 5040 (9) | 4839 (11) |

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 1.

In the formation of the benzoate ladder $[(n\text{-BuSn(O)O}_2\text{CPh})_2(n\text{-BuSn(O}_2\text{CPh})_3)]_2$, as reported elsewhere,[8] $n\text{-BuSnCl}_3$ was used as the starting material and reacted with the silver salt of benzoic acid. This reaction was used here to synthesize the ladder formulation **3**, containing cyclohexane carboxylates, eq 3.

$$6n\text{-BuSnCl}_3 + 10\text{Ag}^+\text{C}_6\text{H}_{11}\text{CO}_2^- + 4\text{H}_2\text{O} \rightarrow [(n\text{-BuSn(O)O}_2\text{CC}_6\text{H}_{11})_2(n\text{-BuSn(O}_2\text{CC}_6\text{H}_{11})_3)]_2 + 10\text{AgCl} + 8\text{HCl} \quad (3)$$

Other than the chloro derivative **2**, the drum and ladder compounds are prepared in high yield, >70%. All are soluble in organic solvents and show characteristic infrared spectra. Drum compounds **1** and **4** exhibit a symmetrical doublet for the carboxylate stretching frequency, $\nu_{\text{COO}}$, centered near 1550 cm$^{-1}$ and a single Sn–O stretch, $\nu_{\text{Sn-O}}$, near 600 cm$^{-1}$. In contrast, the open-drum structures **2** and **3** show an unsymmetrical $\nu_{\text{COO}}$ doublet in the same region as that for the drums and the presence of two Sn–O stretches near 600 cm$^{-1}$.

The drum compounds are thermally quite stable. For example, the cyclopentanecarboxylic acid drum (**1**) was heated at 300 °C for 3 h in vacuum. The material obtained was soluble in $\text{CDCl}_3$, and $^{119}$Sn NMR showed a single line at −491.4 ppm, compared to that of the starting material at −485.8 ppm. The shift is presumably due to loss of solvent molecules present in the crystal in the starting material.

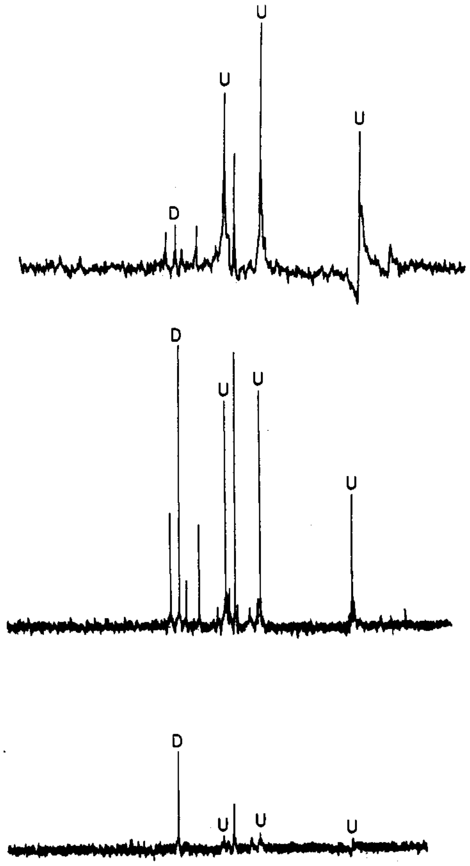
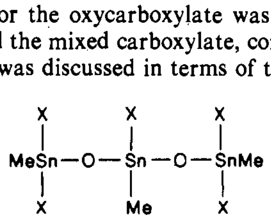


**Figure 6.** $^{119}$Tin NMR spectra of $[(n\text{-BuSn(O)O}_2\text{CC}_6\text{H}_{11})_2(n\text{-BuSn(O}_2\text{CC}_6\text{H}_{11})_3)]_2$ (**3**) in $\text{CDCl}_3$, indicating hydrolysis to a "drum" form. The frequencies, which are listed in Table V, remain the same from spectrum to spectrum. The upper spectrum is for a sample containing $\text{P}_4\text{O}_{10}$, added to reduce hydrolysis relative to the sample used for the middle spectrum, which has no added drying agent. The lower spectrum was recorded on the latter sample 1 week later. D identifies the line due to the drum formulation and U, the lines due to the unfolded drum. The remainder are lines due to intermediates.

