Reactions of Dimethyl Sulfite with Diorganotin Oxides. One-Pot Synthesis of Methoxydiorganotin Methanesulfonates through the Arbuzov Rearrangement, Spectroscopic Characterization of These Compounds and Their Derivatives, and X-ray Crystal Structures of *n*-$Bu_2Sn(X)OS(O)_2Me$ (X = acac, bzbz, OH)

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One-pot reactions of diorganotin oxides, R_2SnO, with dimethyl sulfite under reflux conditions (125−127 °C) proceed via the Arbuzov rearrangement at the sulfur center, yielding the corresponding methoxydiorganotin methanesulfonates, $R_2Sn(OMe)OS(O)_2Me$ [R = *n*-Pr (**1**), *n*-Bu (**2**), *i*-Bu (**3**), c-Hx (**4**)], as white, hygroscopic solids. These compounds react with β-diketones [acetylacetone (Hacac), benzoylacetone (Hbzac), and dibenzoylmethane (Hbzbz)] to afford mixed-ligand organotin derivatives, $R_2Sn(X)OS(O)_2Me$ [X = acac, R = *n*-Pr (**5**), *n*-Bu (**6**); X = bzac, R = *n*-Pr (**7**), *n*-Bu (**8**); X = bzbz, R = *n*-Pr (**9**), *n*-Bu (**10**), *i*-Bu (**11**)]. Selective hydrolysis of the Sn−OMe bond in **1**−**3** occurs, resulting in the isolation of (μ-hydroxo)diorganotin methanesulfonates, $R_2Sn(OH)OS(O)_2Me$ [R = *n*-Pr (**12**), *n*-Bu (**13**), *i*-Bu (**14**)]. All the compounds are characterized by elemental analyses and IR, multinuclear (^1H, ^{13}C, and ^{119}Sn) NMR, and mass spectra. Unequivocal evidence of the presence of the methanesulfonate group is provided by the X-ray crystal structures of **6**, **10**, and **13**. [For **6**: trigonal space group $R\bar{3}$ (No. 148), a = 28.664(1) Å, c = 13.056(1)Å, Z = 18. For **10**: triclinic space group $P\bar{1}$ (No. 2), a = 13.056(3) Å, b = 14.062(3) Å, c = 16.282(3) Å, Z = 4. For **13**: triclinic space group $P\bar{1}$ (No. 2), a = 9.089(2) Å, b = 12.040(2) Å, c =13.894(2) Å, Z = 2]. For **6** and **10**, the solid-state structural analyses reveal dimeric structures with a bridging bidentate methanesulfonate group forming a centrosymmetric eight-membered ring. Compound **13** possesses a polymeric sheet structure with repeating 20-membered macrocycles (including two four-membered $[Sn(OH)]_2$ rings) by virtue of the bridging bidentate methanesulfonate groups. A search for a possible pathway to give Arbuzov-rearranged products **1**−**4** leads us to speculate that there is an initial catalytic transformation of dimethyl sulfite to methyl methanesulfonate via intermediate compounds, $Bu_2Sn(OMe)_2$ (**A**) and $[Bu_2SnOMe]_2O$ (**B**). **A** and **B** subsequently react with methyl methanesulfonate to give **1**−**4**.

Introduction

Dimethyl sulfite is known to exhibit a wide range of reactivities toward various substrates, and its use as alkylating, alkoxylating, acetalizing, and transetherification reagents has been reported for a long time.[1] A few recent reports on the reactivity of dimethyl sulfite under gas-phase conditions described its ubiquitous behavior toward different nucleophiles, the reactivity being largely dependent on the natures and structures of the nucleophilic substrates.[2] Dimethyl sulfite also undergoes isomerization (Arbuzov rearrangement) to methyl methanesulfonate in the presence of organic tertiary amines, methyl iodide, etc. Mechanistic studies of such catalyzed processes have also been reported.[1,3,4]

In spite of the versatility of dimethyl sulfite as a useful reagent, its utility in the domain of organometallic chemistry remains practically unexplored. In our endeavor to understand the behavior of dimethyl sulfite toward organotin reagents of nucleophilic character, we have chosen diorganotin oxides as a case study. Interestingly, the reactions of dimethyl sulfite with diorganotin oxides afford one-pot syntheses of the corresponding methoxydiorganotin methanesulfonates, $R_2Sn(OMe)OS(O)_2Me$ [R = *n*-Pr (**1**), *n*-Bu (**2**), *i*-Bu (**3**), c-Hx (**4**)]. By virtue of the presence of the reactive Sn−OMe bond, these compounds can be easily transformed into hitherto unknown mixed-ligand diorganotin methanesulfonates, $R_2Sn(X)OS(O)_2Me$ [X = β-dik (**5**−**11**), OH (**12**−**14**)]. The results also provide the first example of an organotin compound-mediated Arbuzov rearrangement at the sulfur center. The details are reported herein.

Results and Discussion

Synthetic Methods. The reactions of R_2SnO (R = *n*-Pr, *n*-Bu, *i*-Bu, c-Hx) with excess of dimethyl sulfite under reflux conditions (125−127 °C) were accompanied by slow dissolution of the diorganotin oxides, resulting in clear, homogeneous

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solutions in ~20 h. A longer heating period was optimized to afford the compounds **1**−**4** as white, hygroscopic solids in 56−70% yields (eq 1). These reactions did not take place below

$$R_2SnO + MeOS(O)OMe \xrightarrow{125-127\ ^\circ C,\ 40-45\ h} R_2Sn(OMe)OS(O)_2Me \quad (1)$$
$$\mathbf{1-4}$$

R = *n*-Pr (**1**), *n*-Bu (**2**), *i*-Bu (**3**), c-Hx (**4**)

the reflux temperature of dimethyl sulfite (125−127 °C), while no significant changes in yields were observed at temperatures up to 150 °C.

By virtue of the presence of the reactive Sn−OMe bond, compounds **1**−**4** are found to be excellent precursors to new mixed-ligand diorganotin methanesulfonates. Thus treatment of dichloromethane solutions of **1**−**3** with 1 equiv of acetylacetone (Hacac), benzoylacetone (Hbzac), or dibenzoylmethane (Hbzbz), followed by the usual workup, gave the corresponding (*β*diketonato)diorganotin methanesulfonates, **5**−**11**, in 74−84% yields (eq 2). Compounds **1**−**3** were susceptible to selective hydrolysis

$$R_2Sn(OMe)OS(O)_2Me \xrightarrow[CH_2C_{12},\ room\ temp,\ 4\ h]{\beta\text{-Hdik}} R_2Sn(\beta\text{-dik})OS(O)_2Me + MeOH \quad (2)$$
$$\mathbf{5-11}$$

β-dik	R
acac	*n*-Pr (**5**); *n*-Bu (**6**)
bzac	*n*-Pr (**7**); *n*-Bu (**8**)
bzbz	*n*-Pr (**9**); *n*-Bu (**10**); *i*-Bu (**11**)

of the Sn−OMe bond in moist methanol (95:5 v/v methanol/H_2O) to afford the corresponding (*μ*-hydroxo)diorganotin methanesulfonates, **12**−**14**, in 62−64% yields (eq 3).

$$R_2Sn(OMe)OS(O)_2Me \xrightarrow[room\ temp,\ 24\ h]{methanol/H_2O} R_2Sn(\mu\text{-}OH)OS(O)_2Me \quad (3)$$

R = *n*-Pr (**12**), *n*-Bu (**13**), *i*-Bu (**14**)

Though synthetic procedures involving hemihydrolysis and subsequent condensation to afford stannoxanes are well-established,[5] isolation and structural determination of bifunctional organotin compounds of the type $R_2Sn(OH)X$ (X = Cl, F, I,[6] nitrate,[7] acetate,[8] thiophosphinate/thiophosphonate,[9,10] perchlorate,[11] *N*-sulfonamide,[12] etc.) were achieved only recently. However, there is no report of an organotin analogue with an alkanesulfonate functional group. Compounds **12**−**14** are thus important additions to this family of organotin compounds.

