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Recipe for New Diorganostannates, $[R_2Sn(OS(O)_2R^1)_4]^{2-}$, Bearing Alkanesulfonate Groups Using Dialkyl Sulfite as the Reagent

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A one-pot reaction between di-*n*-propyl/di-*n*-butyltin oxide, dialkyl sulfite, and triethylamine or tetra-*n*-alkylammonium iodide proceeds under ambient conditions (110–120 °C, 20 h) via sulfur-centered Arbuzov rearrangement to afford the corresponding dianionic tetraalkanesulfonato diorganostannates $[R_2Sn(OSO_2Me)_4]\cdot 2Et_3NMe$ [R = *n*-Pr (**1**), *n*-Bu (**2**)] as well as $[n\text{-}Bu_2Sn(OSO_2R^1)_4]\cdot 2R^2_4N$ [R^1 = Me, Et, *n*-Pr; R^2 = Et (**3**, **5**, and **7**), *n*-Bu (**4**, **6**, and **8**)]. X-ray crystal structures of **2** and **3** reveal a monomeric motif of the dianion, with methanesulfonate groups acting as unidentate ligands. The ^{119}Sn NMR spectral studies suggest the existence of pentacoordinated tin species in solution.

Anionic organotin derivatives, also termed “stannates”, have been extensively studied in the past.[1] The Lewis acidic nature of tetracoordinated tin as well as its affinity to expand its coordination number to 5, 6, or 7 has been frequently utilized for the synthesis of many stable mono-, di-, and triorganostannates with a variety of substituents such as halogens,[2] carboxylates,[3] fluoro/chlorosulfates,[4] etc., on the tin center. Studies have also been reported on the selective anion binding capability of “tailor-made” organotin hosts with high-nuclearity tin centers as Lewis acids.[5] The identity of in situ generated pentaorganostannates such as $[Me_5Sn]^-Li$ and $[Me_{5-m}Ph_mSn]^-Li$ has been gleaned by NMR spectroscopic studies and implicates these hypervalent intermediates in the reactions involving Li/Sn exchange.[6] The utility of the tin “ate” complexes $[Bu_2SnI_2H]Li$ and $[Bu_2SnIHBr]MgBr$ generated in situ has been reported in regio/stereoselective reduction of various enals and aliphatic alkynes.[7]

In recent years, we have undertaken a systematic study to unveil the synthetic, structural, and bonding aspects of mixed-ligand diorganotinalkanesulfonate derivatives. In this context, we reported a novel synthetic protocol for diorganotin(alkoxy)(alkanesulfonate)s (Chart 1) involving dialkyl sulfite as the reagent.[8] This approach proved to be very convenient to directly generate the alkanesulfonate moiety from dialkyl

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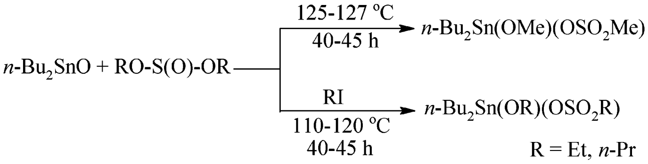
Chart 1



sulfite via sulfur-centered Arbuzov rearrangement. The reactivity behavior of this class of tin ester derivatives has been studied in some detail.[8,9] In this context, the synthesis of the first structurally authenticated example of dimeric, trifunctional diorganostannate salts, $[R_2Sn(OH)(OSO_2Me)(NO_3)]_2{\cdot}2Bu_4N$ (R = *n*-Bu, *n*-Pr), has been achieved by the addition reaction between diorganotin(hydroxy)methanesulfonate and tetra-*n*-butylammonium nitrate.[9c] The formation of these stannates has been rationalized by considering comparable nucleophilicity of the nitrate and methanesulfonate ions, which prevents an ionic metathesis pathway.

The work presented herein relates to the synthesis and structural characterization of new bis(tetraalkylammonium) diorganostannates, $[R_2Sn(OSO_2R^1)_4]{\cdot}2R^2{}_4N$ (**1**−**8**), and further underlines the scope of dialkyl sulfite as the reagent for tin−alkanesulfonate bond formation. A viable route to the stannates **1**−**4** involves a one-pot reaction between di-*n*-propyl/di-*n*-butyltin oxide and dimethyl sulfite in the presence of 2 equiv of either triethylamine or tetraalkylammonium iodide, while the analogous stannates **5**−**8** bearing ethane/*n*-propanesulfonate moieties on the tin center are accessible from the reaction of di-*n*-butyltin oxide with diethyl/di-*n*-propyl sulfite only in the presence of tetraalkylammonium iodide (eqs 1 and 2).[10]

$$R_2SnO + 4MeO{-}S(O){-}OMe + 2Et_3N \xrightarrow[20\ \text{h}]{110-120\ ^\circ\text{C}} [R_2Sn\{OS(O)_2Me\}_4]{\cdot}2Et_3NMe + MeOMe \quad [R = n\text{-Pr } (\mathbf{1}),\ n\text{-Bu } (\mathbf{2})] \tag{1}$$