**$^{119}$Sn NMR Data.** Hydrolytically, the drum formulations are more stable than the open-drum forms. The hydrolysis reaction in eq 4 illustrates this. Lambourne[3] first demonstrated the reversibility of this type of reaction by synthesizing one from the other and vice versa, where R and R′ were methyl groups, although his composition for the oxycarboxylate was trimeric, $[\text{MeSn(O)O}_2\text{CMe}]_3$, and the mixed carboxylate, corresponding to our ladder structure, was discussed in terms of the formula

$$[(\text{R}'\text{Sn(O)O}_2\text{CR})_2\text{R}'\text{Sn(O}_2\text{CR})_3]_2 + 2\text{H}_2\text{O} \rightarrow [\text{R}'\text{Sn(O)O}_2\text{CR}]_6 + 4\text{RCO}_2\text{H} \quad (4)$$



$$\begin{array}{ccccc} \text{X} & & \text{X} & & \text{X} \\ | & & | & & | \\ \text{MeSn} & -\text{O}- & \text{Sn} & -\text{O}- & \text{SnMe} \\ | & & | & & | \\ \text{X} & & \text{Me} & & \text{X} \end{array}$$

where X = $\text{RCO}_2$.

Our investigation using $^{119}$Sn NMR establishes the retention of the drum and ladder structures in solution and shows their interconversion according to eq 4.

Figure 6 displays $^{119}$Sn NMR spectra of a sample of ladder compound **3** in slightly moist $\text{CDCl}_3$. Hydrolysis is evident as the drum peak at −486 ppm grows in intensity relative to signals assigned to the ladder. The top spectrum when compared to the middle spectrum shows the relative absence of the drum form in the presence of $\text{P}_2\text{O}_5$ added to reduce the rapid hydrolysis process. The lower spectrum, taken on the same sample as that for the

**Table II.** Selected Bond Lengths (Å) and Bond Angles (deg) for [$n$-BuSn(O)$O_2CC_5H_9$]$_6$·$C_6H_6$ (**1**)[a]

| | | | | | |
|---|---|---|---|---|---|
| Sn1–CA1 | 2.15 (1) | Sn2–CB1 | 2.16 (1) | Sn3–CC1 | 2.10 (1) |
| Sn1–O1 | 2.094 (6) | Sn2–O2 | 2.082 (7) | Sn3–O3 | 2.075 (7) |
| Sn1–O3′ | 2.082 (6) | Sn2–O1 | 2.093 (7) | Sn3–O2 | 2.088 (7) |
| Sn1–O2 | 2.086 (7) | Sn2–O3 | 2.092 (7) | Sn3–O1′ | 2.081 (6) |
| O11–Sn1 | 2.167 (7) | O21–Sn2 | 2.167 (8) | O31–Sn3 | 2.155 (8) |
| O12–Sn3′ | 2.172 (8) | O22–Sn1 | 2.173 (8) | O32–Sn2 | 2.161 (9) |
| C11–O11 | 1.25 (1) | C21–O21 | 1.25 (1) | C31–O31 | 1.21 (2) |
| C11–O12 | 1.25 (1) | C21–O22 | 1.25 (1) | C31–O32 | 1.33 (2) |
| O1–Sn1–CA1 | 176.1 (4) | O2–Sn2–CB1 | 175.2 (4) | O3–Sn3–CC1 | 176.3 (4) |
| O11–Sn1–O2 | 160.7 (3) | O21–Sn2–O3 | 158.9 (3) | O3–Sn3–O1′ | 160.5 (3) |
| O22–Sn1–O3′ | 160.3 (3) | O32–Sn2–O1 | 160.0 (3) | O12′–Sn3–O2 | 158.1 (3) |
| O3′–Sn1–O2 | 103.4 (3) | O1–Sn2–O3 | 104.4 (3) | O2–Sn3–O1′ | 104.7 (3) |
| O1–Sn1–O2 | 77.9 (3) | O2–Sn2–O1 | 78.0 (2) | O3–Sn3–O2 | 78.1 (3) |
| O1–Sn1–O3′ | 77.7 (3) | O2–Sn2–O3 | 77.8 (3) | O3–Sn3–O1′ | 78.1 (2) |
| CA1–Sn1–O3′ | 100.3 (4) | CB1–Sn2–O3 | 98.2 (4) | CC1–Sn3–O1′ | 100.0 (5) |
| CA1–Sn1–O2 | 99.5 (4) | CB1–Sn2–O1 | 100.5 (4) | CC1–Sn3–O2 | 99.4 (4) |
| CA1–Sn1–O11 | 94.6 (3) | CB1–Sn2–O21 | 97.5 (4) | CC1–Sn3–O31 | 93.7 (5) |
| CA1–Sn1–O22 | 94.8 (4) | CB1–Sn2–O32 | 93.9 (4) | CC1–Sn3–O12′ | 96.6 (4) |
| O1–Sn1–O11 | 88.6 (3) | O2–Sn2–O21 | 87.0 (3) | O3–Sn3–O31 | 88.9 (3) |
| O1–Sn1–O22 | 88.0 (3) | O2–Sn2–O32 | 88.6 (3) | O3–Sn3–O12′ | 86.6 (3) |
| O11–Sn1–O22 | 79.3 (3) | O21–Sn2–O32 | 77.9 (3) | O31–Sn3–O12′ | 77.8 (3) |
| O11–Sn1–O3′ | 86.8 (3) | O21–Sn2–O1 | 86.5 (3) | O31–Sn3–O2 | 86.4 (3) |
| O22–Sn1–O2 | 86.5 (3) | O32–Sn2–O3 | 87.0 (3) | O12′–Sn3-O1′ | 87.0 (3) |
| Sn3′–O1–Sn2 | 132.0 (3) | Sn1–O2–Sn3 | 133.1 (3) | Sn2–O3–Sn1′ | 133.2 (3) |
| Sn1–O1–Sn3′ | 100.0 (3) | Sn2–O2–Sn1 | 100.5 (3) | Sn3–O3–Sn2 | 100.1 (3) |
| Sn1–O1–Sn2 | 99.8 (3) | Sn2–O2–Sn3 | 100.0 (3) | Sn3–O3–Sn1′ | 100.6 (3) |

