

Transesterification reaction of 2-methoxycarbonylethyltin hydroxide

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Abstract: The title compound, $\text{CH}_3\text{OCOCH}_2\text{CH}_2\text{SnCl}_2(\text{OH})$ (**1**), readily undergo transesterification into the corresponding analogues, $\text{ROCOCH}_2\text{CH}_2\text{SnCl}_2(\text{OH})$ ($\text{R} = \text{CH}_3\text{CH}_2$, **2**; $\text{CH}_3\text{CH}_2\text{CH}_2$, **3**; $\text{CH}_2=\text{CHCH}_2$, **4**), when reacted with an alcohol ROH under reflux. The structural features of these compounds have been described, and the possible mechanism of the transesterification reaction has been suggested.

Supporting information: FT-IR, ^1H NMR, X-Ray, Cif file.

Keywords: organotin, 2-methoxycarbonylethyltin hydroxide, crystal structure, intramolecular catalysis, transesterification.

1. INTRODUCTION

Organotin compounds are widely used as the reaction catalysts, PVC stabilizers, biocides, and wood preservatives [1]. Transesterification is a very important reaction in organic synthesis as well as in industry. However, it is very often catalyzed for a better efficiency, higher reaction rates and milder conditions [2]. Organotin compounds such as organotin oxides, alkoxides, carboxylates, chlorides, and tetraorganodistannoxanes are already used as transesterification catalysts [2-6]. However, no attention was paid to transesterifications of monoalkyldichlorotin hydroxides in the literature. Monoalkyldichlorotin hydroxides can be obtained by the hydrolysis of monoalkyltin trichlorides [7,8]. 2-Alkoxy carbonylethyltin trichlorides [9] are the monoalkyltin trichlorides directly prepared from the reaction of acrylates with SnCl_4/HCl in high yields. Previously, we reported the hydrolysis of 2-methoxycarbonylethyltin trichloride and the crystal structure of 2-methoxycarbonylethyltin hydroxide (**1**) [10]. Here, we continue to report transesterification reaction of **1**, and the crystal and molecular structure of $\text{CH}_3\text{CH}_2\text{OCOCH}_2\text{CH}_2\text{SnCl}_2(\text{OH})$.

2. EXPERIMENTAL

All chemicals were of reagent grade and were used without further purification. 2-methoxycarbonylethyltin hydroxide was prepared according to the reported method [10]. Carbon and hydrogen analyses were determined using a Perkin Elmer 2400 Series II elemental analyzer. IR spectra were recorded on a Nicolet 470 FT-IR spectrophotometer using KBr discs in the range $4000\text{--}400\text{ cm}^{-1}$. ^1H NMR spectral data were collected using a Bruker Avance DMX500 NMR spectrometer with CD_3COCD_3 (or CD_3SOCD_3 or CDCl_3) as solvent and TMS as internal standard.

2.1 Transesterification of 1

Transesterification of **1** was performed by refluxing **1** (0.60 g, 2 mmol) in 50 mL ethanol (or 1-propanol or allyl alcohol) for 3 h. The solution was concentrated at reduced pressure and cooled. The white solid obtained was filtered and washed with ether. The analytical and physical data of compounds **2**, **3**, and **4** are as follows.

$\text{CH}_3\text{CH}_2\text{OCOCH}_2\text{CH}_2\text{SnCl}_2(\text{OH})$ (**2**): yield, 82%. M.p. 148.2-149.4 °C. Anal. Found: C, 19.34; H, 3.13. Calcd for $\text{C}_5\text{H}_{10}\text{Cl}_2\text{O}_3\text{Sn}$: C, 19.51; H, 3.28%. IR(KBr)/ cm^{-1} : 3420 (broad, OH), 1645 [vs, $\nu(\text{C}=\text{O})$], 1262, 1236 [vs, $\nu(\text{C}-\text{O})$], 534 [m, $\nu(\text{Sn}-\text{O})$]. ^1H NMR (500 MHz, CD_3COCD_3)/ δ : 1.33 (t, 3H, $J = 7.2$ Hz, CH_3), 1.60 (t, 2H, $J = 7.4$ Hz, CH_2Sn), 2.90 (t, 2H, $J = 7.4$ Hz, CH_2CO), 3.16 (s, 1H, OH), 4.51 (q, 2H, $J = 7.2$ Hz, OCH_2).

