Reactivity behavior of (hydroxy)diorganotin(IV)methanesulfonates with ionic nucleophiles - synthesis and structural characterization of novel diorganostannate salts, 

\[ \text{[R}_2\text{Sn(I-OH)(OSO}_2\text{Me})(\text{ONO}_2)\text{]}_2\text{2Bu}_4\text{N} \]

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Abstract

The reaction of \( \text{R}_2\text{Sn(OH)}\text{OSO}_2\text{Me} \) [\( \text{R} = \text{n-Pr} \) (1a), or \( \text{n-Bu} \) (1b)] with one equivalent of \( \text{Bu}_4\text{NNO}_3 \) in \( \text{CH}_2\text{Cl}_2 \) proceeds via nucleophilic addition of \( \text{NO}_3^- \) ion to the Lewis acidic tin center and results in the formation of novel diorganostannates, \( \text{[R}_2\text{Sn(I-OH)(OSO}_2\text{Me})(\text{ONO}_2)\text{]}_2\text{2Bu}_4\text{N} \) [\( \text{R} = \text{n-Pr} \) (2a), \( \text{n-Bu} \) (2b)]. The molecular structure of 2b comprises of hydroxy-bridged dimer with monodentate methanesulfonate and nitrate groups bonded to each tin atom. Analogous reactions of the tin precursor, 1b with strong nucleophiles such as \( \text{Bu}_4\text{NX} \) (X \( = \text{F}^-, \text{OAc}^- \)) and \( \text{RLi} \) (R =\( \text{M-Bu} \), \( \text{Me} \)) favor ionic metathesis pathway involving Sn-OSO\(_2\)Me bond cleavage. This approach provides a simple and facile synthetic route for triorganotin oxides, \( \text{(R}_2\text{R}_0\text{Sn)}_2\text{O} \) (\( \text{R} = \text{R}_0 = \text{N-Bu} \), \( \text{R} = \text{N-Bu} \), \( \text{R}_0 = \text{Me} \)).

Keywords: Diorganostannate; Methanesulfonate; Ionic metathesis; Organotin oxide

1. Introduction

The property of organotin (IV) compounds, \( \text{R}_2\text{SnX}_2 \) (X = halogen) to act as Lewis acids has been frequently utilized to synthesize a large number of trihalodiorganostannates, \( \text{[R}_2\text{SnX}_3]^- \) [1] as well as tetrahalodiorganostannates, \( \text{[R}_2\text{SnX}_4]^2^- \) [2]. Recently, Tudela et al. [3] have reported solvent dependence on the formation of these class of compounds. It has been shown that the reaction of \( \text{Me}_2\text{SnBr}_2 \) with \( \text{Et}_4\text{NBr} \) in \( \text{CHCl}_3/\text{hexane} \) mixture yields \( \text{[Me}_2\text{SnBr}_2]_2(\text{Et}_4\text{N})2 \) while \( \text{[Me}_2\text{SnBr}_3](\text{Et}_4\text{N}) \) is exclusively formed in water. Extensive studies have been reported on selective anion binding capability of "tailormade" organotin hosts with high nuclearity tin centers as Lewis acids [4]. This has led to the isolation of wide structural diversity of diorganostannate derivatives. In contrast, anionic derivatives bearing functional ligands other than halogen on the tin atom are much less known. The identity of"ate" complexes, \( \text{[Bu}_2\text{SnL}_2\text{H}]\text{Li} \) and \( \text{[Bu}_2\text{SnL}_2\text{HBr}]\text{MgBr} \) generated in situ has been gleaned by \(^{119}\text{Sn} \text{NMR spectroscopy and their utility in regio/stereoselective reduction of various enals and aliphatic alkynes has been reported [5]. The diorganostannates bearing carboxylate ligands such as, } \text{^A}\text{Sn} \text{tC}_7\text{H}_3\text{C}_3\text{Is}^\text{A}-\text{X}^\text{N} \text{(X = Cl, F)}^\text{3-} \) [6] and \( \text{[Me}_2\text{Sn(OAc)}_3]\text{Me}_2\text{N} \) [7] have also been structurally characterized and examined for their antitumor activity.

