Inorg. Chem. **2006**, *45*, 9166–9168

Inorganic Chemistry
Communication

Expanding the Scope of Sulfur-Centered Arbuzov Rearrangement in Diethyl/Di-*n*-propyl Sulfite for the Synthesis of Mixed-Ligand Di-*n*-butyltin Alkanesulfonates[†]

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Received July 24, 2006

A one-pot reaction between di-*n*-butyltin oxide and diethyl/di-*n*-propyl sulfite in the presence of an equimolar amount of alkyl iodide proceeds via sulfur-centered Arbuzov rearrangement to afford the corresponding di-*n*-butyltin (alkoxy)alkanesulfonates $n\text{-}Bu_2Sn(OR')OS(O)_2R$ [R = R′ = Et (**1**), *n*-Pr (**2**); R = Me, R′ = Et (**3**), *n*-Pr (**4**)]. The compounds **1** and **3** react with methylphosphonic acid under mild conditions to give $[n\text{-}Bu_2Sn(OS(O)_2R)OP(O)(OH)Me]_n$ [R = Et (**5**), Me (**6**), respectively].

Organotin sulfonates represent an important family of organotin ester derivatives with a number of applications in organic synthesis.[1] Their catalytic activity is primarily associated with the weakly coordinating nature of the sulfonate ion, which makes its coordination mode very flexible and sensitive to the chemical environment around the Lewis acidic tin center. Recently, a number of diorganotin triflate assemblies including oxotin cations have been isolated and their structural characterization reveals a variety of associated motifs such as coordination polymers and supramolecular arrays by virtue of the ubiquitous coordination behavior of the ligand.[2] A few related structurally authenticated examples of diorganotin esters derived from sterically hindered mono- and disubstituted arenesulfonic acids emphasize the role of hydrogen bonding in the construction of supramolecular motifs.[3] These are generally prepared by dehydration reaction of the appropriate sulfonic acid with diorganotin oxide or treatment of diorganotin halides with the silver salt of the sulfonic acid, although other methods such as solvolysis or insertion reaction between tetraorganotin and SO_3 are also known.[4]

On the other hand, the chemistry of organotin sulfonates derived from alkanesulfonic acids still remains in a state of dormancy, despite the first reported synthesis of dialkyltin bis(ethanesulfonate) by Anderson in 1962.[5] It has been our endeavor to develop new synthetic protocols for diorganotin alkanesulfonates associated with a co-ligand of ambidentate character. In this context, we have recently reported the synthesis of (methoxy)diorganotin methanesulfonates from a one-pot reaction between diorganotin oxide and dimethyl sulfite (eq 1). Interestingly, these reactions proceed via Arbuzov-type rearrangement at the sulfur center in dimethyl sulfite. These compounds react chemoselectively with protic ligands such as β-diketones and carboxylic acids to afford new mixed-ligand diorganotin methanesulfonates, $R_2Sn(X)OSO_2Me$ (X = acac, carboxylate).[6]

$$R_2SnO + MeOS(O)OMe \xrightarrow[40-45\ \text{h}]{125-127\ °\text{C}} R_2Sn(OMe)OS(O)_2Me \tag{1}$$
$$R = n\text{-Pr},\ n\text{-Bu},\ i\text{-Bu},\ c\text{-Hx}$$

These results have stimulated our research interest toward exploring the synthetic utility of this procedure and expanding the scope of higher dialkyl sulfites in the synthesis of

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[†] Dedicated to Professor Suraj P. Narula.

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10.1021/ic061377u CCC: $33.50

mixed-ligand organotin alkanesulfonate derivatives. Following our earlier approach,[6a] a direct reaction between di-*n*-butyltin oxide and excess diethyl/di-*n*-propyl sulfite was investigated under thermal conditions (130−140 °C). It was observed that no reaction occurred even after prolonged heating for 72 h. Surprisingly, however, these reactions, when carried out in the presence of 1 equiv of ethyl/*n*-propyl iodide, proceed smoothly under mild conditions and provide a useful one-pot synthetic route to the corresponding di-*n*-butyltin (alkoxy)alkanesulfonates **1** and **2**, respectively (eq 2). It is striking to note that analogous reactions between di-*n*-butyltin oxide, diethyl/di-*n*-propyl sulfite, and methyl iodide afford the formation of di-*n*-butyltin (alkoxy)methanesulfonates **3** and **4** (eq 3). The presence of an alkanesulfonate group in **1**−**4** strongly suggests the occurrence of sulfur-centered Arbuzov rearrangement in diethyl/di-*n*-propyl sulfite.