$\text{CH}_3\text{CH}_2\text{CH}_2\text{OCOCH}_2\text{CH}_2\text{SnCl}_2(\text{OH})$ (**3**): yield, 78%. M.p. 143.1-144.2 °C. Anal. Found: C, 22.47; H, 3.58. Calcd for $\text{C}_6\text{H}_{12}\text{Cl}_2\text{O}_3\text{Sn}$: C, 22.40; H, 3.76%. IR(KBr)/ cm^{-1} : 3418 (broad, OH), 1645 [vs, $\nu(\text{C}=\text{O})$], 1263, 1236 [vs, $\nu(\text{C}-\text{O})$], 535 [m, $\nu(\text{Sn}-\text{O})$]. ^1H NMR (500 MHz, CD_3SOCD_3)/ δ : 0.90 (t, 3H, $J = 7.0$ Hz, CH_3), 1.66 (sex, 3H, $J = 7.0$ Hz, CH_2), 1.91 (t, 2H, $J = 7.6$ Hz, CH_2Sn), 2.89 (t, 2H, $J = 7.6$ Hz, CH_2CO), 4.20 (t, 2H, $J = 7.0$ Hz, OCH_2).

$\text{CH}_2=\text{CHCH}_2\text{OCOCH}_2\text{CH}_2\text{SnCl}_2(\text{OH})$ (**4**): yield, 73%. M.p. 103.6-104.5 °C. Anal. Found: C, 22.42; H, 3.06. Calcd for $\text{C}_6\text{H}_{10}\text{Cl}_2\text{O}_3\text{Sn}$: C, 22.54; H, 3.15%. IR(KBr)/ cm^{-1} : 3338 (broad, OH), 1664 [vs, $\nu(\text{C}=\text{O})$], 1644 [vs, $\nu(\text{C}=\text{C})$], 1262, 1227 [vs, $\nu(\text{C}-\text{O})$], 545 [m, $\nu(\text{Sn}-\text{O})$]. ^1H NMR (500 MHz, CDCl_3)/ δ : 1.69 (s, 1H, OH), 2.20 (t, tH, $J = 7.6$ Hz, CH_2 , CH_2Sn), 2.94 (t, 2H, $J = 7.6$ Hz, CH_2CO), 4.93 (d, 2H, $J = 7.6$ Hz, OCH_2), 5.29-5.45 (m, 2H, $\text{H}_2\text{C}=\text{C}$), 5.92-6.06 (m, 1H, =CH).

2.2 X-ray crystallography

The colorless single crystal of **2** was obtained from ethanol by slow evaporation at room temperature. Diffractions measurements were performed on a Bruker Smart Apex imaging-plate area detector fitted with graphite monochromatized Mo-K α radiation (0.71073 Å) using the j and w scan technique. The structures were solved by direct-methods and refined by a full-matrix least squares procedure based on F^2 using SHELXL-97. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at calculated positions. One carbon atom (C5) of ethyl group was found to be disordered over two positions with site occupancy factors of 0.515(17):0.485(17). Crystal data, collection procedures and refinement results are summarized in Table S1. Crystallographic data have been deposited

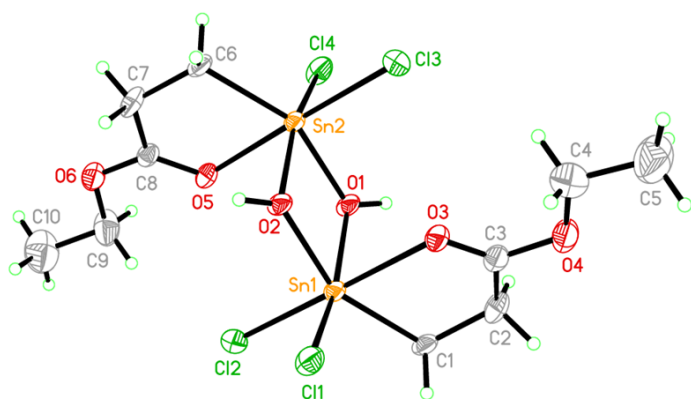
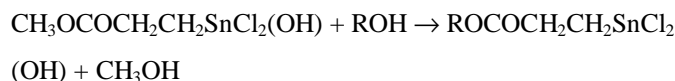


Figure 1. The molecular structure of **2**.

with the Cambridge Crystallographic Data Centre, CCDC 956294.