Characterization. All the compounds obtained above are white to pale yellow solids and are soluble in chloroform, dichloromethane, acetonitrile, THF, etc. They have been characterized by IR, multinuclear (^1H, ^{13}C, and ^{119}Sn) NMR, and mass spectra and by elemental analyses (Experimental Section). Selected spectroscopic data are discussed here. ^1H NMR spectra of **1**−**4** reveal a singlet at *δ* 3.60−3.45 due to the OMe group. Another singlet at *δ* 2.85−2.80 is attributed to SMe protons and provides clear evidence of the presence of the methanesulfonate group. ^{119}Sn NMR spectra in $CDCl_3$ show a single resonance in each case with the chemical shifts lying in the range *δ* −178.9 to −181.7 (for **1**−**3**) and at *δ* −262.7 (for **4**). $^1J(^{13}C-^{119}Sn)$ values for these compounds are observed between 571 and 590 Hz. These NMR data are comparable with those of closely related disubstituted organotin derivatives such as $Bu_2Sn(OMe)OAc$ [$^1J(^{13}C-^{119}Sn)$ = 666 Hz], $Bu_2Sn(Cl)OMe$ [$^1J(^{13}C-^{119}Sn)$ = 622 Hz], $Bu_2SnCl(Et_2dtc)$ [$\delta(^{119}Sn)$ −200; Et_2dtc = diethyldithiocarbamate], etc. and also with those of many other organotin compounds[13−16] for which apparently five-coordinated tin structures in solution have been proposed. For **5**−**11**, ^1H NMR spectra reveal −CH protons of the *β*-diketonato ligand at *δ* 6.85−5.70, suggesting chelation.[17,18] ^{119}Sn NMR spectra [$\delta(^{119}Sn)$ −231.0 to −274.0] as well as $^1J(^{13}C-^{119}Sn)$ values of 603−626 Hz may point to a six-coordinated tin in the structures for these compounds. ^{13}C and ^{119}Sn NMR spectra of **12**−**14** reveal more complex behavior (Experimental Section) than is normally expected from the solid-state structure given below, giving credence to the possible structural changes in solution. The literature also records similar behavior for many stannoxane derivatives.[19,20]

Molecular Structures of 6, 10, and 13. Several attempts to obtain suitable X-ray-quality crystals for **1**−**4** were not successful. However, unequivocal evidence of the existence of the methanesulfonate group and therefrom evidence for the postulated occurrence of a sulfur-centered Arbuzov rearrangement in the title reactions were obtained by X-ray crystal structure determinations of compounds **6**, **10**, and **13**. Two crystallographically independent molecules have been characterized in the refined structure of **10**. The atomic-labeling schemes for **6**, **10**, and **13** are shown in the ORTEP plots of Figures 1, 2, and 3b, respectively. Crystal data for these compounds are collected in Table 1, while selected bond lengths and angles are summarized in Tables 2−4, respectively.

Compounds **6** and **10** crystallize in trigonal and triclinic systems with space groups $R\bar{3}$ and $P\bar{1}$, respectively. As is evident from Figures 1 and 2, these compounds adopt dimeric structures, forming a centrosymmetric eight-membered cyclic ring in which each tin atom has a hexacoordinate environment with the chelating bidentate *β*-diketonate group and bridging bidentate methanesulfohnate group. The bidentate mode of coordination of the methanesulfonate group is crystallographically authenticated for the first time though a similar coordination mode for the fluorosulfonate group is known in the polymeric structure of $Me_2Sn[OS(O)_2F]_2$.[21]

In both **6** and **10**, the Sn−O(methanesulfonate) bond lengths [Sn(1)−O(3) 2.431(4), Sn(1)−O(5a)#1 2.379(5) Å for **6**; Sn-

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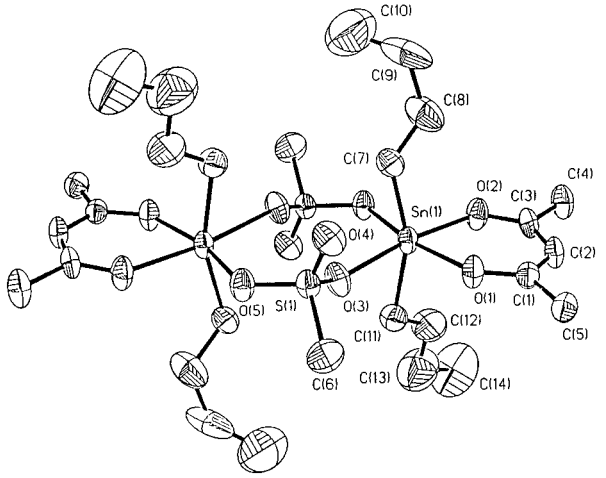

Figure 1. Perspective view of **6** with the atomic-numbering scheme. Thermal ellipsoids are at the 30% probability level.

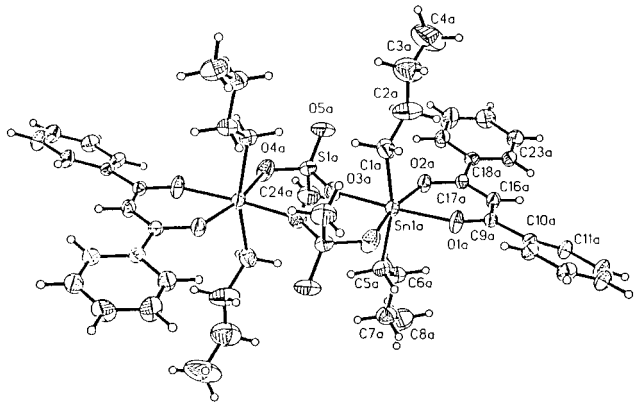

Figure 2. Molecular structure of **10** (first molecule in the asymmetric unit) with the atom-labeling scheme. Thermal ellipsoids are at the 30% probability level.

(1a)−O(3a) 2.383(7), Sn(1a)−O(4a)#1 2.456(8), Sn(1b)−O(3b) 2.255(7), Sn(1b)−O(5b)#1 2.651(7) Å for **10**] are appreciably longer than the Sn−O (*β*-dik) distances [Sn(1)−O(1) 2.157(5), Sn(1)−O(2) 2.117(4) Å for **6**; Sn(1a)−O(1a) 2.151(6), Sn(1a)−O(2a) 2.134(7), Sn(1b)−O(1b) 2.106(7), Sn(1b)−O(2b) 2.157(6) Å for **10**]. However, these are comparable to the corresponding Sn−O bond distances reported for hydroxodi-*n*-butyltin perchlorate [2.425(5) Å][11] and hydroxodimethyltin nitrate [2.30(3) Å],[7] reflecting appreciable ionic character for these bonds. Sn−C and S−O bond distances are normal.[21−23] The presence of the S−C bond [1.721(7) Å for **6**; 1.744(13), 1.742(11) Å for **10**] conclusively proves the identity of methanesulfonate group in these compounds. The Sn···Sn bond distances (4.816−4.986 Å) are much longer than some of the van der Waals radii.[24] Both **6** and **10** adopt distorted octahdral geometry around tin atoms with in-plane disposition of the largest ∠O−Sn−O [O(2)−Sn(1)−O(3) 168.0(2), O(1)−Sn(1)−O(5a)#1 164.2(1)° for **6**; O(1a)−Sn(1a)−O(3a) 165.6(3), O(2a)−Sn(1a)−O(4a)#1 166.8(3), O(2b)−Sn(1b)−O(3b) 166.6(3), O(1b)−Sn(1b)−O(5b)#1 173.3(3)° for **10**] and the bent butyl groups [C(7)−Sn(1)−C(11) 159.8(3)° for **6**; C(5a)−Sn(1a)−C(1a) 162.1(4), C(1b)−Sn(1b)−C(5b) 159.0(5)° for **10**]. The planar angles of the SnO_4 core group sum to 360 ± 0.1° in these compounds. The O−S−O angles of the methanesulfonate groups are similar to those found in other related organotin derivatives.[21−23]

The crystal structure of **13** (triclinic, $P\bar{1}$ space group) is regarded as consisting of a polymeric sheet parallel to (001) with a 20-membered macrocyclic repeating unit (Figure 3a).