[a] Numbers in parentheses are estimated standard deviations. Atoms are labeled to agree with Figures 1 and 2.

middle spectrum, indicates a high percentage of conversion of the ladder to the drum for **3**. The relative equality of the integrated intensities of the three signals labeled U, as well as the constancy in their relative intensities with time, as more drum forms, confirms their assignment to the unfolded-drum structure. The signal at −532 ppm appears to be associated with an intermediate along the hydrolysis path. Additional intermediates are assigned to signals near the drum peak.

Additional support for these assignments are seen in a more broad context by comparing $^{119}$Sn NMR data on related unfolded-drum compositions. These data are listed in Table V. Included are data for the ladders [(R′Sn(O)$O_2CR)_2$R′Sn($O_2CR)_3$]$_2$, where R′ = $n$-Bu, R = Ph for **5**, R′ = $n$-Bu, R = Me for **6**, and R′ = Me, R = $C_6H_{11}$ for **7**.[8]

The spectra show a consistent pattern with the signals for the single methyl derivative (**7**) shifted to lower field relative to the $n$-butyl ladders. Both **2** and **5**, which are closely related, show multiplets assigned to pairs of tin atoms in the ladder structure.

The reason for the appearance of multiplets is not clear. However, the presence of closely related ladder conformations whose interconversion with each other is restricted is a possible explanation.

In all cases the assignment within the ladder is the same; i.e., the terminal pair of tin atoms are assigned to the highest field signal, and progressively lower field signals are assigned to interior pairs of tin atoms located, respectively, at distances closer to the center of the open-drum structure. This assignment is consistent with the fact that the environment of the interior tin atoms most closely resembles that in the drum structure, which has a $^{119}$Sn chemical shift at −486 ppm. As Figure 6 emphasizes, the $^{119}$Sn peak at −532 ppm for **3** appears as a major intermediate. Signals in this region are present in the spectra of all samples except that for the chloro derivative (**2**), which also lacks a high-field signal in the 600–630 ppm region.

The action of excess cyclopentanecarboxylic acid on a $CDCl_3$ solution of the cyclopentane drum (**1**) causes its single signal at −485.8 ppm to disappear and gives rise to the two minor and two major intensity peaks listed in Table V. These peaks correspond to formation of the ladder and the intermediate at −536.5 ppm in the region assigned to the other ladder derivatives. These NMR experiments have shown that the hydrolysis process given in eq 4 is reversible; i.e., a drum forms from a ladder composition, and in the presence of excess acid, the drum can be opened up to yield the ladder formulation.