RESULTS AND DISCUSSION

Compound **1** readily converted into the corresponding 2-alkoxycarbonylethyltin analogues, $\text{ROCOCH}_2\text{CH}_2\text{SnCl}_2(\text{OH})$ (**2-4**), with yields of 73-82% when refluxed in an alcohol ROH.



R = CH_3CH_2 , **2**; $\text{CH}_3\text{CH}_2\text{CH}_2$, **3**; $\text{CH}_2=\text{CHCH}_2$, **4**

Table 1. Selected bond lengths (Å) and angles (°) of **2**

Sn(1)-O(1)	2.170(5)	Sn(2)-O(5)	2.330(6)	Sn(3)-Cl(5)	2.495(2)
Sn(1)-O(2)	1.986(4)	Sn(2)-C(6)	2.141(7)	Sn(3)-Cl(6)	2.324(2)
Sn(1)-O(3)	2.358(6)	Sn(2)-Cl(3)	2.423(2)	Sn(4)-O(10)	2.020(5)
Sn(1)-C(1)	2.122(7)	Sn(2)-Cl(4)	2.425(2)	Sn(4)-O(10) ^{#2}	2.181(5)
Sn(1)-Cl(1)	2.424(2)	Sn(3)-O(7)	2.026(4)	Sn(4)-O(11)	2.235(6)
Sn(1)-Cl(2)	2.427(3)	Sn(3)-O(7) ^{#1}	2.183(5)	Sn(4)-C(16)	2.114(8)
Sn(2)-O(1)	1.981(5)	Sn(3)-O(8)	2.270(6)	Sn(4)-Cl(8)	2.327(3)
Sn(2)-O(2)	2.162(5)	Sn(3)-C(11)	2.120(7)	Sn(4)-Cl(7)	2.500(3)
O(2)-Sn(1)-C(1)	154.9(3)	O(2)-Sn(2)-O(5)	85.6(2)	O(7)-Sn(3)-Cl(5)	88.21(15)
O(2)-Sn(1)-O(1)	69.72(18)	O(1)-Sn(2)-Cl(3)	93.22(17)	C(11)-Sn(3)-Cl(5)	104.3(2)
C(1)-Sn(1)-O(1)	93.2(3)	C(6)-Sn(2)-Cl(3)	108.6(2)	O(7) ^{#1} -Sn(3)-Cl(5)	159.71(14)
O(2)-Sn(1)-O(3)	85.6(2)	O(2)-Sn(2)-Cl(3)	95.82(16)	O(8)-Sn(3)-Cl(5)	83.21(16)
C(1)-Sn(1)-O(3)	73.9(3)	O(5)-Sn(2)-Cl(3)	176.96(15)	Cl(6)-Sn(3)-Cl(5)	94.00(9)
O(1)-Sn(1)-O(3)	83.8(2)	O(1)-Sn(2)-Cl(4)	92.03(15)	O(10)-Sn(4)-C(16)	156.8(3)
O(2)-Sn(1)-Cl(1)	91.89(15)	C(6)-Sn(2)-Cl(4)	100.5(2)	O(10)-Sn(4)-O(10) ^{#2}	72.4(2)
C(1)-Sn(1)-Cl(1)	101.1(2)	O(2)-Sn(2)-Cl(4)	160.70(14)	C(16)-Sn(4)-O(10) ^{#2}	92.3(3)
O(1)-Sn(1)-Cl(1)	159.81(15)	O(5)-Sn(2)-Cl(4)	85.79(16)	O(10)-Sn(4)-O(11)	79.6(2)
O(3)-Sn(1)-Cl(1)	86.61(16)	Cl(3)-Sn(2)-Cl(4)	92.02(10)	C(16)-Sn(4)-O(11)	81.8(3)
O(2)-Sn(1)-Cl(2)	93.65(17)	O(7)-Sn(3)-C(11)	155.7(3)	O(10) ^{#2} -Sn(4)-O(11)	85.2(2)
C(1)-Sn(1)-Cl(2)	107.0(3)	O(7)-Sn(3)-O(7) ^{#1}	72.9(2)	O(10)-Sn(4)-Cl(8)	98.34(18)
O(1)-Sn(1)-Cl(2)	96.67(16)	C(11)-Sn(3)-O(7) ^{#1}	90.9(3)	C(16)-Sn(4)-Cl(8)	100.5(3)
O(3)-Sn(1)-Cl(2)	178.90(15)	O(7)-Sn(3)-O(8)	79.88(19)	O(10) ^{#2} -Sn(4)-Cl(8)	95.70(18)
Cl(1)-Sn(1)-Cl(2)	92.63(10)	C(11)-Sn(3)-O(8)	81.1(3)	O(11)-Sn(4)-Cl(8)	177.47(16)
O(1)-Sn(2)-C(6)	154.2(3)	O(7) ^{#1} -Sn(3)-O(8)	86.1(2)	O(10)-Sn(4)-Cl(7)	88.37(17)
O(1)-Sn(2)-O(2)	69.99(18)	O(7)-Sn(3)-Cl(6)	98.22(16)	C(16)-Sn(4)-Cl(7)	103.2(3)
C(6)-Sn(2)-O(2)	93.7(3)	C(11)-Sn(3)-Cl(6)	101.5(2)	O(10) ^{#2} -Sn(4)-Cl(7)	159.12(17)
O(1)-Sn(2)-O(5)	84.8(2)	O(7) ^{#1} -Sn(3)-Cl(6)	95.99(16)	O(11)-Sn(4)-Cl(7)	83.36(18)
C(6)-Sn(2)-O(5)	73.9(3)	O(8)-Sn(3)-Cl(6)	176.65(16)	Cl(8)-Sn(4)-Cl(7)	95.10(11)