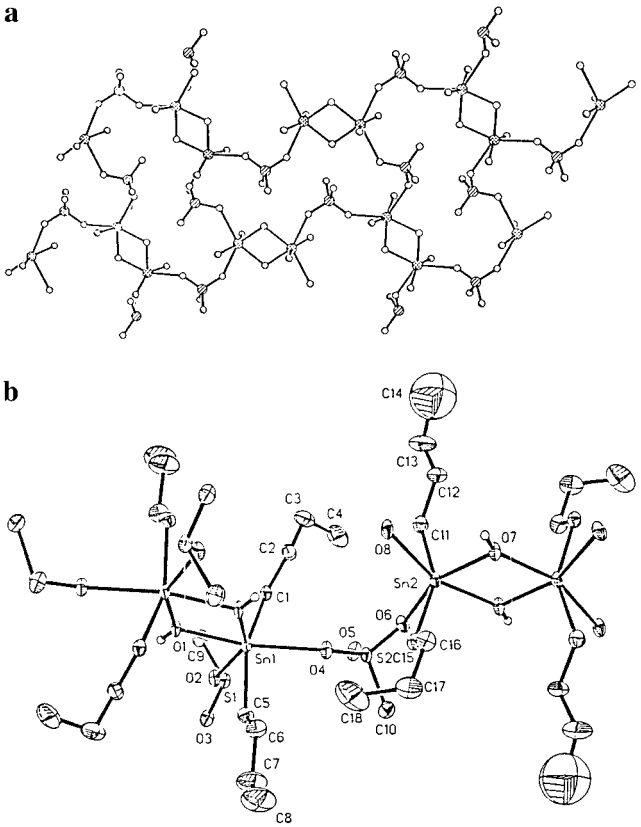

Figure 3. (a) Perspective view of **13** with the molecular sheet parallel to (001) showing the macrocycle. Only the tin-bonded carbons of the butyl group are shown. (b) Projection of a part of the structure of **13** with the atomic-labeling scheme showing the $Sn_2(OH)_2$ ring along with the bridging methanesulfonate group.

Table 1. Summary of Crystallographic Data for Compounds **6**, **10**, and **13**[a]

	6	**10**	**13**
empirical formula	$C_{14}H_{28}O_5SSn$	$C_{24}H_{32}O_5SSn$	$C_{18}H_{44}O_8S_2Sn_2$
fw	427.1	551.25	690.02
T,°C	23(2)	23(2)	23(2)
λ, Å	0.710 73	0.710 73	0.710 73
space group	$R\bar{3}$ (No. 148)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	28.664(1)	13.056(3)	9.089(2)
b, Å	28.664(1)	14.062(3)	12.040(2)
c, Å	13.056(1)	16.28213)	13.894(2)
α, deg	90	80.87(3)	91.67(2)
β, deg	90	71.00(3)	90.26(2)
γ, deg	120	66.25(3)	105.88(2)
V, Å^3	9290.0(8)	2586(2)	1461.6(5)
Z	18	4	2
ρ_{calcd}, g cm^{-3}	1.374	1.402	1.568
μ, cm^{-1}	13.53	18.88	10.87
final *R* indices	$R = 0.0373$	$R = 0.0565$	$R = 0.0330$
$[I > 2\sigma(I)]$	$R_w = 0.0587$	$R_w = 0.1424$	$R_w = 0.0854$
R indices	$R = 0.0447$	$R = 0.1366$	$R = 0.0687$
(all data)	$R_w = 0.0615$	$R_w = 0.4410$	$R_w = 0.2378$

[a] For **6**: $R = \sum||F_o| - |F_c||/\sum F_o$; $R_w = \sum(w^{1/2}|F_o - |F_c||)/\sum(w^{1/2}F_o)$. For **10** and **13**: $R = (\sum||F_o| - |F_c||/\sum|F_o|)$; $R_w = \sum w(F_o^2 - F_c^2)^2/\sum w[(F_o^2)^2]^{1/2}$.

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for **6**[a]

Sn(1)−O(1)	2.157(5)	Sn(1)−O(5a)#1	2.379(5)
Sn(1)−O(2)	2.117(4)	S(1)−O(3)	1.458(6)
Sn(1)−O(3)	2.431(4)	S(1)−O(4)	1.433(7)
Sn(1)−C(7)	2.096(7)	S(1)−O(5)	1.460(4)
Sn(1)−C(11)	2.113(7)	S(1)−C(6)	1.721(7)
O(1)−Sn(1)−O(2)	84.1(2)	C(7)−Sn(1)−O(5a)#1	87.5(3)
O(1)−Sn(1)−O(3)	83.9(2)	C(11)−Sn(1)−O(5a)#1	85.8(3)
O(2)−Sn(1)−O(3)	168.0(2)	O(3)−S(1)−O(4)	114.5(3)
O(1)−Sn(1)−C(7)	97.5(3)	O(3)−S(1)−O(5)	108.8(3)
O(2)−Sn(1)−C(7)	98.2(2)	O(4)−S(1)−O(5)	113.6(3)
O(3)−Sn(1)−C(7)	83.3(2)	O(3)−S(1)−C(6)	106.3(4)
O(1)−Sn(1)−C(11)	94.1(3)	O(4)−S(1)−C(6)	107.7(4)
O(2)−Sn(1)−C(11)	99.4(2)	O(5)−S(1)−C(6)	105.3(3)
O(3)−Sn(1)−C(11)	81.5(2)	Sn(1)−O(1)−C(1)	128.0(5)
C(7)−Sn()−C(11)	159.8(3)	Sn(1)−O(2)−C(3)	128.5(5)
O(1)−Sn(1)−O(5a)#1	164.2(1)	Sn(1)−O(3)−S(1)	152.4(4)
O(2)−Sn(1)−O(5a)#1	80.3(2)	S(1)−O(5)−Sn(1a)	121.8(3)
O(3)−Sn(1)−O(5a)#1	111.6(2)		

[a] Symmetry transformation used to generate equivalent atoms: (#1) $1 - x, -y, 1 - z$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **10**[a]

Sn(1a)−C(5a)	2.094(11)	Sn(1a)−C(1a)	2.096(12)
Sn(1a)−O(2a)	2.134(7)	Sn(1a)−O(1a)	2.151(6)
Sn(1a)−O(3a)	2.383(7)	Sn(1a)−O(4a)#l	2.456(8)
O(4a)−Sn(1a)#1	2.456(8)	Sn(1b)−C(1b)	2.088(12)
Sn(1b)−O(1b)	2.106(7)	Sn(1b)−C(5b)	2.108(13)
Sn(!b)−O(2b)	2.157(6)	Sn(1b)−O(3b)	2.255(7)
Sn(1b)−O(5b)#l	2.651(7)		
C(Sa)−Sn(1a)−C(1a)	162.1(4)	C(2a)−C(1a)−Sn(1a)	114.8(9)
C(1a)−Sn(1a)−O(2a)	96.8(4)	C(1b)−Sn(1b)−O(1b)	101.9(4)
C(1a)−Sn(1a)−O(1a)	96.7(4)	O(1b)−Sn(1b)−C(5b)	98.3(5)
C(Sa)−Sn(1a)−O(3a)	83.7(4)	O(1b)−Sn(1b)−O(2b)	82.4(3)
O(2a)−Sn(1a)−O(3a)	82.6(3)	C(1b)−Sn(1b)−O(3b)	86.6(4)
C(5a)−Sn(1a)−O(4a)#1	83.1(4)	C(5b)−Sn(1b)−O(3b)	89.7(4)
O(2a)−Sn(1a)−O(4a)#1	166.8(3)	C(9b)−O(1b)−Sn(1b)	127.9(6)
O(3a)−Sn(1a)−O(4a)#1	110.6(3)	S(1b)−O(3b)−Sn(1b)	144.3(4)
C(17a)−O(2a)−Sn(1a)	130.7(6)	C(6b)−C(5b)−Sn(1b)	115.9(13)
S(1a)−O(4a)−Sn(1a)#1	124.5(4)	C(8b)−C(7b)−C(6b)	127(4)
C(5a)−Sn(1a)−O(2a)	98.6(4)	C(1b)−Sn(1b)−C(Sb)	159.0(5)
C(5a)−Sn(1a)−O(1a)	94.1(4)	C(1b)−Sn(1b)−O(2b)	91.4(4)
O(2a)−Sn(1a)−O(1a)	83.7(2)	C(5b)−Sn(1b)−O(2b)	96.7(4)
C(1a)−Sn(1a)−O(3a)	89.3(4)	O(1b)−Sn(1b)−O(3b)	85.0(3)
O(1a)−Sn(1a)−O(3a)	165.6(3)	O(2b)−Sn(1b)−O(3b)	166.6(3)
C(1a)−Sn(1a)−O(4a)#1	84.0(4)	C(17b)−O(2b)−Sn(1b)	127.5(6)
O(1a)−Sn(1a)−O(4a)#1	83.2(3)	C(2b)−C(1b)−Sn(1b)	115.2(10)
C(9a)−O(1a)−Sn(1a)	128.5(6)	O(1b)−Sn(1b)−O(5b)#1	173.3(3)
S(1a)−O(3a)−Sn(1a)	158.1(5)		

[a] Symmetry transformation used to generate equivalent atoms: (#1) $-x, -y, -z$.