The mechanistic rationale for the sulfur-centered Arbuzov rearrangement in dimethyl sulfite as observed for **1** and **2** parallels those proposed earlier for triethylamine-catalyzed isomerization of dimethyl sulfite, wherein the formation of the $[Et_3NMe][OS(O)OMe]$ ion pair has been suggested as the reactive intermediate, which subsequently undergoes methylation at the sulfur center to yield methyl methanesulfonate.[11] For **3**−**8**, the formation of ethyl ethanesulfonate/*n*-propyl propanesulfonate (**A**) is believed to follow a similar mechanism albeit in the presence of the iodide ion, which promotes C−O bond cleavage in higher dialkyl sulfites. This proposition as well as the proposed intermediates such as **B** and **C** finds analogy with those reported earlier for the reaction between di-*n*-butyltin oxide, diethyl/di-*n*-propyl sulfite, and alkyl iodide (Chart 2).[8] In the present case, it is believed that the presence of a quaternary ammonium ion seems to be the driving force for subsequent addition of alkanesulfonate groups on the tin center associated with the intermediate **C** to afford stable diorganostannates, **3**−**8**.

$$n\text{-}Bu_2SnO + 4R^1O{-}S(O){-}OR^1 + 2R^2{}_4NI \xrightarrow[20\ \text{h}]{110-120\ ^\circ\text{C}} [n\text{-}Bu_2Sn\{OS(O)_2R^1\}_4]{\cdot}2R^2{}_4N + 2R^1I + R^1OR^1 \quad [R^1 = Me,\ R^2 = Et\ (\mathbf{3}),\ n\text{-Bu}\ (\mathbf{4});\ R^1 = Et,\ R^2 = Et\ (\mathbf{5}),\ n\text{-Bu}\ (\mathbf{6});\ R^1 = n\text{-Pr},\ R^2 = Et\ (\mathbf{7}),\ n\text{-Bu}\ (\mathbf{8})] \tag{2}$$

The identities of **1**−**8** have been established by IR, multinuclear (^{1}H, ^{13}C, and ^{119}Sn) NMR, and electrospray ionization mass spectrometry (ESI-MS; negative mode) spectral data. The $\nu(SO_3)$ absorptions appear at 1050−1060 and 1180−1200 cm^{-1} in the IR spectra of all of the compounds. For **1**−**4**, the ^{1}H NMR spectra reveal a singlet at δ 2.8−3.0 due to SCH_3 protons, whereas a quartet (for **5** and **6**) and a triplet (for **7** and **8**) at δ 2.8−3.0 ($^3J_{H-H}$ = 6.6−7.8 Hz) are ascribed to SCH_2 protons. The corresponding $^{13}C\{^1H\}$ NMR resonances appear at δ 39.1−53.7. For **1** and **2**, the presence of an N−Me group is confirmed by characteristic ^{1}H and ^{13}C NMR signals at δ 3.1 and 46.2−46.5, respectively, while the corresponding signals for the NCH_2 moiety appear at δ 3.2−3.5 ($^3J_{H-H}$ = 7.2−8.2 Hz) and 51.8−58.5 in the spectra of all of the compounds. The integral intensity of ^{1}H NMR signals for each compound is consistent with the proposed composition. ^{119}Sn NMR spectra in a $CDCl_3$ solution at room temperature display a single resonance at δ −291 to −328 for **1**−**4** and δ −242 to −265 for **5**−**8**. The solid-state ^{117}Sn NMR spectra (cross-polarization magic-angle-spinning) for compounds **2**, **6**, and **8** exhibit isotropic chemical shift values at δ −413, −394, and −399, respectively. These values are found to be shifted significantly upfield ($\Delta\delta$ = 114−136) in comparison to those found in the solution state. These results suggest the existence of pentacoordinated tin species in solution.[2b,12] An attendant argument that the octahedral geometry found in the solid state is not retained in solution comes from the $^1J(^{13}C-^{119}Sn)$ coupling constants for the *n*-butyl groups. Calculation of the C−Sn−C bond angle,[13] according to $|^1J(^{13}C-^{119}Sn)| = 9.99\ (\pm 0.73)\Theta - 746\ (\pm 100)$ for *n*-Bu_2Sn compounds, leads to values of 147° (±10°) for compounds **1**−**4** and of 138° (±10°) for compounds **5**−**8**, in contrast to the nearly

