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Structure and Transesterification Reaction of Methyl 3-(Phenyldihalostannyl)propionates

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Abstract: The title compounds, $PhX_2SnCH_2CH_2CO_2Me$ (X = Cl, **1a**; Br, **1b**; I, **1c**), readily underwent transesterification into the corresponding analogues, $PhX_2SnCH_2CH_2CO_2R$ when reacted with an alcohol ROH. The structural features of these compounds were described, and the possible mechanism of the novel transesterification was suggested.

Keywords: Organotin dihalide, 3-(phenyldihalostannyl)propionate, transesterification reaction, crystal structure.

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[1]. Organotin compounds as organotin oxides, alkoxides, carboxylates and tetraorganodistannoxanes are already used as transesterification catalysts[1-3], however, no attention was paid to transestrifications of 3-(phenyldihalostannyl)propionates in the literature. In this paper, we report the structures and transesterifications of **1a-c**.

The compounds **1a-c** obtained by the reaction of methyl 3-triphenylstannyl-propionate with YX (ICl, Br_2, or I_2) in 1:2 molar ratio at room temperature readily converted into the corresponding 3-(phenyldihalostannyl)propionate analogues with yields of 64-90% when refluxed in an alcohol ROH. The results were listed in **Table 1**[4].

$$Ph_3SnCH_2CH_2CO_2Me + 2YX \rightarrow PhX_2SnCH_2CH_2CO_2Me + 2PhY$$
$$PhX_2SnCH_2CH_2CO_2Me + ROH \rightarrow PhX_2SnCH_2CH_2CO_2R + MeOH$$

X = Cl, **a**; Br, **b**; I, **c**. Y = I, Br. R = Me, **1**; Et, **2**; *n*-Pr, **3**; *i*-Pr, **4**.

Table 1 The yield (%) and melting point (°C) of the compounds **1a-c**, **2a-c**, **3a-c**, **4a-c**

No.	mp °C	yield %	No.	mp °C	yield %	No.	mp °C	yield %
1a	121-2	79.3	**2b**	84-5	78.6	**3c**	61-2	77.3
1b	118-9	69.2	**2c**	70-1	89.6	**4a**	137-8	67.2
1c	77-8	67.4	**3a**	62-4	87.2	**4b**	102-3	70.4
2a	104-6	90.3	**3b**	50-1	74.5	**4c**	104-5	64.4

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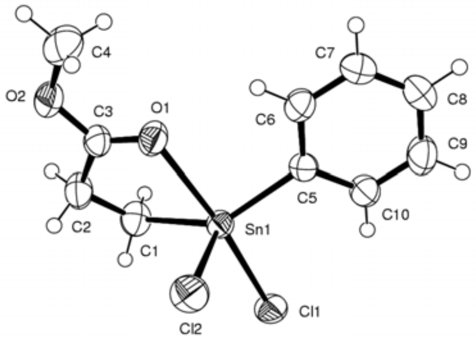
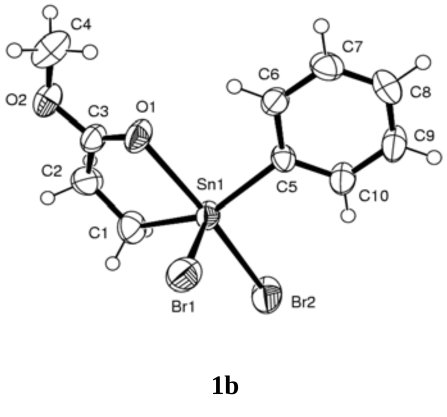
Compared with ν (C=O) (~1730m^{-1}) of a free ester group, the ν (C=O) (~1650 cm^{-1}) in these compounds indicate that the carbonyl oxygen atom is coordinated intramolecularly to the tin atom[5]. The δ (^{1}H and ^{13}C) values of C=O and OCH_n (n = 1, 2, 3) in these compounds show a downfield shift relative to those of the fatty acid ester because the coordination of carbonyl to tin causes the deshielding of $COOCH_n$. The results of X-ray single crystal diffraction of **1a** and **1b** are completely in agreement with the spectral analysis (see **Figure 1**)[6]. The compounds **1a** and **1b** contain a five-membered chelate ring formed *via* carbonyl oxygen to tin coordination (the Sn–O bond length is 2.432(3) Å for**1a** and 2.407(4) Å for **1b**, respectively.). The geometry about tin atom is a distorted trigonal bipyramid with two carbons (C1 and C5) and a halogen in equatorial sites and another halogen and carbonyl oxygen in axial positions.