Each macrocyclic unit has six tin atoms connecting each other through four bridging bidentate methanesulfonate groups. Four of these tin atoms of the ring are also involved in the formation of a μ-hydroxo-bridged four-membered $[Sn(OH)]_2$ ring, while the remaining form analogous four-membered rings with two tin atoms of the neighboring macrocycles. All the tin atoms possess six-coordinate distorted octahedral geometry. Analyses of the microstructural data reveal that Sn−O(methanesulfonate) bond distances [Sn(1)−O(4) 2.429(4), Sn(2)−O(8) 2.410(4) Å] are comparable to the similar Sn−O bond distances observed in compounds **6** and **10** [2.651(7)−2.225(7) Å] and thus point to an appreciable ionic character for this bond in the present compound too. The bond angles [C(1)−Sn(1)−C(5) 151.4(3), C(11)−Sn(2)−C(15) 151.9(3), O(1)−Sn(1)−O(4) 154.8(2), O(7)−Sn(2)−O(6) 152.1(2), O(1)#1−Sn(1)−O(2) 150.97(14), O(7)#2−Sn(2)−O(8) 155.1(2)°] show a severely distorted octahedral geometry around each tin atom. The planar angles of the SnO_4 core sum to 359.5/359.8° with the bent C−Sn−C group occupying the trans position. This situation is similar to those observed in the crystal structures of **6** and **10** described above. The S−O, S−C, and Sn−C bond distances as well as the O−S−O and O−S−C bond angles are quite typical of other structurally related sulfonate derivatives.[21−23] Another structural feature of the compound is the incorporation of two centrosymmetric $[Sn_2(OH)_2]$ rings in each repeating subunit of the polymer framework. The important bond lengths and bond angles associated with the cyclic ring are as follows: Sn(1)−O(1) 2.112(4), Sn(1)−O(1)#1 2.086(4), Sn(2)−O(7) 2.085(4), Sn(2)−O(7)#2 2.122(4) Å; Sn(1)#1−O(1)−Sn(1) 108.3(2), O(1)#1−Sn(1)−O(1) 71.7(2), Sn(2)−O(7)−Sn(2)#2 107.9(2), O(7)−Sn(2)−O(7)#2 72.1(2)°. The tin atoms are separated by 3.402(4) Å. Although, these parameters are close to those of existing organotin analogues,[6−12] the molecular architecture arising from simultaneous methanesulfonate- and hydroxo-bridged frameworks involving three neighboring tin atoms as observed here is unprecedented. The hydroxo-bridged diorganotin derivatives known so far are discrete dimers.[6−12] Additionally, strong hydrogen-bonding interactions between the hydrogen atoms of the hydroxyl groups and the oxygen atoms of adjacent methanesulfonate groups are evident from the H(1a)···O(3′) 1.915(2) and H(7a)···O(5″) 1.914(3) Å distances. The observed angles are ∠O(1)−H(1a)···O(3′) 156.8 and ∠O(7)−H(7a)···O(5″) 152.4°.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **13**[a]

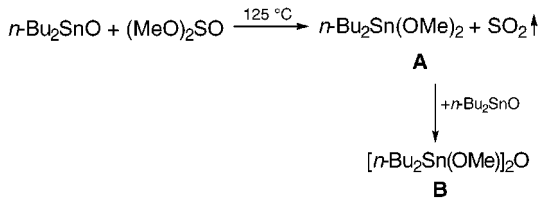
Sn(1)−O(1)#1	2.086(4)	Sn(1)−O(1)	2.112(4)
Sn(1)−C(1)	2.116(7)	Sn(1)−C(5)	2.127(7)
Sn(1)−O(4)	2.429(4)	Sn(1)−O(2)	2.489(4)
Sn(2)−O(7)	2.085(4)	Sn(2)−C(11)	2.119(8)
Sn(2)−C(15)	2.123(7)	Sn(2)−O(7)#2	2.122(4)
Sn(2)−O(8)	2.410(4)	Sn(2)−O(6)	2.492(4)
O(7)−Sn(2)#2	2.122(4)		
O(1)#1−Sn(1)−O(1)	71.7(2)	O(1)#1−Sn(1)−C(1)	102.3(2)
O(1)−Sn(1)−C(1)	99.7(2)	O(1)#1−Sn(1)−C(5)	103.3(2)
O(1)−Sn(1)−C(5)	100.5(2)	C(1)−Sn(1)−C(5)	151.4(3)
O(1)#1−Sn(1)−O(4)	83.1(2)	O(1)−Sn(1)−O(4)	154.8(2)
C(1)−Sn(1)−O(4)	87.9(2)	C(5)−Sn(1)−O(4)	82.4(2)
O(1)#1−Sn(1)−O(2)	150.97(14)	O(1)−Sn(1)−O(2)	79.29(14)
C(1)−Sn(1)−O(2)	84.3(2)	C(5)−Sn(1)−O(2)	79.7(2)
O(4)−Sn(1)−O(2)	125.7(2)	O(7)−Sn(2)−C(11)	102.8(2)
O(7)−Sn(2)−C(15)	102.1(2)	C(11)−Sn(2)−C(15)	151.9(3)
O(7)−Sn(2)−O(7)#2	72.1(2)	C(11)−Sn(2)−O(7)#2	100.7(2)
C(15)−Sn(2)−O(7)#2	99.1(2)	O(7)−Sn(2)−O(8)	83.2(2)
C(11)−Sn(2)−O(8)	82.4(2)	C(15)−Sn(2)−O(8)	87.9(2)
O(7)#2−Sn(2)−O(8)	155.1(2)	O(7)−Sn(2)−O(6)	152.1(2)
C(11)−Sn(2)−O(6)	79.7(2)	C(15)−Sn(2)−O(6)	84.4(2)
O(7)#2−Sn(2)−O(6)	80.2(2)	O(8)−Sn(2)−O(6)	124.4(2)
Sn(1)#1−O(1)−Sn(1)	108.3(2)	Sn(2)−O(7)−Sn(2)#2	107.9(2)

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x + 1, -y + 1, -z$; (#2) $-x, -y + 1, -z + 1$.

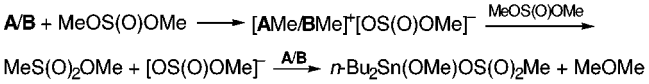
Mechanism of the Arbuzov Rearrangement: Formation of 1−4. A tentative pathway of the formation of methoxydi-*n*-butyltin methanesulfonate, **2**, was followed by monitoring the progress of the reaction (eq 1) with time. The ^{119}Sn NMR spectrum of this reaction mixture reveals two major products, i.e. *n*-$Bu_2Sn(OMe)_2$ (**A**) [$\delta(^{119}Sn)$ −162.7] and [*n*-$Bu_2Sn(OMe)]_2O$ (**B**) [$\delta(^{119}Sn)$ −172.8, −186.6], along with small amounts of **2** (<5%) by comparison to authentic chemical shifts of these species.[19,25] When the reaction was quenched at intervals of 25, 35, and 45 h, the concentration of **2** was found to increase with the progress of the reaction. Thereafter, the yield did not materially change. These observations suggest **A** and **B** as possible intermediates. The formation of **A** may be considered

(25) Smith, P. J.; White, R. F. M.; Smith, L. *J. Organomet. Chem.* **1972**, *40*, 341.

Scheme 1



Scheme 2



to be due to both the alkylating and alkoxylating behavior of dimethyl sulfite,[1] while **B** is known to result from the redistribution reaction[26] of $Bu_2Sn(OMe)_2$ and Bu_2SnO (Scheme 1).

Although direct reaction of dimethyl sulfite with **A** or **B** was found to yield compound **2** (see Experimental Section), the role of **A** and **B** in inducing the Arbuzov rearrangement is not yet clearly understood. In view of the known ubiquitous reactivity of dimethyl sulfite toward nucleophilic substrates,[2] it may be thought that methoxydi-*n*-butyltin methyl sulfite, $Bu_2Sn(OMe)$-OS(O)OMe (**C**), is initially formed by SO_2 insertion[27] (dimethyl sulfite is also a source of SO_2 in some of its reactions) into an Sn−O bond of $Bu_2Sn(OMe)_2$ and later undergoes an intramolecular Arbuzov rearrangement to yield **2**. This speculation is not favorable, as an isolated reaction[27] between preformed **C** and dimethyl sulfite under identical conditions (125 °C, 40 h) does not yield compound **2**. Alternatively, the nucleophilic assistance of **A** and/or **B** in the transformation of dimethyl sulfite to methyl methanesulfonate at the initial step can be invoked similarly to the rearrangement of dimethyl sulfite by tertiary nitrogen bases, methyl iodide,[3,4] etc. The reaction may proceed via an ionic mechanism (Scheme 2). This possibility is likely to be favored because the reactions of methyl methanesulfonate with **A** or **B** produce compound **2** much more readily (∼30 min) as compared to the similar direct reactions of **A** and **B** with dimethyl sulfite (20−22 h). In the former reactions, di-*n*-butyltin bis(methanesulfonate) is also formed in ∼18% yield. However, all efforts to detect the formation of methyl methanesulfonate during the course of these reactions failed.