Symmetry code: #1 -x+1, -y+2, -z; #2 -x+2, -y, -z+1.

The compounds **2-4** are white solid, and can be soluble in alcohols. In their IR, the strong and broad band appeared at 3338–3420 cm^{-1} is assigned to the stretching vibration of hydroxyl group, $\nu(\text{OH})$. Compared with $\nu(\text{C}=\text{O})$ ($\sim 1730\text{m}^{-1}$) of a free ester group, the $\nu(\text{C}=\text{O})$ of these compounds shifted to low frequency and appeared in the range of 1645 to 1664 cm^{-1} , indicating that the carbonyl oxygen atom was coordinated intramolecularly to the tin atom [11]. The fact that there is almost no variation of $\nu(\text{C}=\text{O})$ between the pure compound (in KBr discs) and a solution of ethanol for **2** indicates the intramolecular $\text{C}=\text{O} \rightarrow \text{Sn}$ coordination still remains in solution [11]. This was further supported by the d value of CH_2O protons (4.51 ppm) in CD_3COCD_3 appeared at the lower magnetic field compared with that in ethyl propionate (4.13 ppm). The coordination of carbonyl oxygen to tin causes the de-shielding of CH_2O protons.

The molecular structure of **2** is shown in Figure 1. The selected bond lengths and bond angles are listed in Table 1. The compound crystallizes in triclinic space group $P-1$ and the asymmetric unit contains four $\text{CH}_3\text{CH}_2\text{OCOCH}_2\text{CH}_2\text{SnCl}_2(\text{OH})$ molecules which slightly differ from each other. Compound **2** exists as a six-coordinated dimer with bridging hydroxyl groups. Each tin atom is coordinated by two chloride atoms occupying mutually *cis* positions and an oxygen atom from intramolecular carbonyl group. The remaining positions in the distorted octahedral coordination geometry about each tin atom are occupied by two μ_2 -hydroxide groups. The major distortions in the tin atom geometries may be traced to the acute angles induced by the Sn_2O_2 ring [O(1)–Sn(1)–O(2) 69.72(18)°, O(1)–Sn(2)–O(2) 69.99(18)°, O(7)–Sn(3)–O(7)^{#1} 72.9(2)°, O(10)–Sn(2)–O(10)^{#2} 