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(10) In a typical procedure, di-*n*-propyl/di-*n*-butyltin oxide (0.75/0.85 g, 3.39 mmol), dimethyl sulfite (3.73 g, 33.90 mmol), and triethylamine (0.69 g, 6.78 mmol) was refluxed at 110−120 °C for 3−4 h under a nitrogen atmosphere, resulting in complete dissolution of the diorganotin oxide. The reaction mixture was heated for another 16 h to ensure completion of the reaction. The contents were cooled to room temperature, and diethyl ether (30 mL) was added to precipitate a white solid in each case and identified as **1** and **2**, respectively. Following the same procedure as that above, the reaction of di-*n*-butyltin oxide (0.50 g, 2.01 mmol), dimethyl/diethyl/di-*n*-propyl sulfite (2.21/2.77/3.34 g, 20.10 mmol), and tetraethyl/tetra-*n*-butylammonium iodide (1.03/1.48 g, 4.02 mmol) affords the corresponding stannates **3**−**8**.

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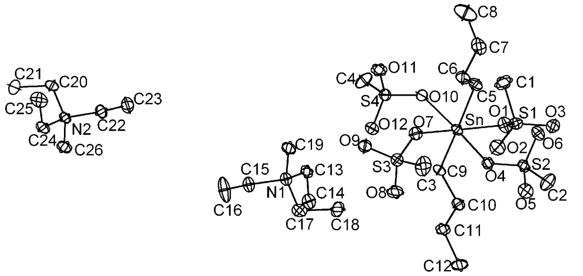
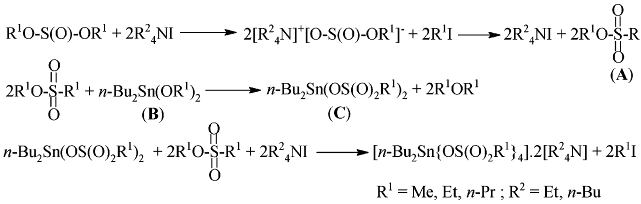


Figure 1. Crystal structure of **2**. The thermal ellipsoids are set at 30% probability, and the hydrogen atoms are omitted for clarity. Selected bond length (Å) and angles (deg): O1−Sn 2.268(18), O4−Sn 2.226(17), O7−Sn 2.197(18), O10−Sn 2.293(17), C5−Sn 2.110(3), C9−Sn 2.106(2); O4−Sn−O1 86.56(6), O7−Sn−O4 87.08(6), O7−Sn−O10 88.49(6), O1−Sn−O10 97.86(6), C9−Sn−C5 170.09(10).

Chart 2



trans disposition of the *n*-butyl groups with a C−Sn−C angle of 170.09(10)° (vide infra) in the crystal structure of compound **2**. The negative ion ESI-MS spectrum of each compound in an acetonitrile solution shows an isotopic cluster pattern corresponding to the $[R_2Sn(OSO_2R^1)_3]^-$ ion as the predominant peak.

The single-crystal X-ray diffraction analysis of **2** and **3** reveals that the structural motif of the dianion in each case is identical and consists of a discrete monomer in which the tin atom adopts a distorted octahedral geometry by virtue of four uniquely disposed monodentate methanesulfonate groups, with the SnO_4 core defining the basal plane ($360 \pm 0.01°$ for **2** and $360 \pm 0.11°$ for **3**). The ORTEP view of **2** is shown in Figure 1. The *n*-butyl groups adopt nearly trans disposition with C−Sn−C angles of 170.09(10)° (for **2**) and 169.38(6)° (for **3**). The Sn−O$_{\text{methanesulfonate}}$ bond lengths (2.19−2.29 Å) are comparable with those observed for polymeric di-*n*-butyltin bis(methanesulfonate) [Sn−O = 2.272(11) Å][9b] and lie at the upper end of the normal range accepted for the Sn−O covalent bond (1.9−2.1 Å).[14] The presence of methanesulfonate groups in the dianionic stannate moiety is a clear manifestation of the occurrence of sulfur-centered Arbuzov rearrangement in dimethyl sulfite. The metrical parameters associated with tetraalkylammonium cations are quite similar to those reported earlier.[2d,3a]

In conclusion, the synthesis of dianionic stannates **1**−**8** bearing methane/ethane/*n*-propanesulfonate groups on the tin center has been achieved by utilizing the affinity of dialkyl sulfites to isomerize into the corresponding alkanesulfonate moiety in the presence of triethylamine or tetraalkylammonium iodide. These stannates are considered as important additions to the rare family of tin−alkanesulfonate derivatives with exclusive monodentate bonding of the alkanesulfonate groups. We are currently investigating the synthesis and structural aspects of related stannates derived from mono- and triorganotin precursors.

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Supporting Information Available: Spectroscopic data for **1**−**8**, ORTEP view of **3**, and X-ray crystallographic data in CIF format [for CCDC-660450 (**2**) and CCDC-660449 (**3**)]. This material is available free of charge via the Internet at http://pubs.acs.org.

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