Conclusions

The reactions between dimethyl sulfite and the diorganotin oxides R_2SnO (R = *n*-Pr, *n*-Bu, *i*-Bu, c-Hx) proceed via an Arbuzov type rearrangement at the sulfur center, yielding the corresponding methoxydiorganotin methanesulfonates, **1**−**4**, in one-pot syntheses. This new strategy underlines the possible synthetic utility of dimethyl sulfite in organometallic chemistry. The preferential reactivity of the Sn−OMe group in these compounds toward β-diketones and hydrolysis favors the isolation of hitherto unknown mixed-ligand diorganotin derivatives of the types $R_2Sn(X)OS(O)_2Me$ [X = β-dik (**5**−**11**); X = OH (**12**−**14**)]. The X-ray crystal structures of **6**, **10**, and **13** authenticate the existence of the methanesulfonate group with uncommon structural motifs and provide the first example of a crystallographically substantiated bridging bidentate character for the methanesulfonate group. A search for the possible pathway for the formation of **1**−**4** leads us to speculate that the following occur: (i) initial formation of $Bu_2Sn(OMe)_2$ (**A**) and $[Bu_2Sn(OMe)]_2O$ (**B**); (ii) Arbuzov type rearrangements of dimethyl sulfite to methyl methanesulfonate in the presence of **A** and **B**; and (iii) in situ reactions of **A** and **B** with methyl methanesulfonate.

Experimental Section

General Considerations. All reactions were conducted under an inert atmosphere of nitrogen. Solvents were dried using standard techniques (*n*-hexane over calcium hydride; chloroform and dichloromethane over P_2O_5). Glassware was dried in an oven at 110−120 °C and further flame-dried under vacuum prior to use.

Commercial compounds such as tin(IV) chloride, di-*n*-butyltin oxide, acetylacetone, benzoylacetone, and dibenzoylmethane were used as supplied. Literature methods were used to prepare di-*n*-propyl-, diisobutyl-, and dicyclohexyltin oxides,[28] di-*n*-butyltin dimethoxide,[29] 1,1,3,3-tetra-*n*-butyl-1,3-dimethoxystannoxane,[26] methoxydi-*n*-butyltin methyl sulfite,[27] dimethyl sulfite,[30] and methyl methanesulfonate.[3]

^{1}H NMR spectra were collected on a Bruker AM-300 spectrometer, and ^{13}C and ^{119}Sn NMR spectra were obtained on a Bruker AMX-400 spectrometer at frequencies of 100.6 and 149.2 MHz, respectively. ^{1}H and ^{13}C NMR spectra are referenced to the residual protons of the solvent, while ^{119}Sn NMR spectra are quoted with respect to tetramethyltin. Infrared spectra were routinely obtained for Nujol/hexachlorobutadiene mulls on a Perkin-Elmer (model 1430) ratio recording spectrophotometer using NaCl/KBr optics. Mass spectra (EI, 70 eV) were obtained on a VG Analytical 70-S mass spectrometer. Elemental analyses (C, H) were performed on a Perkin-Elmer model 2400 CHN elemental analyzer. Sulfur and tin were estimated by gravimetric methods.[31]

Preparation of Methoxydiorganotin Methanesulfonates (1−4). The syntheses of **1**−**4** were essentially the same. In a typical procedure, the diorganotin oxide (5.20 mmol) and dimethyl sulfite (5.50 g, 4.2 mL, 50.0 mmol) were heated at 125−127 °C on a constant-temperature oil bath for 40−45 h. To the resulting clear solution was added with stirring *n*-hexane (for **1**, **2**, and **4**) or isooctane (for **3**) (∼75 mL). The white solid obtained in each case was filtered off, washed with the solvent, and dried under vacuum.

***n*-$Pr_2Sn(OMe)OS(O)_2Me$ (1).** This compound was obtained as a white solid. Yield: 1.15 g, 67%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.45 (s, 3H, OCH_3), 2.85 (s, 3H, SCH_3), 1.80 (m, 8H, $SnCH_2CH_2$), 1.10 (t, 6H, CH_3). ^{13}C{^{1}H} NMR (100.61 MHz, $CDCl_3$): δ 53.3 (OCH_3), 39.5 (SCH_3), 28.6 (C_1, $^1J(^{13}C-^{119/117}Sn)$ = 585/560 Hz), 18.3 (C_2, $^2J(^{13}C-^{119}Sn)$ = 36 Hz), 18.2 (C_3, $^3J(^{13}C-^{119}Sn)$ = 106 Hz). ^{119}Sn{^{1}H} NMR (149.21 MHz, $CDCl_3$): δ −181.7. IR (Nujol, cm^{-1}): 1250, 1120, 1070 ($\nu(SO_3)$). Mass spectrum (EI, 70 eV): *m*/*z* 215 $[SnOS(O)_2Me]^+$, 95 $[MeSO_3]^+$, 79 $[MeSO_2]^+$, 64 $[SO_2]^+$. Anal. Calcd for $C_8H_{20}O_4SSn$: C, 29.02; H, 6.09; S, 9.68; Sn, 35.86. Found: C, 28.72; H, 6.00; S, 9.48; Sn, 35.72.

***n*-$Bu_2Sn(OMe)OS(O)_2Me$ (2).** This compound was isolated as a white solid. Yield: 1.30 g, 69.8%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.50 (s, 3H, OCH_3), 2.85 (s, 3H, SCH_3), 1.74 (m, 8H, $SnCH_2CH_2$), 1.41 (m, 4H, CH_2) 1.00 (t, 6H, CH_3). ^{13}C{^{1}H} NMR (100.61 MHz, $CDCl_3$): δ 53.3 (OCH_3), 39.4 (SCH_3), 26.1 (C_1, $^1J(^{13}C-^{119/117}Sn)$ = 590/564 Hz), 26.5 (C_2, $^2J(^{13}C-^{119}Sn)$ = 34 Hz), 26.6 (C_3, $^3J(^{13}C-^{119}Sn)$ = 108 Hz), 13.4 (C_4). ^{119}Sn{^{1}H} NMR (149.2 MHz, $CDCl_3$): δ −181.4. IR (Nujol, cm^{-1}): 1250, 1125, 1075 ($\nu(SO_3)$). Mass spectrum (EI, 70 eV): *m*/*z* 329 $[M - OMe]^+$, 215 $[SnOSO_2Me]^+$, 95 $[MeSO_3]^+$, 79 $[MeSO_2]^+$, 64 $[SO_2]^+$. Anal. Calcd for $C_{10}H_{24}O_4SSn$: C, 33.45; H, 6.73; S, 8.93; Sn, 33.06. Found: C, 33.32; H, 6.67; S, 8.64; Sn, 33.22.

***i*-$Bu_2Sn(OMe)OS(O)_2Me$ (3).** This compound was obtained as a white solid. Yield: 1.05 g, 56.4%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.58 (s, 3H, OCH_3), 2.80 (s, 3H, SCH_3), 2.25 (m, 2H, CH), 1.72 (d, 4H, $SnCH_2$), 1.04 (d, 12H, CH_3). ^{13}C{^{1}H} NMR (100.61 MHz, $CDCl_3$): δ 53.0 (OCH_3), 39.6 (SCH_3), 37.6 (C_1, $^1J(^{13}C-^{119/117}Sn)$ =

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571/546 Hz), 25.5 (C_2, $^2J(^{13}C-^{119}Sn)$ = 26 Hz), 26.3 (C_3, $^3J(^{13}C-^{119}Sn)$ = 80 Hz). $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): δ −178.9. IR (Nujol, cm^{-1}): 1275, 1150, 1080 ($\nu(SO_3)$). Anal. Calcd for $C_{10}H_{24}O_4SSn$: C, 33.45; H, 6.73; S, 8.93; Sn, 33.06. Found: C, 33.17; H, 6.70; S, 8.70; Sn, 33.22.