72.4(2)°, symmetry code: #1 $-x+1, -y+2, -z$; #2 $-x+2, -y, -z+1$.] and five-membered chelate C_3SnO ring [C(1)–Sn(1)–O(3) 73.9(3)°, C(6)–Sn(2)–O(5) 73.9(3)°, C(11)–Sn(3)–O(8) 81.1(3)°, C(16)–Sn(4)–O(11) 81.8(3)°]. The Sn–O distances within the four-membered rings are not symmetrical, with the bond *trans* to a chlorine atom longer than that *trans* to a carbon atom (for example, Sn(1)–O(1) 2.170(5) Å, Sn(1)–O(2) 1.986(4) Å). The Sn–O lengths in the five-membered chelate rings are Sn(1)–O(3) 2.358(6) Å, Sn(2)–O(5) 2.330(6) Å, Sn(3)–O(8) 2.270(6) Å, and Sn(4)–O(11)

2.235(6) Å, respectively, which are shorter than those of the six-coordinated $\text{EtOCOCH}_2\text{CH}_2\text{SnCl}_3 \cdot \text{OSBu}_2$ [12] and similar to those of the analogues $\text{CH}_3\text{OCOCH}_2\text{CH}_2\text{SnCl}_2(\text{OH})$ [10] and $\text{H}_2\text{NCOCH}_2\text{CH}_2\text{SnCl}_2(\text{OH})$ [13].

The molecules of **2** are linked by the intermolecular O–H...Cl hydrogen bonds [H(1)...Cl(7) 2.38 Å, O(1)...Cl(7) 3.166(5) Å, O(1)–H(1)...Cl(7) 152°; H(2)...Cl(5) 2.37 Å, O(2)...Cl(5) 3.196(5) Å, O(2)–H(2)...Cl(5) 165°; H(7)...Cl(1) 2.49 Å, O(7)...Cl(1) 3.312(5) Å, O(7)–H(7)...Cl(1) 163°; H(10)...Cl(4) 2.41 Å, O(10)...Cl(4) 3.263(5) Å, O(10)–H(10)...Cl(4) 174°; H(1)...Cl(7) 2.38 Å, O(1)...Cl(7) 3.166(5) Å, O(1)–H(1)...Cl(7)^{#1} 152°] to form an infinite zigzag double-chain (Figure 2). The one-dimensional supramolecular chains are further joined by the weaker intermolecular C–H...Cl interactions [H(2A)...Cl(8)^{#3} 2.78 Å, C(2)...Cl(8)^{#3} 3.735(17) Å, C(2)–H(2A)...Cl(8)^{#3} 167°; H(7B)...Cl(6)^{#4} 2.81 Å, C(7)...Cl(6)^{#4} 3.769(12) Å, C(7)–H(7B)...Cl(6)^{#4} 172°; H(12B)...Cl(3)^{#5} 2.71 Å, C(12)...Cl(3)^{#5} 3.612(9) Å, C(12)–H(12B)...Cl(3)^{#5} 155°; H(17A)...Cl(2)^{#6} 2.75 Å, C(17)...Cl(2)^{#6} 3.220(10) Å, C(17)–H(17A)...Cl(2)^{#6} 178°. Symmetry code: #3

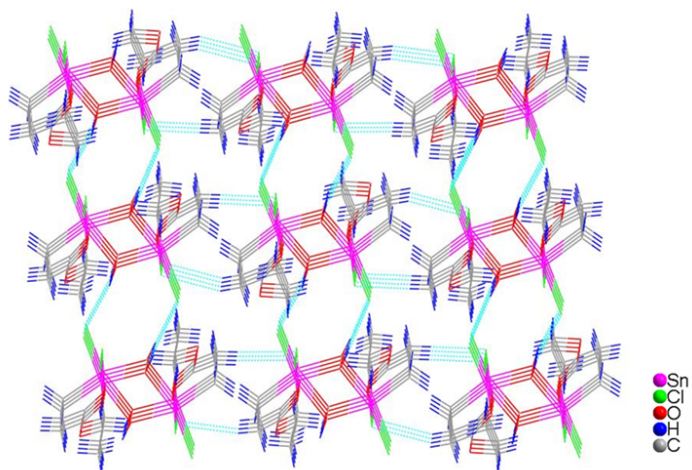


Figure 3. The 3D connectivity formed by the intermolecular O–H...Cl and C–H...Cl interactions in **2**.