We attributed the occurrence of the novel transesterification to the intramolecular Lewis acid catalysis by the electrophilic SnX_2 group (see **Scheme 1**). The coordination of the ester carbonyl to tin atom (C=O→Sn) polarized the carbonyl bond, thereby making the carbonyl carbon more susceptible to attack by a nucleophilic reagent alcohol to form tetrahedral intermediate.

Figure 1 Molecular structure of **1a** and **1b**

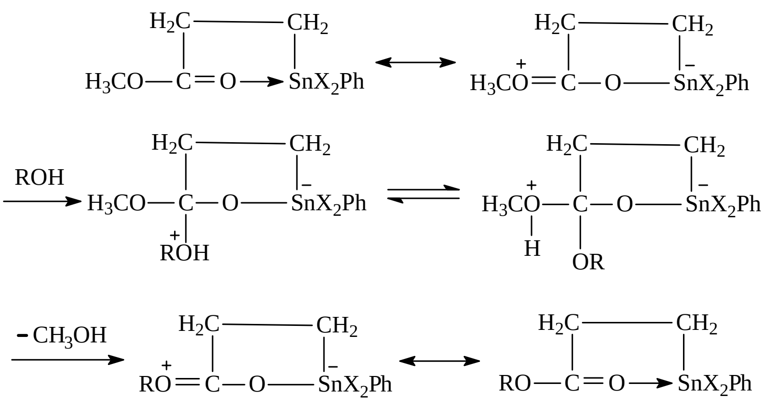


1a



1b

Scheme 1



The reaction with better yields, higher rate and easier operation provides a convenient way for preparing 3-(phenyldihalostannyl)propionates.

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References and Notes

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4. Selected analytical and spectral data: Compound **2a**, Anal. Calcd. for $C_{11}H_{14}Cl_2O_2Sn$: C, 35.92, H, 3.84. Found: C, 35.89, H, 3.62%. IR (KBr) ν: 1652 (C = O), 1234 (C–O) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, δ ppm): 1.34 (t, 3H, *J* = 7.1 Hz, CH_3), 1.97 (t, 2H, *J* = 7.5 Hz, $J(^{119/117}Sn\text{-}^1H)$ = 84.8/81.5 Hz, CH_2Sn), 2.94 (t, 2H, *J* = 7.5 Hz, $J(^{119/117}Sn\text{-}^1H)$ = 140.9/133.3 Hz, CH_2CO), 4.37 (q, 2H, *J* = 7.2 Hz, OCH_2), 7.45-7.52 (m, 3H, *p*-H and *m*-H in ph), 7.91-7.93 (m, 2H, $J(^{119}Sn\text{-}^1H)$ = 88.0 Hz, *o*-H in ph). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 14.20 (CH_3), 22.34 ($J(^{119/117}Sn\text{-}^{13}C)$ = 648.0/619.6 Hz,CH_2Sn), 29.61 ($J(^{119}Sn\text{-}^{13}C)$ = 49.8 Hz, CH_2CO), 64.66 (OCH_2), 129.23 ($J(^{119}Sn\text{-}^{13}C)$ = 89.2 Hz, *m*-C in ph), 131.06 ($J(^{119}Sn\text{-}^{13}C)$ = 17.9 Hz, *p*-C in ph), 135.71 ($J(^{119}Sn\text{-}^{13}C)$ = 63.3 Hz, *o*-C in ph), 141.17 (*i*-C in ph), 181.37 (CO_2).
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6. Crystal structure determinations of **1a** and **1b**: Intensity data were collected at 293 K on a Smart CCD diffractometer. The crystal data were as follows: **1a**, $C_{10}H_{12}Cl_2O_2Sn$, Mr = 353.79, Monoclinic, Space group $P2_1/n$, a = 8.4829(17), b = 13.629(3), c = 11.744(2) Å, β = 109.694(2)°, V = 1278.3(4) $Å^3$, Z = 4, R = 0.0359, *w*R = 0.0856. **1b**, $C_{10}H_{12}Br_2O_2Sn$, Mr = 442.71, Monoclinic, Space group $P2_1/n$, a = 11.025(4), b = 10.853(4), c = 11.335(4) Å, β = 104.129(4)°, V = 1315.1(7) $Å^3$, Z = 4, R = 0.0303, *w*R = 0.0702. The final coordinates, bond lengths and angles of **1a** and **1b** have been deposited in the editorial office of CCL.

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