$(C_6H_{11})_2Sn(OMe)OS(O)_2Me$ (4). This compound was isolated as a white solid. Yield: 1.25 g, 58.4%. ^1H NMR (300 MHz, $CDCl_3$): δ 2.85 (s, 3H, SCH_3), 3.55 (s, 3H, OCH_3), 2.05 (m, 8H, ring H), 1.65 (m, 14H, ring H). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 55.3 (OCH_3), 39.5 (SCH_3), 26.4, 28.6, 30.3, 45.5 (c-Hx carbons). $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): δ −262.7. IR (Nujol, cm^{-1}): 1250, 1140, 1070 ($\nu(SO_3)$). Anal. Calcd for $C_{14}H_{28}O_4SSn$: C, 40.89; H, 6.86; S, 7.79; Sn, 28.87. Found: C, 40.66; H, 6.82; S, 7.57; Sn, 28.38.

Preparation of (*β*-Diketonato)diorganotin Methanesulfonates (5−11). *n*-$Pr_2Sn(acac)OS(O)_2Me$ (5). To a solution of methoxydi-*n*-propyltin methanesulfonate (**1**) (0.70 g, 2.11 mmol) in dichloromethane was added acetylacetone (0.21 g, 0.22 mL, 2.11 mmol), and the clear solution was stirred for 4−5 h at room temperature. The solvent was removed under vacuo, and *n*-hexane was added. The white solid thus obtained was filtered off, washed with *n*-hexane, and dried under vacuum. Recrystallization of the product from a CH_2Cl_2/*n*-hexane mixture afforded **5** as a white solid. Yield: 0.67 g, 79.4%. ^1H NMR (300 MHz, $CDCl_3$): δ 2.90 (s, 3H, SCH_3), 1.80 (m, 8H, $SnCH_2CH_2$), 1.02 (t, 6H, CH_3), 2.17 (s, 6H, CH_3CO), 5.85 (s, 1H, CH). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 39.6 (SCH_3), 29.5 (C_1, $^1J(^{13}C-^{119/117}Sn)$ = 626/600 Hz), 18.1 (C_2, $^2J(^{13}C-^{119}Sn)$ = 36 Hz), 17.7 (C_3, $^3J(^{13}C-^{119}Sn)$ = 103 Hz), 194.6 (CO), 101.9 (=CH), 27.6 (dik CH_3). $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): δ −242.1. IR (Nujol, cm^{-1}): 1250, 1160, 1060 ($\nu(SO_3)$), 1520 (ν(CO)). Mass spectrum (EI, 70 eV): *m*/*z* 357 $[M - Pr]^+$, 305 $[M - OSO_2Me]^+$, 219 $[Sn(acac)]^+$. Anal. Calcd for $C_{12}H_{24}O_5SSn$: C, 36.11; H, 6.06; S, 8.03; Sn, 29.74. Found: C, 36.18; H, 5.94; S, 7.82; Sn, 29.66.

***n*-$Bu_2Sn(acac)OS(O)_2Me$ (6).** This compound was obtained as a white solid according to the procedure described for **5** by reacting methoxydi-*n*-butyltin methanesulfonate, **2** (0.70 g, 1.94 mmol), with acetylacetone (0.19 g, 0.20 mL, 1.94 mmol). Yield: 0.70 g, 84.3%. ^1H NMR (300 MHz, $CDCl_3$): δ 2.87 (s, 3H, SCH_3), 1.74 (m, 8H, $SnCH_2CH_2$), 1.38 (m, 4H, CH_2), 0.92 (t, 6H, CH_3), 2.08 (s, 6H, CH_3CO), 5.70 (s, 1H, CH). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 39.4 (SCH_3), 27.5 (C_1, $^1J(^{13}C-^{119/117}Sn)$ = 621/595 Hz), 26.3 (C_2, $^2J(^{13}C-^{119}Sn)$ = 34 Hz), 28.8 (C_3, $^3J(^{13}C-^{119}Sn)$ = 98 Hz), 13.3 (C_4). $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): δ −239.3. IR (Nujol, cm^{-1}): 1260, 1155, 1060 ($\nu(SO_3)$), 1535 (ν(CO)). Mass spectrum (EI, 70 eV): *m*/*z* 371 $[M - Bu]^+$, 333 $[M - OSO_2Me]^+$, 219 $[Sn(acac)]^+$. Anal. Calcd for $C_{14}H_{28}O_5SSn$: C, 39.36; H, 6.60; S, 7.50; Sn, 27.79. Found: C, 39.10; H, 6.54; S, 7.17; Sn, 27.25.

***n*-$Pr_2Sn(bzac)OS(O)_2Me$ (7).** The reaction of methoxydi-*n*-propyltin methanesulfonate (**1**) (0.64 g, 1.94 mmol) and benzoylacetone (0.31 g, 1.94 mmol) was carried out in a manner similar to that described for **5**. Compound **7** was isolated as a pale yellow solid. Yield: 0.69 g, 77.5%. ^1H NMR (300 MHz, $CDCl_3$): δ 2.88 (s, 3H, SCH_3), 1.82 (m, 8H, $SnCH_2CH_2$), 1.04 (t, 6H, CH_3), 6.18 (s, 1H, CH), 2.21 (s, 3H, CH_3CO), 7.43−7.93 (m, 5H, Ph). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 38.6 (SCH_3), 28.6 (C_1, $^1J(^{13}C-^{119/117}Sn)$ = 621/595 Hz), 17.2 (C_2, $^2J(^{13}C-^{119}Sn)$ 36 Hz), 16.8 (C_3, $^3J(^{13}C-^{119}Sn)$ = 96 Hz), 185.0, 194.7 (CO), 97.3 (CH), 27.4 (dik CH_3), 135.4, 132.0, 127.7, 126.9 (Ph). $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): δ −239.9. IR (Nujol, cm^{-1}): 1250, 1130, 1050 ($\nu(SO_3)$), 1520 (ν(CO)). Mass spectrum (EI, 70 eV): *m*/*z* 419 $[M - Pr]^+$, 367 $[M - OSO_2Me]^+$, 301 $[Pr_2SnOS(O)_2Me]^+$, 281 $[Sn(bzac)]^+$. Anal. Calcd for $C_{17}H_{26}O_5SSn$: C, 44.27; H, 5.68; S, 6.95; Sn, 25.74. Found: C, 44.11; H, 5.57; S, 6.82; Sn, 25.54.

***n*-$Bu_2Sn(bzac)OS(O)_2Me$ (8).** This compound was isolated as a pale yellow solid from the reaction of **2** (0.70 g, 1.94 mmol) and benzoylacetone (0.31 g, 1.94 mmol) by following a procedure similar to that described for **5**. Yield: 0.72 g, 75.5%. ^1H NMR (300 MHz, $CDCl_3$): δ 2.90 (s, 3H, SCH_3), 1.76 (m, 8H, $SnCH_2CH_2$), 1.40 (m, 4H, CH_2), 0.90 (t, 6H, CH_3), 6.20 (s, 1H, CH), 2.25 (s, 3H, CH_3CO), 7.40−7.96 (m, 5H, Ph). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 39.7 (SCH_3), 26.9 (C_1, $^1J(^{13}C-^{119/117}Sn)$ = 615/589 Hz), 28.4 (C_2, $^2J(^{13}C-^{119}Sn)$ = 34 Hz), 26.3 (C_3, $^3J(^{13}C-^{119}Sn)$ = 99 Hz), 13.5 (C_4), 186.1, 195.5 (CO), 98.1 (CH), 26.6 (dik CH_3), 136.2, 132.8, 128.6, 127.7 (Ph). $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): δ −246.3. IR (Nujol, cm^{-1}): 1260, 1140, 1060 ($\nu(SO_3)$), 1520 (ν(CO)). Mass spectrum (EI, 70 eV): *m*/*z* 433 $[M - Bu]^+$, 395 $[M - OSO_2Me]^+$, 281 $[Sn(bzac)]^+$. Anal. Calcd for $C_{19}H_{30}O_5SSn$: C, 46.64; H, 6.18; S, 6.55; Sn, 24.26. Found: C, 46.47; H, 6.11; S, 6.41; Sn, 23.90.