**Structural Details.** For **1**, both the hexameric "drum" and the benzene of solvation have crystallographic $C_i$ symmetry. The molecular geometry of the hexamer is very similar to that found for the previously reported phenyltin cyclohexanoate analogue,[7] having idealized $S_6$ molecular symmetry. The geometry of the stannoxane framework of the molecule is shown in Figure 2, where it can be seen that the six-membered rings have a chair conformation. Each Sn atom is bonded to three framework oxygen atoms, where the Sn–O bonds are all of comparable strength and have lengths ranging from 2.075 (7) to 2.093 (7) Å. The oxygen atoms of the framework are trivalent and have a distorted pyramidal geometry. The sum of the three Sn–O–Sn angles about these oxygen atoms ranges from 331.8 to 333.9°. The Sn atoms, which are all chemically equivalent, are hexacoordinated, with the coordination sphere being completed by an $n$-butyl group and two oxygen atoms from different carboxylate groups. Each of the six four-membered rings of the core is spanned by a carboxylate group that forms a symmetrical bridge between two Sn atoms. The Sn–O bonds to the bridging carboxylate atoms are longer than the core bonds and range from 2.155 (8) to 2.173 (8) Å.

The "unfolded-drum" or "ladder" compound **2** has crystallographic $C_i$ symmetry. This corresponds to the ideallized molecular symmetry, and therefore, there are three chemically inequivalent types of Sn atoms in the molecule, although all are hexacoordinated. The oxygen atoms in the open form can be subdivided into two types, as in the case of the drum molecule: trivalent framework oxygen atoms and the divalent oxygen atoms of the bridging carboxylate ligands. In this case, however, there is an anomaly in the Sn–O bond lengths of the framework, which range from 2.012 (3) to 2.066 (3) Å with the exception of the Sn1–O2 bond length of 2.123 (3) Å. This is comparable to the values for the bridging carboxylate groups where the Sn–O bond lengths range from 2.116 (3) to 2.234 (3) Å.

The geometry about the oxygen atoms of the framework of the open form tends toward planarity. In this case the sums of the angles about the trivalent oxygen atoms are 357.4° for O1 and 355.3° for O2. The geometry about the Sn atoms is best described as distorted octahedral, the distortions being occasioned by the constraints imposed by the geometric requirements of the framework and, to a lesser extent, the bridging carboxylate groups.

The general structural features of the "ladder" [($n$-BuSn(O)$O_2CC_6H_{11})_2$($n$-BuSn($O_2CC_6H_{11})_3$)]$_2$ (**3**), shown in Figure 4, are very similar to that found for **2**, the principal difference being

**Table III.** Atomic Coordinates in Crystalline $[(n\text{-BuSn(O)O}_2\text{CPh})_2(n\text{-BuSn(Cl)(O}_2\text{CPh})_2)]_2$ (**2**)[a]

