Synthesis, Structure and Transesterification of the Derivatives of β-Alkoxycarbonylethyltin Trichlorides with Diethyldithiocarbamate

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Abstract: The derivatives of β-alkoxycarbonylethyltin trichlorides with diethyldithiocarbamate, $ROCOCH_2CH_2Sn(S_2CNEt_2)Cl_2$, were synthesized and characterized by the means of elemental analysis, IR, ^1H NMR and X-ray single crystal diffraction. The structural features of the compounds were described, and the possible mechanism of transesterification for compound **2a** was suggested.

Keywords: β-Aalkoxycarbonylethyltin trichloride, diethyldithiocarbamate, crystal structure, transesterification.

β-Alkoxycarbonylethyltin trichlorides, $ROCOCH_2CH_2SnCl_3$ **1**, a novel type of mono-organotin compounds containing ester group, have received considerable attention since Hutton *et al* reported their synthesis[1-4]. Their spectral data showed that the center tin atom was penta-coordinated with intramolecular ester carbonyl oxygen to tin coordination and the intramolecular coordination can be broken by external bidentate donor, such as 2,2'-bipyridyl, 1,10-phenanthroline, *etc.*[1-4]. The adducts of **1** with neutral donor, for example, dimethylsulfoxide, hexamethylphosphoramide, 2,2'-bipyridyl and 1,10-phenanthroline, have been reported[2-4], but their derivatives with dithiocarbamate have not been described so far in the literature. In this paper, we report the synthesis, structure and transesterifi-cation of the derivatives of **1** with diethyldithiocarbamate. The reaction equations were as follows:

$$\underset{\mathbf{1}}{ROCOCH_2CH_2SnCl_3} + NaS_2CNEt_2 \rightarrow \underset{\mathbf{2}}{ROCOCH_2CH_2Sn(S_2CNEt_2)Cl_2} + NaCl$$

$$\underset{\mathbf{2a}}{MeOCOCH_2CH_2Sn(S_2CNEt_2)Cl_2} + ROH \rightarrow \underset{\mathbf{2b\text{-}2g}}{ROCOCH_2CH_2Sn(S_2CNEt_2)Cl_2} + MeOH$$

a, R = Me; **b**, Et; **c**, n-Pr,; **d**, allyl; **e**, n-Bu; **f**,cyclohexyl; **g**, benzyl.

Experimental

Compounds type **1** were prepared according to literature procedures[1,5]. The physical data of **1f** and **1g** were listed in **Table 1**.

Preparation method of **2**: A solution of $NaS_2CNEt_2{\bullet}3H_2O$ (1.13 g, 5 mmol) dissolved in 80 mL of CH_2Cl_2 was added dropwise to an equimolar solution of **1** (5 mmol) in 30 mL of CH_2Cl_2. The reaction mixture was stirred for an hour under reflux, and then cooled to about 0°C. Formed NaCl was removed by filtration. The colorless filtrate was concentrated to *ca*. 20 mL by evaporation under reduced pressure, and then addition of petroleum ether (b.p. 30-60°C) (*ca*. 10 mL) gave colorless crystals **2**, which were recrystallized from dichloromethane-petroleum ether (b.p. 30-60°C) (1:1, v/v). The yield, melting point and spectral data for **2a-2g** were listed in **Table 1**.

Transesterification of **2a**: **2a** (1.10 g, 3 mmol) was dissolved in 50 mL ROH and refluxed for 2h, then concentrated by evaporation under reduced pressure. The resultant solid was recrystallized from dichloromethane-petroleum ether (b.p. 30-60°C) (1:1, v/v) to obtain transesterification products of **2a**. The yields of **2b-2g** were 90.6%, 84.9%, 82.4%, 88.2%, 66.5% and 61.4%, respectively.