In recent years, we have been interested in the development of new synthetic strategies for functional organotin derivatives and reported on the preparation
and structural characterization of (hydroxy)diorganotin (IV)methanesulfonates, \( R_2\text{Sn(OH)OSO}_2\text{Me} \) (\( R = \text{n-Pr}, \text{N-BU}, \text{etc.} \)) [8]. The reaction chemistry of these bifunctional tin compounds has attracted our attention. It has been demonstrated that the selective dehydration reaction involving Sn-OH group with carboxylic acids results in the isolation of diorganotin carboxylates [9], which are not accessible by classical route. Another interesting aspect concerns the reactivity of these tin precursors towards the ionic nucleophiles. In the present work, preliminary investigations on this aspect have been undertaken. While the reaction of 1a or 1b with \( \text{Bu}_4\text{NNO}_3 \) results in the isolation of novel diorganotin carboxylates, \( 2a \) or \( 2b \), the use of strong nucleophiles such as \( \text{Bu}_4\text{NX} \) (\( X = \text{F}, \text{OAc} \)) and \( \text{RLi} \) (\( R = \text{N-BU}, \text{Me} \)) favor ionic metathesis reaction involving Sn-\( \text{OSO}_2\text{Me} \) bond cleavage. The results obtained from these studies are reported herein.

2. Results and discussion

The synthesis of \( [R_2\text{Sn(l-OH)(OSO}_2\text{Me)(ONO}_2\text{)}]_2 \) \( 2\text{Bu}_4\text{N} \) (\( R = \text{n-Pr (2a)}, \text{N-BU (2b)} \)) is accessible from the reaction of (hydroxy)diorganotin methanesulfonates (1a or 1b) with one equivalent of tetra-n-butylammonium nitrate (Eq. (1)). These compounds are moderately sensitive to moisture and are soluble in common organic solvents such as chloroform, dichloromethane, methanol, acetonitrile, etc.

\[
2R_2\text{Sn(OH)(OSO}_2\text{Me)(ONO}_2\text{)}]_2 + 2\text{Bu}_4\text{NNO}_3 \rightarrow \text{R} = \text{n-Pr, n-Bu}
\]

The single crystals of \( 2b \) suitable for X-ray structure were obtained upon cooling solution of the compound in dichloromethane at 4 °C for several days. The compound crystallizes with two independent molecules in the unit cell of which only one is shown in Fig. 1. The relevant crystal data are given in Table 1, while selected bond distances and angles are given in Table 2. The anion in each molecule adopts a centrosymmetric hydroxy-bridged dimeric structure with highly distorted octahedral geometry around each tin atom. The SnO\( _4 \) coordination sphere formed by two bridging OH, a monodentate methanesulfonate and a nitrate group is planer (360° ± 1). Principle differences between the two molecules in the unit cell appear in the Sn-O (methanesulfonate and nitrate) bond distances and O-Sn-O/C-Sn-C angles. A comparison of these metrical parameters with those of the precursor Sn-O (methanesulfonate) = 2.410(4) Å [8] reveals significant elongation of Sn-O (methanesulfonate) bond distance in the stannate \( \text{Sn(1A)-O(2A)} = 2.451(6) \text{Sn(1B)-O(2B)} = 2.552(7) \text{Å} \) and suggests appreciable ionic character. The angle C(5A)-Sn(1A)-C(1A) = 159.6(3)°/C(5B)-Sn(1B)-C(1B) = 153.3(4)° is much larger than observed in the tin precursor 1b [C-Sn-C = 151.4(3)°].

Secondary interactions such as intramolecular hydrogen bonding [O(3A)-••H-O(1A) = 2.694 Å, O(3B)-••H-O(1B) = 2.780 Å] as well as intermolecular C-H••O...
The products obtained in these reactions are shown as:
pathway involving the cleavage of Sn-OSO₂Me bond. Reactions invariably proceed via an ionic metatheses tin precursors. This is evident by studying the reactions found to substantially alter the reaction chemistry of the NO₃⁻ ion.

A change in the ¹¹⁹Sn NMR values was observed upon addition of another equivalent amount of Bu₄NX to 1a or 1b suggesting that the tin precursor binds only one NO₃⁻ ion.