| atom type[b] | $10^4x$ | $10^4y$ | $10^4z$ |
|---|---|---|---|
| Sn1 | –568.8 (2) | 840.8 (2) | 13.7 (2) |
| Sn2 | 1331.8 (2) | 2094.8 (2) | 2275.0 (2) |
| Sn3 | 775.8 (3) | 3939.4 (2) | 1317.0 (2) |
| Cl | –1255 (1) | 3593 (1) | 999 (1) |
| O1 | 749 (2) | 736 (2) | 857 (2) |
| O2 | 381 (2) | 2443 (2) | 1306 (2) |
| O11 | –1565 (3) | 274 (3) | 988 (2) |
| O12 | –304 (3) | 1295 (3) | 2596 (2) |
| O21 | 471 (3) | 1472 (2) | –909 (2) |
| O22 | 520 (3) | 3148 (3) | –337 (2) |
| O31 | 2874 (3) | 2899 (3) | 1915 (3) |
| O32 | 2634 (3) | 4215 (3) | 1606 (4) |
| O41 | 1647 (3) | 3621 (3) | 3547 (2) |
| O42 | 1023 (3) | 4599 (3) | 2948 (2) |
| CA1 | –2074 (4) | 780 (4) | –863 (4) |
| CA2 | –3235 (5) | –56 (7) | –941 (7) |
| CA3 | –4263 (6) | –35 (9) | –1588 (9) |
| CA4 | –5374 (9) | –938 (10) | –1827 (12) |
| CB1 | 2231 (5) | 1747 (5) | 3346 (4) |
| CB2 | 3475 (6) | 2647 (7) | 3992 (6) |
| CB3 | 4037 (8) | 2482 (10) | 4815 (8) |
| CB4 | 5231 (10) | 3500 (13) | 5503 (10) |
| CC1 | 1523 (5) | 5534 (5) | 1315 (4) |
| CC2 | 2107 (6) | 6520 (5) | 2385 (5) |
| CC3 | 2573 (7) | 7642 (6) | 2387 (7) |
| CC4 | 2987 (10) | 8597 (6) | 3484 (8) |
| C11 | –1285 (4) | 539 (4) | 1951 (4) |
| C12 | –2182 (4) | –89 (4) | 2342 (4) |
| C13 | –3179 (5) | –1070 (5) | 1628 (5) |
| C14 | –3990 (6) | –1678 (6) | 2003 (6) |
| C15 | –3828 (7) | –1332 (8) | 3038 (7) |
| C16 | –2842 (7) | –377 (6) | 3748 (6) |
| C17 | –2031 (5) | 223 (5) | 3385 (5) |
| C21 | 557 (4) | 2327 (4) | –1010 (3) |
| C22 | 637 (4) | 2363 (4) | –2021 (3) |
| C23 | 569 (6) | 1470 (5) | –2849 (4) |
| C24 | 681 (8) | 1558 (6) | –3778 (5) |
| C25 | 779 (7) | 2480 (6) | –3873 (5) |
| C26 | 813 (6) | 3354 (5) | –3085 (5) |
| C27 | 745 (4) | 3308 (4) | –2142 (4) |
| C31 | 3188 (4) | 3685 (4) | 1649 (4) |
| C32 | 4329 (4) | 3999 (4) | 1408 (4) |
| C33 | 4910 (6) | 5038 (6) | 1421 (7) |
| C34 | 5967 (6) | 5306 (7) | 1162 (8) |
| C35 | 6391 (6) | 4533 (8) | 875 (6) |
| C36 | 5821 (5) | 3533 (7) | 867 (5) |
| C37 | 4781 (5) | 3248 (5) | 1151 (5) |
| C41 | 1422 (4) | 4433 (4) | 3669 (3) |
| C42 | 1627 (4) | 5236 (4) | 4742 (4) |
| C43 | 2163 (6) | 5166 (5) | 5589 (4) |
| C44 | 2324 (8) | 5923 (6) | 6581 (5) |
| C45 | 1912 (9) | 6712 (5) | 6727 (5) |
| C46 | 1381 (8) | 6765 (6) | 5906 (5) |
| C47 | 1242 (6) | 6030 (4) | 4907 (4) |

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 3.

a replacement of the Cl atom in **2** by a pendant cyclohexanoate group. Like **2**, the molecule of **3** has crystallographic $C_i$ symmetry. Again the Sn–O bond lengths of the bridging carboxylates are in general longer (averaging 2.15 (3) Å) than the Sn–O framework bonds (averaging 2.06 (2) Å).

It is interesting to note that the bond angles at the "pyramidal" framework oxygen atoms in drum **1** average 100.4 (3)° in the distannoxane ring and are at 133.2 (3)° in the tristannoxane ring (Figure 2). This compares with an average bond angle at oxygen within the distannoxane ring of 102.9 (1)° in unfolded drum **2**, which has nearly planar oxygen atoms and slightly shorter Sn–O framework bonds, averaging 2.063 (3) Å for **2** compared to 2.086 (7) Å for **1**. The average Sn–O bridging carboxylate bond length is the same in the two structures, at 2.166 (8) Å in **1** and at 2.166 (3) Å in **2**. Although the same number of bonds are conserved in the hydrolysis of an unfolded drum of type **3** to a drum structure, eq 4, the entropy change is favorable.

**Table IV.** Selected Bond Lengths (Å) and Bond Angles (deg) for $[(n\text{-BuSn(O)O}_2\text{CPh})_2(n\text{-BuSn(Cl)(O}_2\text{CPh})_2)]_2$ (**2**)[a]