$$\mathrm{Bu_2SnO + ROS(O)OR + RI \xrightarrow[40-45\ h]{100-110\ °C} Bu_2Sn(OR)OS(O)_2R} \qquad (2)$$
$$\mathrm{R = Et\ (\mathbf{1}),\ \mathit{n}\text{-}Pr\ (\mathbf{2})}$$

$$\mathrm{Bu_2SnO + ROS(O)OR + MeI \xrightarrow[40-45\ h]{100-110\ °C} Bu_2Sn(OR)OS(O)_2Me} \qquad (3)$$
$$\mathrm{R = Et\ (\mathbf{3}),\ \mathit{n}\text{-}Pr\ (\mathbf{4})}$$

The key mechanistic steps involved in this transformation are conceived to be similar to those reported earlier[6a] for the direct reaction between Bu_2SnO and dimethyl sulfite, where the formation of ion pair $[AMe]^+[OSO_2Me]^-$ [**I**; A = $\{Bu_2Sn(OMe)\}_2O$] has been suggested as the intermediate. Nevertheless, the role of alkyl iodide in the present reactions is indeed intriguing[7] and is not completely understood yet. Brook et al. have reported that quaternary ammonium iodide also catalyzes Arbuzov rearrangement in dimethyl sulfite to afford methyl methanesulfonate.[8] By analogy, it is thus speculated that the formation of **1**−**4** may follow a mechanism in which the formation of the ion pair similar to that of **I** is initiated by iodide-ion-promoted C−O bond cleavage in diethyl/di-*n*-propyl sulfite. The anion subsequently undergoes alkylation at the sulfur center preferentially by the alkyl iodide to produce the corresponding alkyl alkanesulfonate. The latter proposition is expected on the basis of the stronger alkylating power of alkyl iodide in comparison to dialkyl sulfite.[8] Thus, the formation of the methanesulfonate moiety in **3** and **4** may be rationalized by the intermediate formation of ethyl methanesulfonate and propyl methanesulfonate as the reactive species.

The identity of **1**−**4** has been established by IR and multinuclear (^{1}H, ^{13}C, and ^{119}Sn) NMR spectral studies. The ^{1}H NMR spectrum of each compound reveals distinct signals at δ 2.8−2.9 and 3.6−3.7 for SCH_2/SCH_3 and OCH_2 protons arising from alkanesulfonate and alkoxy groups, respectively. The observed 1:1 integral ratio of these groups corroborates well with the composition of **1**−**4**. The corresponding ^{13}C{^{1}H} NMR resonances for these groups appear at δ 46.20/61.48 (for **1**), 53.89/67.66 (for **2**), 39.44/61.54 (for **3**), and 39.60/67.27 (for **4**). ^{119}Sn NMR spectra in a $CDCl_3$ solution display a single resonance in each case in a narrow chemical shift region (^{119}Sn NMR: δ −180 to −182). These results along with ^1J (^{119}Sn−^{13}C) data (580−593 Hz) are consistent with those observed for di-*n*-butyltin (methoxy)methanesulfonate[6a] and suggest an associated structure for these compounds by virtue of the presence of strong coordinating ligands. It must be mentioned that structural motifs of these compounds could not be established because of the lack of suitable quality crystals for X-ray crystallography. Nevertheless, fast atom bombardment (FAB) mass spectra of **1**−**4** reveal structurally important fragment ions that are derived from dimeric/trimeric entities by the predominant loss of OR or R (R = Et or *n*-Pr) groups (see the Experimental Section). For **2** and **3**, the spectral data are convincing in establishing the identity of the monomer from the observed $[M + H]^+$ ions at *m*/*z* 417 and 374, respectively.