***n*-$Pr_2Sn(bzbz)OS(O)_2Me$ (9).** This compound was prepared from **1** (0.64 g, 1.94 mmol) and dibenzoylmethane (0.43 g, 1.94 mmol) by a procedure analogous to that used to synthesize **5**. Compound **9** was isolated as a pale yellow solid. Yield: 0.78 g, 77.1%. ^1H NMR (300 MHz, $CDCl_3$): δ 2.90 (s, 3H, SCH_3), 1.81 (m, 8H, $SnCH_2CH_2$), 1.01 (t, 6H, CH_3), 6.85 (s, 1H, CH), 7.40−8.20 (m, 10H, Ph). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 39.7 (SCH_3), 28.5 (C_1, $^1J(^{13}C-^{119/117}Sn)$ = 618/592 Hz), 17.2 (C_2, $^2J(^{13}C-^{119}Sn)$ = 32 Hz), 17.3 (C_3, $^3J(^{13}C-^{119}Sn)$ = 96 Hz), 187.2 (CO), 95.0 (CH), 133.1, 128.7, 127.9 127.1 (Ph). $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): δ −270.6. IR (Nujol, cm^{-1}): 1260, 1135, 1055 ($\nu(SO_3)$), 1515 (ν(CO)). Mass spectrum (EI, 70 eV): *m*/*z* 481 $[M - Pr]^+$, 429 $[M - OSO_2Me]^+$, 343 $[Sn(bzbz)]^+$, 215 $[SnOSO_2Me]^+$. Anal. Calcd for $C_{22}H_{28}O_5SSn$: C, 50.50; H, 5.39; S, 6.12; Sn, 22.68. Found: C, 50.38; H, 5.41; S, 6.18; Sn, 22.81.

***n*-$Bu_2Sn(bzbz)OS(O)_2Me$ (10).** The reaction between methoxydi-*n*-butyltin methanesulfonate (**2**) (0.70 g, 1.94 mmol) and dibenzoylmethane (0.43 g, 1.94 mmol) was conducted in CH_2Cl_2 under the same conditions as described for **5**. Compound **10** was obtained as a pale yellow solid. Yield: 0.89 g, 82.8%. ^1H NMR (300 MHz, $CDCl_3$): δ 2.91 (s, 3H, SCH_3), 1.78 (m, 8H, $SnCH_2CH_2$), 1.40 (m, 4H, CH_2), 1.0 (t, 6H, CH_3), 6.80 (s, 1H, CH), 7.45−8.20 (m, 10H, Ph). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 39.7 (SCH_3), 27.0 (C_1, $^1J(^{13}C-^{119/117}Sn)$ = 610/585 Hz), 26.6 (C_2, $^2J(^{13}C-^{119}Sn)$ = 32 Hz), 26.3 (C_3, $^3J(^{13}C-^{119}Sn)$ = 97 Hz), 13.5 (C_4), 187.2 (CO), 95.0 (CH), 133.1, 128.7, 127.9, 127.1 (Ph). $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): δ −274.0. IR (Nujol, cm^{-1}): 1280, 1130, 1050 ($\nu(SO_3)$), 1510 (ν(CO)). Mass spectrum (EI, 70 eV): *m*/*z* 495 $[M - Bu]^+$, 438 $[M - 2Bu]^+$, 343 $[Sn(bzbz)]^+$, 215 $[SnOSO_2Me]^+$. Anal. Calcd for $C_{24}H_{32}O_5SSn$: C, 52.28; H, 5.85; S, 5.81; Sn, 21.53. Found: C, 52.07; H, 5.76; S, 5.66; Sn, 20.81.

***i*-$Bu_2Sn(bzbz)OS(O)_2Me$ (11).** This compound was isolated as a pale yellow solid from the reaction of **3** (0.70 g, 1.94 mmol) and dibenzoylmethane (0.43 g, 1.94 mmol) by following a procedure similar to that described for **5**. Yield: 0.79 g, 73.5%. ^1H NMR (300 MHz, CCl_3): δ 2.95 (s, 3H, SCH_3), 2.20 (m, 2H, CH), 1.70 (d, 4H, $SnCH_2$), 1.05 (d, 12H, CH_3), 6.80 (s, 1H, *β*-dik CH), 7.50−8.15 (m, 10H, Ph). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 39.7 (SCH_3), 37.0 (C_1, $^1J(^{13}C-^{119/117}Sn)$ = 603/577 Hz), 25.5 (C_2, $^2J(^{13}C-^{119}Sn)$ = 27 Hz), 26.0 (C_3, $^3J(^{13}C-^{119}Sn)$ = 82 Hz), 186.9 (CO), 95.0 (dik CH), 133.1, 128.8, 128.0, 126.6 (Ph). $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): δ −231.7. IR (Nujol, cm^{-1}): 1280, 1135, 1050 ($\nu(SO_3)$), 1520 (ν(CO)). Mass spectrum (EI, 70 eV): *m*/*z* 495 $[M - i\text{-}Bu]^+$, 343 $[Sn(bzbz)]^+$, 215 $[SnOSO_2Me]^+$. Anal. Calcd for $C_{24}H_{32}O_5SSn$: C, 52.28; H, 5.85; S, 5.81; Sn, 21.53. Found: C, 51.92; H, 5.80; S, 5.62; Sn, 20.88.

Preparation of (*μ*-Hydroxo)diorganotin Methanesulfonates (12−14). In a typical procedure, methoxydi-*n*-propyltin, methoxydi-*n*-butyltin, or methoxydiisobutyltin methanesulfonate (**1**, **2**, or **3**) (1.32, 1.43, or 1.43 g; 4.00 mmol) was dissolved in ∼50 mL of moist methanol (95:5 methanol/water) and the clear solution was stirred under atmospheric conditions for 24 h. Thereafter, solvent was stripped off under vacuo. To the resulting viscous mass was added a mixture of *n*-hexane and solvent ether (4:1) with constant stirring. A white solid was obtained in each case, which was filtered off, washed with solvent ether, and dried under vacuo. Recrystallization of the product from a CH_2Cl_2/*n*-hexane mixture afforded the corresponding hydroxodialkyltin methanesulfonate (**12**, **13**, or **14**).

***n*-$Pr_2Sn(OH)OS(O)_2Me$ (12).** The compound was obtained as a white solid. Yield: 0.81 g, 64.2%. ^1H NMR (300 MHz, $CDCl_3$): δ 2.85 (s, 3H, SCH_3), 1.81 (m, 8H, $SnCH_2CH_2$), 1.10 (t, 6H, CH_3), 4.85 (br, 1H, OH). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 39.5 (SCH_3), 32.5, 31.7, 30.3, 29.7, 29.4, 27.5, 18.6, 18.3 ($SnCH_2CH_2CH_3$). $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): δ −188.2, −182.9, −176.4, −175.6, −169.9, −163.1. IR (Nujol, cm^{-1}): 1280, 1250, 1200, 1140, 1065, 1040 ($\nu(SO_3)$), 3350 (ν(OH)). Mass spectrum (EI, 70 eV): *m*/*z* 353 $[PrSn(OSO_2Me)_2]^+$, 311 $[HSn(OSO_2Me)_2]^+$, 301 $[M - OH]^+$, 215

$[SnOSO_2Me]^+$. Anal. Calcd for $C_7H_{18}O_4SSn$: C, 26.52; H, 5.72; S, 10.11; Sn, 37.44. Found: C, 26.22; H, 5.55; S, 9.92; Sn, 37.11.

***n*-$Bu_2Sn(OH)OS(O)_2Me$ (13).** This compound was isolated as a white solid. Yield: 0.94 g, 68.4%. ^1H NMR (300 MHz, $CDCl_3$): δ 2.80 (s, 3H, SCH_3), 1.72 (m, 8H, $SnCH_2CH_2$), 1.42 (m, 4H, CH_2), 1.05 (t, 6H, CH_3), 5.30 (br, 1H, OH). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 39.5 (SCH_3), 30.5, 29.6, 27.2, 26.8, 26.6, 26.0 ($SnCH_2CH_2CH_2$), 13.5 (CH_3). $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): δ −189.3, −182.9, −175.3, −172.8, −168.3, −162.7. IR (Nujol, cm^{-1}): 1260, 1230, 1200, 1150, 1080 ($\nu(SO_3)$), 3380 (ν(OH)). Mass spectrum (EI, 70 eV): *m*/*z* 367 $[BuSn(OSO_2Me)_2]^+$, 329 $[M - OH]^+$, 311 $[HSn(OSO_2Me)_2]^+$, 215 $[SnOSO_2Me]^+$. Anal. Calcd for $C_9H_{22}O_4SSn$: C, 31.33; H, 6.42; S, 9.29; Sn, 34.40. Found: C, 31.17; H, 6.28; S, 9.11; Sn, 34.48.

***i*-$Bu_2Sn(OH)OS(O)_2Me$ (14).** This compound was obtained as a white solid. Yield: 0.86 g, 62.5%. ^1H NMR (300 MHz, $CDCl_3$): δ 2.76 (s, 3H, SCH_3), 2.15 (m, 2H, CH), 1.64 (d, 4H, CH_2), 0.95 (d, 12H, CH_3), 5.1 (br, 1H, OH). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 39.2 (SCH_3), 37.0, 36.6, 26.4, 26.0, 25.8 (*i*-Bu). $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): δ −176.9, −171.6, −148.0. IR (Nujol, cm^{-1}): 1255, 1205, 1190, 1150, 1090 ($\nu(SO_3)$), 3320 (ν(OH)). Anal. Calcd for $C_9H_{22}O_4SSn$: C, 31.33; H, 6.42; S, 9.29; Sn, 34.40. Found: C, 31.01; H, 6.31; S, 8.99, Sn, 34.25.