| | | | |
|---|---|---|---|
| O1–Sn1 | 2.055 (3) | O31–Sn2 | 2.116 (3) |
| O1–Sn2 | 2.053 (3) | O32–Sn3 | 2.234 (3) |
| O1–Sn1′ | 2.068 (3) | O42–Sn3 | 2.127 (3) |
| O2–Sn1 | 2.123 (3) | O41–Sn2 | 2.148 (3) |
| O2–Sn2 | 2.066 (3) | Cl–Sn3 | 2.422 (1) |
| O2–Sn3 | 2.012 (3) | C11–O11 | 1.264 (5) |
| Sn1–CA1 | 2.139 (4) | C11–O12 | 1.260 (5) |
| Sn2–CB1 | 2.133 (5) | C21–O21 | 1.258 (5) |
| Sn3–CC1 | 2.126 (5) | C21–O22 | 1.255 (5) |
| O11–Sn1 | 2.178 (3) | C31–O31 | 1.261 (5) |
| O12–Sn2 | 2.179 (3) | C31–O32 | 1.241 (5) |
| O21–Sn1 | 2.181 (3) | C41–O41 | 1.268 (5) |
| O22–Sn3 | 2.162 (3) | C41–O42 | 1.244 (5) |
| Sn1–O1–Sn1′ | 105.0 (1) | O2–Sn2–O41 | 88.6 (1) |
| Sn1–O1–Sn2 | 103.2 (1) | O2–Sn2–O12 | 76.6 (1) |
| Sn2–O1–Sn1′ | 149.2 (1) | O2–Sn2–O31 | 90.5 (1) |
| Sn1–O2–Sn2 | 105 (1) | CB1–Sn2–O1 | 105.6 (2) |
| Sn3–O2–Sn2 | 127.3 (1) | CB1–Sn2–O41 | 89.0 (2) |
| Sn3–O2–Sn1 | 127.5 (1) | CB1–Sn2–O12 | 90.0 (2) |
| CA1–Sn1–O1 | 173.6 (2) | CB1–Sn2–O31 | 93.1 (2) |
| O11–Sn1–O21 | 177.8 (1) | O1–Sn2–O12 | 90.2 (1) |
| O2–Sn1–O1′ | 150.1 (1) | O1–Sn2–O31 | 89.4 (1) |
| O1–Sn1–O2 | 75.4 (1) | O41–Sn2–O12 | 86.9 (1) |
| O1–Sn1–O1′ | 75.0 (1) | O41–Sn2–O31 | 92.7 (1) |
| O1–Sn1–O11 | 84.4 (1) | O32–Sn3–Cl | 178.57 (9) |
| O1–Sn1–O21 | 94.9 (1) | O22–Sn3–O42 | 175.4 (1) |
| CA1–Sn1–O2 | 108.7 (2) | CC1–Sn3–O2 | 168.6 (2) |
| CA1–Sn1–O1′ | 101.2 (1) | Cl–Sn3–O2 | 92.81 (9) |
| CA1–Sn1–O11 | 90.7 (2) | Cl–Sn3–O22 | 90.7 (1) |
| CA1–Sn1–O21 | 90.2 (2) | Cl–Sn3–O42 | 90.4 (1) |
| O2–Sn1–O11 | 88.2 (1) | Cl–Sn3–CC1 | 98.3 (2) |
| O2–Sn1–O21 | 89.5 (1) | O32–Sn3–O2 | 85.8 (1) |
| O1′–Sn1–O11 | 92.3 (1) | O32–Sn3–O22 | 89.1 (2) |
| O1′–Sn1–O21 | 89.6 (1) | O32–Sn3–O42 | 89.6 (2) |
| CB1–Sn2–O2 | 175.8 (2) | O32–Sn3–CC1 | 83.1 (2) |
| O12–Sn2–O31 | 177.0 (1) | O2–Sn3–O42 | 87.8 (1) |
| O1–Sn2–O41 | 165.1 (1) | O2–Sn3–O22 | 87.7 (1) |
| O2–Sn2–O1 | 76.6 (1) | CC1–Sn3–O42 | 94.5 (2) |
| | | CC1–Sn3–O22 | 89.8 (2) |

[a] Numbers in parentheses are estimated standard deviations. Atoms are labeled to agree with Figure 3.

**Ladder to Drum Conversion.** It is interesting to speculate how the drum structure is formed from the ladder. The implication is that the energy difference between the two basic structures is relatively small. By way of illustration, we apply the hydrolysis process to ladder formulation **3**. Mechanistically, for this example, a conservation is expected in the number of bonds to be broken and formed in executing the hydrolysis of eq 4. A minimum of nine Sn–carboxylate oxygen bonds are required to be cleaved. During this cleavage the Sn–carboxylate oxygen bonds must assume cis positions at the tin atoms. These chelating groups are in trans positions in the open-drum structure. The bonds formed in completing the conversion to the drum structure with this constraint consist of three Sn–carboxylate oxygen bonds and six Sn–O bonds.