Nucleophilicity of the anionic reagents has been found to substantially alter the reaction chemistry of the tin precursors. This is evident by studying the reactions of 1b with Bu₄NX (F, OAc) or RLi (n-Bu, Me). These reactions invariably proceed via an ionic metatheses pathway involving the cleavage of Sn-OSO₂Me bond. The products obtained in these reactions are shown as:

| Bond lengths | | |
| Sn(1A)-C(1A) | 2.130(8) | Sn(1B)-C(1B) | 2.150(9) |
| Sn(1A)-O(1A) | 2.130(5) | Sn(1B)-O(1B) | 2.136(5) |
| Sn(1A)-C(5A) | 2.117(8) | Sn(1B)-C(5B) | 2.105(9) |
| Sn(1A)-O(5A) | 2.418(5) | Sn(1B)-O(5B) | 2.383(6) |
| Sn(1A)-O(2A) | 2.451(6) | Sn(1B)-O(2B) | 2.552(7) |
| Sn(1A)-O(1A)#1 | 2.118(5) | Sn(1B)-O(1B)#2 | 2.104(6) |

| Bond angles | | |
| C(5A)-Sn(1A)-C(1A) | 159.6(3) | C(5B)-Sn(1B)-C(1B) | 153.3(4) |
| O(1A)#1-Sn(1A)-O(1A) | 71.8(2) | O(1B)#2-Sn(1B)-O(1B) | 71.83(3) |
| O(1A)-Sn(1A)-O(5A) | 74.95(18) | O(1B)-Sn(1B)-O(5B) | 74.2(2) |
| O(5A)-Sn(1A)-O(2A) | 130.95(18) | O(5B)-Sn(1B)-O(2B) | 136.6(2) |
| O(1A)#1-Sn(1A)-O(2A) | 82.4(2) | O(1B)-Sn(1B)-O(2B) | 77.5(2) |

*#1 -x, y+1, -z, #2 -x, -y, z+1.

The identity of these products has been confirmed by comparison of IR, ¹H, and ¹¹⁹Sn NMR spectral data with those of the known compounds previously reported in literature [14].

A final comment concerns the formation of the stannates, 2a and 2b. Complexation of the NO₃⁻ ion to the tin center of 1a or 1b can be rationalized by considering coordinative dissociation of bridging bidentate methanesulfonate in the tin precursors [8]. It appears that the nucleophilicity of NO₃⁻ and MeSO₃⁻ ions being comparable [15] inhibits the ionic metathesis pathway. Nevertheless, the use of organometallic reagents such as RLi may also be of significant synthetic utility in the formation of mixed triorganotin oxides. This aspect is presently being investigated in our laboratory.

3. Experimental

All reactions were conducted in an inert atmosphere of nitrogen. Solvents were dried using standard techniques (dichloromethane and n-hexane over P₂O₅, diethyl ether over sodium benzenophene). Glassware was dried in an oven at 110-120 °C and further flame dried under vacuum prior to use. The precursors, (hydroxy)di-n-propyl/di-n-butyltin(IV)methanesulfonates [8] and di-n-propyltin oxide [16] were prepared using literature methods, while the reagents such as Bu₄NX (X = NO₃, F, OAc) and RLi (R = Bu, Me) were obtained commercially (Aldrich). ¹H, ¹³C and ¹¹⁹Sn NMR spectra.
were recorded on Bruker DPX-300 at 300, 75.46 and 111.88 MHz, respectively. $^1$H and $^{13}$C chemical shifts are quoted with respect to the residual protons of the solvent, while $^{119}$Sn NMR data are given using tetramethylditin as internal standard. The IR spectra were recorded on Nicolet protege 460 E.S.P. spectrophotometer using KBr optics. Elemental analysis (C, H and N) was performed on a Perkin-Elmer model 2400CHN elemental analyzer. Tin was estimated gravimetrically [17].

3.1. Reactions of (hydroxy)diorganotin methanesulfonate with tetrabutylammonium nitrate

To a stirred suspension of (hydroxy)di-n-propyltin(IV)methanesulfonate (0.69 g, 2.16 mmol) or (hydroxy)di-n-butyltin(IV)methanesulfonate (0.75 g, 2.16 mmol) in dichloromethane (~50 ml) was added a solution of Bu$_4$NNO$_3$ (0.65 g, 2.16 mmol) in the same solvent. The clear reaction mixture was stirred for 12-15 h, at room temperature. The resulting solution was concentrated under vacuum and n-hexane was added. A white solid, thus obtained in each case was filtered and dried in vacuum.