The identity of these compounds has been further supported by their reactivity behavior toward oxyphosphorous acid. Thus, the reaction of **1** or **3** with an equimolar quantity of methylphosphonic acid in dichloromethane proceeds under mild conditions to afford the mixed-ligand tin esters **5** and **6** respectively (eq 4). The chemoselective reactivity of the Sn−OEt group in the precursor tin complexes toward methylphosphonic acid is in accordance with the more basic character of the ethoxide group as compared to the alkanesulfonate group. The identity of each compound is established by IR, multinuclear NMR spectroscopy (see the Supporting Information), and X-ray crystallography.

$$\mathrm{Bu_2Sn(OEt)OS(O)_2R \xrightarrow[RT,\ 6\ h]{MeP(O)(OH)_2} Bu_2Sn\{OP(O)(OH)Me\}OS(O)_2R} \qquad (4)$$
$$\mathrm{R = Et\ (\mathbf{5}),\ Me\ (\mathbf{6})}$$

X-ray crystal structures of **5** and **6** reveal the presence of ethanesulfonate and methanesulfonate groups, respectively, and provide strong evidence in favor of sulfur-centered Arbuzov rearrangement in diethyl sulfite during the formation of compounds **1** and **3**. The molecular structures of both **5** and **6** (Figures 1 and 2) correspond to a centrosymmetric dimer based on an eight-membered ring formed by the bridging bidentate mode of the hydrogenmethylphosphonate group [**5**, Sn1−O1 2.067(4) Å, Sn1−O2′ 2.064(3) Å; **6**, Sn1−O1 2.076(6) Å, Sn1−O2′ 2.099(6) Å]. However, significant differences between the two structures arise as a result of varying disposition of the alkanesulfonate group around the tin atoms. For **5**, the ethanesulfonate groups act in the bridging bidentate mode to form a weak bond with a tin atom of the neighboring dimer [Sn1−O4 2.543(4) Å, Sn1−O5′ 2.627(7) Å].[9] This results in the formation of 1-D polymer chains comprising alternate eight-membered rings being formed by the hydrogenmethylphosphonate and ethanesulfonate ligands, respectively. On the other hand, the

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(7) In a control experiment, the reaction between diethyl/di-*n*-propyl sulfite and ethyl/*n*-propyl iodide does not produce the corresponding alkyl alkanesulfonate. For a related reference, see: Bissinger, W. E.; Kung, F. E.; Hamilton, C. W. *J. Am. Chem. Soc.* **1948**, *70*, 3940.

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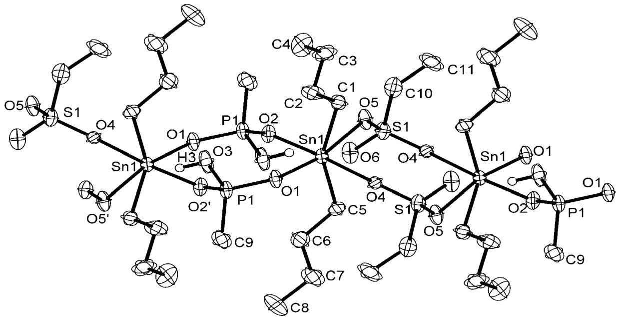

Figure 1. Crystal structure of **5**. The thermal ellipsoids are set at 30% probability, and the hydrogen atoms (except for H3) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn1−O1 2.067(4), Sn1−O2′ 2.064(3), Sn1−O4 2.543(4), Sn1−O5′ 2.627(7); O2′−Sn1−O1 89.28(14), O5′−Sn1−O2′ 78.66(14), O5′−Sn1−O4 112.72(13), O1−Sn1−O4 79.08(13), C1−Sn1−C5 154.0(2).