Crystal structure determinations of **1f** and **2b**: The single crystal structures of **1f** and **2b** were determined on a Bruker P4 fourcircle diffractometer with graphite monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å). The crystal data were as follows: **1f**, $C_9H_{15}Cl_3O_2Sn$, Mr = 380.25, monoclinic, space group $P2_1/c$, a = 10.4443(9), b = 10.4823(7), c = 12.8113(11) Å, α = 90, β = 90.953(8), γ = 90°, V = 1402.39(19) $Å^3$, Z = 4. **2b**, $C_{10}H_{19}Cl_2NO_2S_2Sn$, Mr = 438.97, monoclinic, space group $P2_1/c$, a = 14.881(13), b = 9.5127(10), c = 12.9323(14) Å, α = 90, β = 110.282(6), γ = 90°, V = 1717.1(4) $Å^3$, Z = 4.

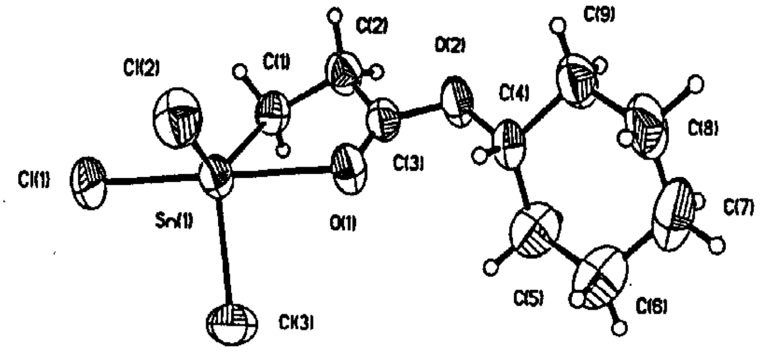
Table 1. The Physical and Spectral Data of the Compounds

No.	m.p. (°C)	yield (%)	IR(ν, cm^{-1})			^{1}HNMR (δ, $CDCl_3$ as solvent)			
			C=O	C-N	C-S	OCH	$COCH_2$	CH_2Sn	NCH_2
1f	161	79.4	1652 vs			5.02 m	2.90 t	2.20 t	
1g	140	68.7	1649 vs			5.41 s	2.96 t	2.23 t	
2a	79-80	84.2	1674 vs	1520 vs	994 s	4.02 s	2.89 t	1.86 t	3.72 q
2b	101	81.3	1678 vs	1528 vs	999 s	4.46 q	2.92 t	1.89 t	3.72 q
2c	65-66	86.5	1670 vs	1518 vs	992 s	4.38 t	2.90 t	1.87 t	3.71 q
2d	49-50	80.7	1678 vs	1522 vs	997 s	4.83 d	2.88 t	1.90 t	3.72 q
2e	35-36	73.2	1668 vs	1525 vs	995 s	4.36 t	2.89 t	1.88 t	3.71 q
2f	104	88.2	1670 vs	1520 vs	990 s	5.09 m	2.88 t	1.87 t	3.72 q
2g	114	78.5	1668 vs	1528 vs	998 s	5.44 s	2.92 t	1.90 t	3.71 q