Reactions Involved in Mechanistic Studies. For a detailed study of the reaction between di-*n*-butyltin oxide and dimethyl sulfite, aliquots of the reaction mixture at intervals of 20, 25, 35, and 45 h were cannula-transferred to an NMR tube. Excess dimethyl sulfite was removed under vacuo, and the remaining contents were subjected to ^{119}Sn NMR studies.

Reaction of *n*-$Bu_2Sn(OMe)_2$ with Dimethyl Sulfite. A mixture of di-*n*-butyltin dimethoxide (1.0 g, 3.38 mmol) and dimethyl sulfite (5.0 g, 4.0 mL, 45.40 mmol) was heated at 125−127 °C for 20−24 h. To the resulting solution was added an *n*-hexane/diethyl ether mixture (1:4 ratio), and the contents were stirred for 4−5 h. The white solid thus obtained was filtered off, washed with an *n*-hexane/diethyl ether mixture, and dried under vacuo. Yield: 0.65 g, 53.4%. Elmental analyses and IR and ^1H, ^{13}C, and ^{119}Sn NMR spectral data for the product are identical to those for **2**.

Reaction of $[n\text{-}Bu_2Sn(OMe)]_2O$ with Dimethyl Sulfite. The reaction between $[n\text{-}Bu_2Sn(OMe)]_2O$ (1.50 g, 2.75 mmol) and dimethyl sulfite (5.0 g, ∼4.0 mL, 45.4 mmol) was carried out under the same conditions as described above for di-*n*-butyltin dimethoxide. Yield: 0.47 g, 48.4%. The solid was identified as compound **2** by spectroscopic studies.

Reaction of *n*-$Bu_2Sn(OMe)_2$ with Methyl Methanesulfonate. A mixture of di-*n*-butyltin dimethoxide (1.50 g, 5.08 mmol) and methyl methanesulfonate (0.77 g, 0.60 mL, 6.99 mmol) was heated at 125−127 °C. After a brief period of 30 min, a white solid was formed. Heating was stopped at this stage, and *n*-hexane/diethyl ether (1:1) was added to the solid. The mixture was stirred for 4−5 h at room temperature and filtered. The insoluble solid obtained was dried under vacuo and identified as $Bu_2Sn(OS(O)_2Me)_2$. Yield: 0.20 g, 18.6%. ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 2.66 (s, 6H, SCH_3), 1.64 (m, 8H, $SnCH_2CH_2$), 1.36 (m, 4H, CH_2), 0.91 (t, 6H, CH_3). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$ + DMSO-d_6): δ 39.6 (SCH_3), 34.2 (C_1, $^1J(^{13}C-^{119/117}Sn)$ = 867/842 Hz), 27.2 (C_2, $^2J(^{13}C-^{119}Sn)$ = 44 Hz), 26.0 (C_3, $^3J(^{13}C-^{119}Sn)$ = 161 Hz), 13.7 (C_4). $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$ + DMSO-d_6): δ −380.9. IR (Nujol, cm^{-1}): 1270, 1190, 1050 ($\nu(SO_3)$). Anal. Calcd for $C_{10}H_{24}O_6S_2Sn$: C, 28.38; H, 5.71; S, 15.15; Sn, 28.05. Found: C, 28.67; H, 5.78; S, 15.26; Sn, 28.11. The filtrate obtained from this reaction was concentrated. Addition of *n*-hexane yielded a white solid which was identified as **2**. Yield: 0.30 g, 32.8%.

Reaction of $[n\text{-}Bu_2Sn(OMe)]_2O$ with Methyl Methanesulfonate. The reaction between $[n\text{-}Bu_2Sn(OMe)]_2O$ (2.18 g, 4.0 mmol) and methyl methanesulfonate (0.4 g, 0.34 mL, 4.08 mmol) was carried out under the same conditions as described above for di-*n*-butyltin dimethoxide. The dichloromethane-soluble product and the dichloromethane-insoluble product were separately identified as **2** and $Bu_2Sn(OSO_2Me)_2$, respectively.

X-ray Crystallography. Crystals of compounds **6**, **10**, and **13** suitable for X-ray diffraction studies were mounted along their largest dimension in sealed capillaries and were used for data collection at ambient temperature [23(2) °C]. The intensity data were collected on a Siemens P4 single-crystal diffractometer (for **6**) or on a Rigaku AFC6S diffractometer (for **10** and **13**) with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). All calculations were performed either on an Iris 4D/35 or on an IBM compatible PC using programs such as TEXSAN,[32] SHELXS86,[33] SHELXL93,[34] and SHELXTL-PC.[35]

For *n*-$Bu_2Sn(acac)OS(O)_2CH_3$ (**6**), the lattice parameters and their standard deviations were obtained by a least-squares fit to 50 reflections (14.8° < 2θ < 29.9°). The data ($0 \le h \le 30$, $-31 \le k \le 0$, $0 \le l \le 14$) were collected in the ω scan mode with a variable scan speed (minimum of 2°/min to a maximum of 30°/min). The data were corrected for Lorentz and polarization effects, and an absorption correction based on ψ scans (T_{max} = 0.96, T_{min} = 0.67; μ = 1.353 mm^{-1}) was also applied. The structure was solved by direct methods using the SHELXTL-PC[35] package of Siemens, which was also used for refinement. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations based on *F*. The hydrogens were stereochemically fixed and were considered as riding (U_{iso} = 0.08 Å^2) on their respective non-hydrogen atoms. A weighting function of the form $w = k/\sigma^2|F_o| + g|F_o|^2$ with k = 1.00 and g = 0.001 635 was employed, and the final refinement converged to an *R* value of 0.0373 (R_w = 0.0587) for 2313 reflections.

For *n*-$Bu_2Sn(bzbz)OS(O)_2CH_3$ (**10**), the data ($0 \le h \le 15$, $-15 \le k \le 16$, $-18 \le l \le 19$) were collected with a constant scan speed of 8°/min in ω, the weak reflections [$I < 5\sigma(I)$] rescanned to a maximum of six times, and the counts accumulated to ensure good counting statistics. The remeasured reflections did not show any crystal decay after 96 h of X-ray exposure time. Cell parameters were obtained from a least-square fit to 25 reflections (20° < 2θ < 40°). Lorentz−polarization corrections and an absorption correction based on ψ scans (T_{max} = 1.00, T_{min} = 0.45; μ =1.087 mm^{-1}) were applied. The structure was solved by the direct methods program SHELXS86[33] and refined with SHELXL93[34] (on F^2). All non-hydrogen atoms except disordered carbon atoms were refined anisotropically. Hydrogen atoms were included in ideal positions with fixed isotropic *U* values of 0.08 Å^2. A weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ with a = 0.0749 and b = 12.76 was used. The butyl groups of molecule B were found to be disordered and were refined with site occupancy factors. The refinement converged to a final *R* value of 0.0565 (R_w = 0.1424).

A suitable crystal of the compound *n*-$Bu_2Sn(OH)OS(O)_2CH_3$ (**13**) was used for data collection ($-10 \le h \le 10$, $0 \le k \le 14$, $-16 \le l \le 16$), and the data collection parameters were the same as those for **10** (T_{max} = 1.00, T_{min} = 0.77; μ = 1.888 mm^{-1}). Intensities for three monitored reflections measured after every 150 reflections decreased by approximately 10% during 72 h of X-ray exposure, and an appropriate scale factor was applied to account for this decay. Unit cell dimensions and cell parameters were obtained by a least-squares fit to 25 reflections (20° < 2θ < 40°). The structure was solved using SHELXS86,[33] and the refinement conditions were the same as those for **10** (in the weighting function, a = 0.0418 and b = 3.17). There was evidence for slight disorder near the C(14) atoms, and fixing the C(13)−C(14) solved the problem to some extent. The final refinement converged to R = 0.033 and R_w = 0.0854, and the difference map was featureless.

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Supporting Information Available: Textual presentations of X-ray experimental details, tables of crystal data, fractional atomic coordinates and *U* values, bond distances and angles, anisotropic displacement parameters, and hydrogen atom coordinates and *U* values, and packing diagrams for **6**, **10**, and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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