It is probable that the first step in the hydrolysis of unfolded drums involves the attack of the terminal tin atoms by water molecules. This leads to the formation of a dihydroxy intermediate, illustrated in Figure 7. While we have not isolated a derivative of this type, the formation of the isostructural dichloro compound **2** lends credence to this suggestion.

As indicated in the intermediate formulation in Figure 7, there remains seven Sn-carboxylate oxygen bonds to be cleaved. From this point, only an account of the bonds breaking and forming to give the drum is possible. Three steps are required to bring this about: (1) The removal of two additional carboxylic acid molecules is required. (2) Since alternate tin atoms from the upper and lower faces of the drum are coupled together by bridging carboxylate groups, the lack of this linkage between tin atoms Sn1 and Sn1′ must be remedied; (3) The intermediate must cyclize such that atoms Sn2, Sn3′, Sn3, and Sn2′ form two distannoxane

**Table V.** $^{119}$Sn Chemical Shifts[a] (ppm) for Drums and Ladders

$[n\text{-BuSn(O)O}_2\text{CR}]_6$[b]

|  | **1** | **4** |
|---|---|---|
| R | $C_5H_9$ | $C_6H_{11}$ |
|  | −485.8 | −486.2 |

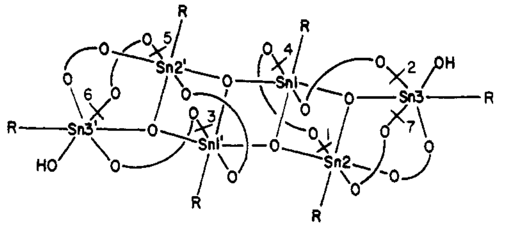
$[(\text{R}'\text{Sn(O)O}_2\text{CR})_2\text{R}'\text{Sn(O}_2\text{CR})_n(\text{Cl})_x]_2$

|  | **1**[c] $n = 3$, $x = 0$ | **3**[d] $n = 3$, $x = 0$ | **2**[e] $n = 2$, $x = 1$ | **5**[f] $n = 3$, $x = 0$ | **6**[g] $n = 3$, $x = 0$ | **7**[h] $n = 3$, $x = 0$ | assignt[i] |
|---|---|---|---|---|---|---|---|
| R′ | *n*-Bu | *n*-Bu | *n*-Bu | *n*-Bu | *n*-Bu | Me |  |
| R | $C_5H_9$ | $C_6H_{11}$ | Ph | Ph | Me | $C_6H_{11}$ |  |
|  |  | −479 |  |  |  |  | I |
|  |  | −486 |  |  | −486 | −465.9 | D |
|  |  | −492 |  |  |  |  | I |
|  |  | −503 |  |  |  |  | I |
|  |  |  | −516.0 | −517 |  |  |  |
|  |  |  | −520.1 | −520 |  |  |  |
|  | −528.3 | −524 | −521.0 | −522 | −522 | −500.9 | U |
|  |  |  | −522.7 | −523 |  |  |  |
|  | −536.5 | −532 |  | −536 | −533 | −515.6 | I |
|  |  |  | −549.8 | −545 |  |  |  |
|  | −546.9 | −552 | −551.1 | −548 | −549 | −527.0 | U |
|  |  |  |  | −550 |  |  |  |
|  | −629.7 | −630 |  | −606 |  | −607.4 | U |
| ref | *j* | *j* | *j* | 8 | 8 | 8 |  |

[a] Relative to $Me_4Sn$ in $CDCl_3$ except **2**, which is a solution in $C_3D_6O$. [b] Values are given for solutions of the pure drum compound. Only a single signal is present. [c] Values here refer to a solution of the pure drum **1**, to which a 10-fold excess of $C_6H_{11}CO_2H$ was added. [d] Values refer to invariant frequencies recorded with time as displayed in Figure 6. [e] Values are listed as components of two multiplets. [f] Similar to data for **2**, components of two multiplets are listed. In addition, two other peaks are recorded. [g] Values are for a sample of **6** that had been standing for 1 week before the $^{119}$Sn spectrum was recorded. [h] Compared to the derivatives containing the *n*-butyl group, **7**, incorporating methyl groups, has signals shifted to lower fields. [i] I = intermediate, D = drum, and U = unfolded drum. [j] This work.

units. In doing this, tin atoms Sn3 and Sn3′ need to be connected by a bridging carboxylate.