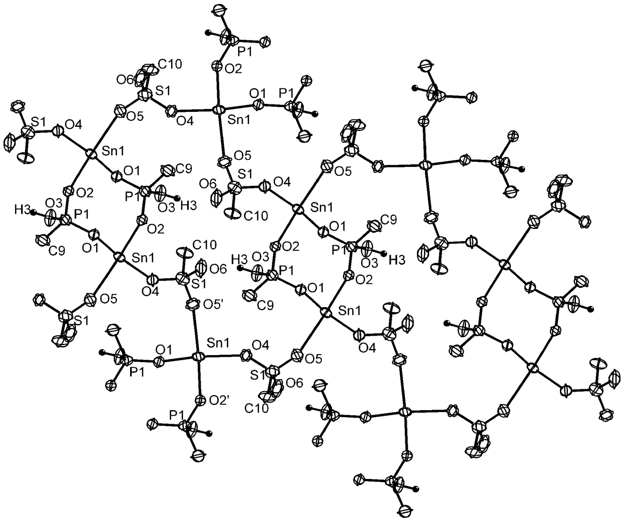

Figure 2. Perspective view of **6** with a molecular sheet parallel to (100) showing the macrocyclic rings. Butyl groups have been omitted for clarity. The thermal ellipsoids are set at 30% probability, and hydrogen atoms (except for H3) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn1−O1 2.076(6), Sn1−O2′ 2.099(6), Sn1−O4 2.471(7), Sn1−O5′ 2.540(7); O1−Sn1−O2′ 89.6(2), O2′−Sn1−O4 85.0(2), O4−Sn1−O5′ 99.9(3), O1−Sn1−O5′ 85.5(3), C1−Sn1−C5 157.2(4).

structure of **6** reveals that the dimeric units are associated with one another by virtue of bridging methanesulfonate groups to give a layer connectivity (parallel to 100) and results in the formation of centrosymmetric 24-membered hexatin macrocyclic rings [Sn1−O4 2.471(7) Å, Sn1−O5′ 2.540(7) Å]. The structures of both **5** and **6** reveal a distorted octahedral geometry around each tin atom, with the basal plane defined by the SnO$_4$ core. The *n*-butyl groups adopt trans disposition with C−Sn−C angles of 154.0(2)° for **5** and 157.2(4)° for **6**. Other metrical parameters for **5** and **6** are consistent with those observed earlier for di-*n*-butyltin bis(methanesulfonate)[6c] and di-*n*-butyltin bis(hydrogenmethylphosphonate).[10] In addition, strong hydrogen-bonding interactions between the hydrogen atom of the hydroxyl group and the oxygen atom of adjacent alkanesulfonate groups are evident [O3−H3 0.82 Å, H3···O6′ 1.83 Å, O3···O6′ 2.629(5) Å, and O3−H3−O6′ 165.3° for **5**; O3−H3 0.82 Å, H3···O6′ 1.81 Å, O3···O6′ 2.588(11) Å, and O3−H3−O6′ 159.0° for **6**].

In conclusion, the work presented herein demonstrates that the reaction between *n*-Bu$_2$SnO and diethyl/di-*n*-propyl sulfite in the presence of an alkyl iodide provides a one-pot synthetic route for the mixed-ligand di-*n*-butyltin (alkoxy)-alkanesulfonates **1**−**4**. A critical step in this approach involves sulfur-centered Arbuzov rearrangement of diethyl/di-*n*-propyl sulfite. These results assume significance in view of the paucity of available synthetic protocols for this class of tin ester derivatives. The isolation of mixed-ligand tin esters **5** and **6** suggests the versatility of these compounds as a synthon for a wide structural variety of organotin alkanesulfonate derivatives. The scope of this new synthetic approach is being further explored in our laboratory.

Acknowledgment. This research was supported by grants from CSIR (India). The financial support from DST (India) for the single-crystal X-ray diffractometer to the Department of Chemistry, Indian Institute of Technology (IIT Delhi), New Delhi, India, is acknowledged. We are grateful to one of the reviewers for useful suggestions. We thank IIT Delhi for providing a Senior Research Fellowship to A.P.S., K. Pavani for crystal data collection, CDRI (Lucknow) for FAB mass spectral data, and SAIF (Panjab University) Chandigarh for ^{119}Sn NMR data.

Supporting Information Available: Synthetic procedures and spectroscopic data for **1**−**6** as well as X-ray crystallographic data in CIF format [for CCDC-611330 (**5**) and CCDC-613251 (**6**)]. This material is available free of charge via the Internet at http://pubs.acs.org.

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