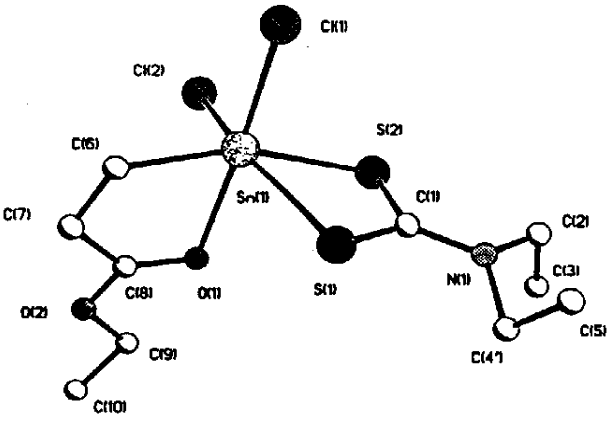
Results and Discussion

The title compounds **2** were obtained by reaction of **1** with NaS_2CNEt_2 with yields of 73.2-88.2% (see **Table 1**). They are soluble in the general organic solvents, such as benzene, alcohol, chloroform, *etc*., but insoluble in saturated hydrocarbon, for example, hexane and petroleum ether. Compared with ν (C=O) (~1735 cm^{-1}) of a free ester group, the ν (C=O) (1650-1680 cm^{-1}) of **1f**, **1g** and **2** indicate that the carbonyl is coordinated intramolecularly to the tin atom[1]. The ν (C–N) and ν (C–S) bands in the regions 1450-1550 and 950-1050 cm^{-1}, respectively, are known to depend on the nature of coordination of the dithiocarbamate ligand. A single band for compounds **2** in each region is indicative of bidentate chelation of the dithiocarbamate ligand[6]. The ^{1}H NMR data also support the presence of carbonyl oxygen to tin coordination in **1f**, **1g** and **2**. The δ values of alkoxyl OCH in **1f**, **1g** and **2** show a downfield shift compared with those in the fatty acid ester because the coordination of carbonyl to tin causes the deshielding of alkoxyl OCH.

Figure 1. Molecular Structures of **1f** and **2b**



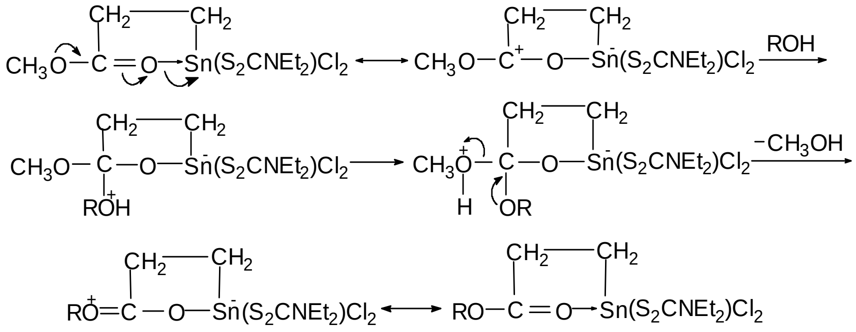
1f



2b

The results of X-ray single crystal diffraction of **1f** and **2b** are completely in agreement with the spectral analysis (see **Figure 1**). The compound **1f** contains a five-membered chelate ring formed *via* carbonyl oxygen to tin coordination (the Sn (1) –O (1) bond length is 2.362 (3) Å) and tin atom is penta-coordinationed with C (1), Cl (2) and Cl (3) in equatorial positions and with O (1) and Cl (1) in axial positions in a distorted trigonal bipyramidal arrangement. The bond angles of C (1) –Sn (1) –Cl (2), C (1) –Sn (1) –Cl (3), Cl (2) –Sn (1) –Cl (3) and O (1)–Sn (1) –Cl (1) are 125.93 (13), 120.70 (13), 107.80 (5) and 176.27 (8)°, respectively. The compound **2b** contains a five-membered chelate ring formed *via* carbonyl oxygen to tin coordination (the Sn (1) –O (1) bond length is 2.392 (3) Å) and a four-membered chelate ring from the bidentate dithiocarbamate (the bond lengths of Sn (1) –S (1) and Sn (1) –S (2) are 2.6371 (13) and 2.4789 (12) Å, respectively). The center tin atom possesses a distorted octahedral geometry with coordinating atoms C (6), O (1), Cl (1), Cl (2), S (1) and S (2). The bond angles of Cl (1) –Sn (1) –O (1), C (6) –Sn (1) –S (2) and Cl (2) –Sn (1) –S (1) are 176.55 (8), 161.40 (13) and 157.25 (5)°, respectively.

The compound **2a** was readily converted into the corresponding analogs **2b-2g** with yields of 61.4-90.6% when refluxed in a corresponding alcohol. The transesterification provided a convenient way for preparing the compounds **2**. We attributed the occurrence of the novel transesterification to the intramolecular Lewis acid catalysis by the electrophilic $SnCl_2$ group. The coordination of the ester carbonyl to tin atom polarized the carbonyl bond, thereby making the carbonyl carbon more susceptible to attack by a nucleophilic reagent alcohol. The possible mechanism of transesterification for **2a** was suggestion as follows.



Acknowledgment

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7. The crystallographic parameters of **1f** and **2b** have been deposited in the editorial office of CCL.

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