3.1.1. [n-Pr$_2$Sn(l-OH) (OSO$_2$Me) (ONO$_2$)$_2$] Bu$_4$N(2a)

Yield: (85%), m.p. 80-83 °C. $^1$H NMR (CDCl$_3$): $\delta$ 3.33 (t, 8H, NCH$_2$), 2.77 (s, 3H, SME), 1.78 (m, 16H, Sn(CH$_2$)$_2$ + NCH$_2$CH$_2$), 1.50 (m, 8H, N(CH$_2$)$_2$CH$_2$), 1.01 (t, 18H, Sn(CH$_2$)$_2$CH$_3$ + N(CH$_2$)$_2$CH$_3$). $^{13}$C($^1$H) NMR (CDCl$_3$): 58.3 (NCH$_2$), 39.2 (SME), 29.2 (SnCH$_2$), 18.1 (SnCH$_2$), 122 (Sn(CH$_2$)$_2$CH$_3$ + N(CH$_2$)$_2$CH$_3$), 23.5 (NCH$_2$CH$_2$), 19.3 (N(CH$_2$)$_2$CH$_2$). $^{119}$Sn NMR (CDCl$_3$): $\delta$ 155, 159, 191, 234. IR (KBr, cm$^{-1}$): 3420 (mOH), 1487, 1386 (mNO$_2$), 1209, 1054 (mSO$_2$), 784 (SMe) Anal. Calc. for C$_3$H$_8$N$_2$O$_2$Sn: C, 44.37; H, 8.68; N, 4.50; Sn, 19.29. Found: C, 44.10; H, 8.75; N, 4.61; Sn, 19.91%.

3.1.2. [n-Bu$_2$Sn(l-OH) (OSO$_2$Me) (ONO$_2$)$_2$] Bu$_4$N(2b)

Yield: (90%), m.p. 72-75 °C. $^1$H NMR (CDCl$_3$): $\delta$ 3.33 (t, 8H, NCH$_2$), 2.77 (s, 3H, SME), 1.65 (m, 16H, Sn(CH$_2$)$_2$ + NCH$_2$CH$_2$), 1.45 (12H, N(CH$_2$)$_2$CH$_2$ + Sn(CH$_2$)$_2$CH$_2$), 1.03 (t, 12H, N(CH$_2$)$_2$CH$_2$), 0.93 (t, 6H, Sn(CH$_2$)$_2$CH$_2$). $^{13}$C($^1$H) NMR (CDCl$_3$): $\delta$ 58.3 (NCH$_2$), 39.2 (SME), 26.5 (SnCH$_2$), 23.5 (SnCH$_2$CH$_2$ + NCH$_2$CH$_2$), 18.1 (SnCH$_2$), 12.2 (SnCH$_2$CH$_2$ + N(CH$_2$)$_2$), 23.5 (NCH$_2$CH$_2$), 19.3 (SnCH$_2$CH$_2$CH$_2$ + N(CH$_2$)$_2$CH$_2$). $^{119}$Sn NMR (CDCl$_3$): $\delta$ 157, 159, 194, 234. IR (KBr, cm$^{-1}$): 3400 (mOH), 1487, 1384 (mNO$_2$), 1210, 1058 (mSO$_2$), 784 (SMe) Anal. Calc. for C$_{25}$H$_{33}$N$_2$O$_3$Sn: C, 46.15; H, 8.92; N, 4.30; Sn, 18.46. Found: C, 46.91; H, 8.33; N, 4.21; Sn, 18.01%.

3.2. Reactions of (hydroxy)di-n-butyltin methanesulfonate with Bu$_4$NX ($X = F^-, OAc^-$)

To a stirred suspension of (hydroxy)di-n-butyltin methanesulfonate, 1b (0.62 g, 1.79 mmol) in dichloromethane was added Bu$_4$NF (1.79 ml (1.0 M/THF), 1.79 mmol). The resulting clear solution was stirred for 8-10 h at room temperature. Thereafter the reaction mixture was concentrated under vacuum and diethyl ether was added to precipitate a white solid identified as tetra-n-butyl ammonium methanesulfonate, Bu$_4$NOSO$_2$Me. Solvent was evaporated from the ether solution to afford [Bu$_4$Sn(F)]$_2$O as a white solid. The reaction of 1b (0.62 g, 1.79 mmol) with Bu$_4$N(OAc) (0.53 g, 1.79 mmol) was performed by following a similar procedure as above. n-Hexane was added to precipitate the salt Bu$_4$NOSO$_2$Me which was filtered and dried under vacuum. The compound [Bu$_4$Sn(OAc)]$_2$O was isolated from the concentrated hexane solution as a white solid.

3.2.1. Bu$_4$NOSO$_2$Me

Yield: (45%), $^1$H NMR (CDCl$_3$): d 3.31 (t, 8H, NCH$_2$), 2.75 (s, 3H, SME), 1.66 (m, 8H, NCH$_2$CH$_2$), 1.44 (m, 8H, N(CH$_2$)$_2$CH$_2$) 1.01 (t, 12H, CH$_3$), IR (KBr, cm$^{-1}$): 2960, 2932 (mCH), 1240, 1193, 1058 (mSO$_2$), 784 (SMe) Anal. Calc. for C$_3$H$_6$N$_2$O$_3$: C, 60.53; H, 11.57; N, 4.15; Found: C, 61.01; H, 11.43; N, 4.21%.