To complete the formation of the drum from the intermediate, the following possible path is presented to aid in visualizing the process:



A pattern of suggested bonds to be cleaved is shown schematically for **3**. The order of bonds cleaved as labeled follows the accompanying discussion. In addition, two O–H bonds are broken and two O–H bonds are formed during expulsion of the two carboxylic acid molecules required to complete the reaction. Hydroxide attack from the Sn3–OH unit on Sn2 could initiate cleavage of the Sn2–O bond labeled 1. The accompanying movement of Sn3 to form a distannoxane bridging group is envisioned to break the Sn3–O bond labeled 2.

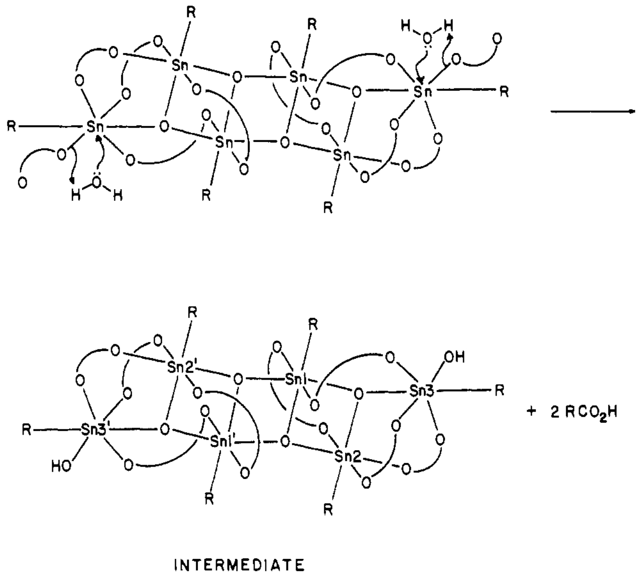
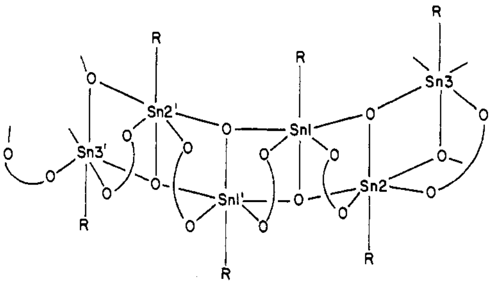


**Figure 7.** Suggested initial intermediate resulting in the hydrolysis of a ladder structure as represented by eq 4.

Pivoting of the dangling end of the carboxylate group so as to form a bridge between Sn1 and Sn1′ causes the bridge between Sn1′ and Sn3′ to break at Sn1′, bond 3. The molecule should start to fold up due to the presence of cis carboxylate linkages at Sn1′. Steric repulsion should now exist between the bridge between Sn1 and Sn2 and the adjacent Sn2′–Sn3′ bridge resulting in cleavage of the trans Sn1–O bond 4 and expulsion of a carboxylic acid molecule. Simultaneously with hydroxide attack at Sn2, hydroxide attack from the Sn3′–OH unit on Sn2′ should cleave Sn–O carboxylate bond 5 as Sn2′ moves into place. With increased folding magnifying steric strain, expulsion of the remaining carboxylic acid molecule to complete the reaction by cleavage of Sn–O bond 6 is possible. This steric effect aided by the process of closing the ends to form the drum is envisioned to cleave Sn3–O bond 7. The latter carboxylate group then pivots to form a new bridge between Sn2 and Sn1. Just prior to formation of the drum, we have the formulation



The conversion to the drum structure is completed by the formation of the stannoxane units, Sn3–O–Sn2′ and Sn2–O–Sn3′ giving rise to the upper and lower tristannoxane faces. The whole process is expected to be a concerted one.

Other processes of bond cleavage and bond formation may be envisioned. However, the number and type of bonds broken and formed should remain the same.

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**Supplementary Material Available:** Listings of anisotropic thermal parameters (Table S1) and additional bond lengths and angles (Table S2) for **1** and anisotropic thermal parameters (Table S3), hydrogen atom parameters (Table S4), additional bond lengths and angles (Table S5), and deviations from selected least-squares mean planes (Table S6) for **2** (10 pages); tables of calculated and observed structure factors (35 pages). Ordering information is given on any current masthead page.