$-x+2, -y+1, -z+1$; #4: $-x+1, -y+1, -z$; #5 $-x+2, -y+1, -z$; #6 $-x+1, -y+1, -z+1$] to complete a form of three-dimensional connectivity (Figure 3).

Hobbs and Smith's study [5] indicated that in the transesterification reaction catalyzed by the monoalkyltin compounds, the coordination of carbonyl group in the ester to the tin catalyst is an important factor influencing its activity. According to the proposed mechanism of transesterification for 2-alkoxycarbonylethyltin trichlorides [5,14], we attributed the occurrence of the novel transesterification of **1** to the intramolecular Lewis acid catalysis by the electrophilic $\text{SnCl}_2(\text{OH})$ group (see Scheme 1). The coordination of the ester carbonyl to tin atom ($\text{C}=\text{O} \rightarrow \text{Sn}$) polarized the carbonyl double bond, thereby making the carbonyl carbon more susceptible to attack by a nucleophilic reagent, alcohol, to form tetrahedral carbon atom intermediate. The reaction with better yields, higher rate and easier operation provides a convenient way for preparing 2-alkoxycarbonylethyltin hydroxide.

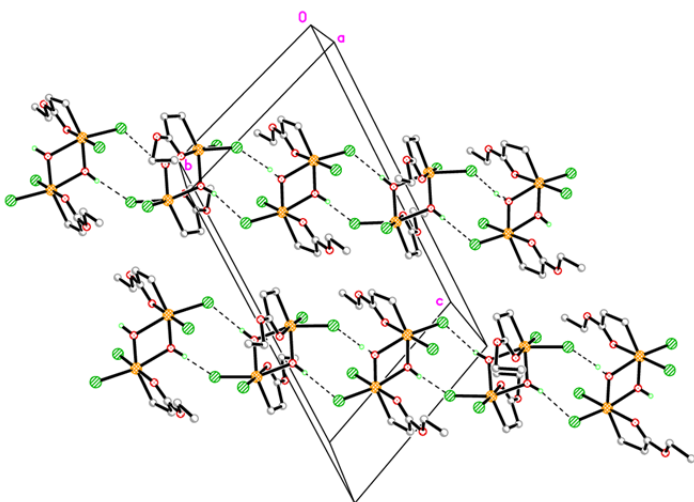
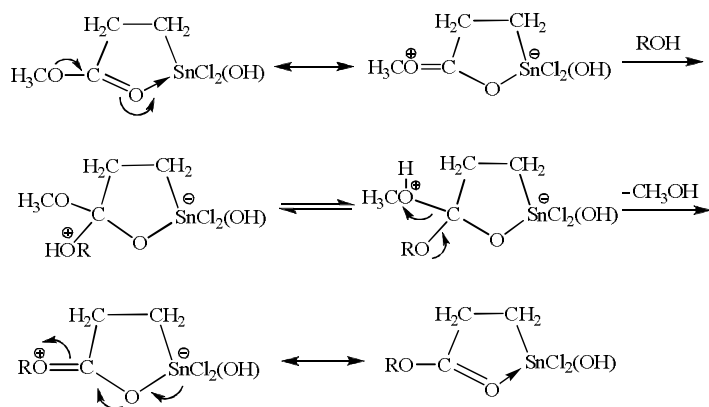


Figure 2. The 1D-chain formed by the intermolecular O–H...Cl hydrogen bonds. All hydrogen atoms except H atoms of hydroxyls are omitted for clarity.



Scheme 1. The suggested mechanism for the transesterification of **1**

Acknowledgments

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