3.2.2. [Bu$_4$Sn(F)$_2$]O

Yield: (41%), m.p. 137-140 °C (Lit. 140 °C). $^1$H NMR (CDCl$_3$): d 0.92 (t, 6H, CH$_3$), 1.20 (m, 8H, CH$_2$CH$_2$), 1.54 (m, 4H, SnCH$_2$). $^{119}$Sn NMR (CDCl$_3$): $\delta$ 160. IR (KBr, cm$^{-1}$): 2959, 2928, 2857 (mCH), 1660 (mSn-O-Sn). Anal. Calc. for C$_3$H$_3$O$_2$F$_2$Sn$_2$: C, 36.78; H, 6.89. Found: C, 36.60; H, 6.75%.

3.2.3. [Bu$_4$Sn(OAc)$_2$]O

Yield: (51%), m.p. 52-53 °C (Lit. 54 °C). $^1$H NMR (CDCl$_3$): d 1.89 (s, 3H, OAc), 0.86 (t, 6H, CH$_3$), 1.30 (m, 8H, CH$_2$CH$_2$), 1.57 (m, 4H, SnCH$_2$). $^{119}$Sn NMR (CDCl$_3$): $\delta$ 215, 226. IR (KBr, cm$^{-1}$): 2961, 2926, 2870 (mCH), 1636, 1559 (mCO$_2$), 1372 (mCO$_2$), 639 (mSn-O-Sn) Anal. Calc. for C$_2$H$_4$O$_2$Sn$_2$: C, 39.86; H, 6.97. Found: C, 39.60; H, 6.74%.

3.3. Reactions of (hydroxy)di-n-butyltin methanesulfonate (1b) with RLi (R = n-Bu, Ph)

To a stirred solution of 1b (0.75 g, 2.16 mmol) in diethyl ether (~75 ml) was added n-BuLi (3.45 ml, 16 M/hexane, 2.16 mmol) or MeLi (2.16 ml, 10 M/THF, 2.16 mmol) at 25 °C. The reaction mixture was stirred for 12 h and subsequently hydrolyzed by 25 ml of water. The organic layer was extracted in each case and kept on anhydrous sodium sulfate. Evaporation of solvent ether
gave (Bu3Sn)2O or (Bu2Me)2SnO as colorless viscous liquids.

3.3.1. \((Bu3Sn)2O\)

Yield: (55%): b.p. 205-210 °C/10 mm (Lit. 210-214 °C/10 mm). \(^1^H\) NMR (CDCl3): d 0.90 (t, 6H, CH₃), 1.37 (m, 8H, (CH₂)₂CH₃), 1.65 (m, 4H, SnCH₂). \(^1^9^7^7^9\)Sn NMR (CDCl3): d 85.6. IR (KBr, cm⁻¹): 2961, 2926, 2870 (mCH), 689 (mSn-O-Sn). Anal. Calc. for C4H5SnO2: C, 48.16; H, 8.17. Found: C, 47.95; H, 8.21%.

3.3.2. \((Bu3MeSn)2O\)

Yield: (50%): b.p. 180-185 °C/10 mm. \(^1^H\) NMR (CDCl3): d 0.91 (t, 6H, CH₃), 1.40 (m, 8H, (CH₂)₂CH₃), 1.71 (m, 4H, SnCH₂), 1.85 (s, 3H, SnCH₃). \(^1^9^7^7^9\)Sn NMR (CDCl3): d 95.0. IR (KBr, cm⁻¹): 2963, 2927, 289 (CH), 680 (mSn-O-Sn). Anal. Calc. for C12H14O2Sn2: C, 42.02; H, 8.17. Found: C, 42.11; H, 8.10%.

3.4. X-ray crystallography

A colorless, block shaped crystal was mounted along with the largest dimension and data were collected on a Bruker SMART APEX diffractometer equipped with a molybdenum sealed tube and a highly oriented graphite monochromator. There were no systematic absences in the data, therefore space group \(P\bar{i}\) was assumed and data, therefore space group \(P\bar{i}\) was assumed and corrected to \(P\bar{i}\).

3.5. References

4. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 204117 for compound 2b. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EC, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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