Convenient Preparation of Hindered Dialkyltin(IV) Derivatives

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Diphenyltin dichloride was reacted with excess Grignard reagent to give dialkyldiphenyltin derivatives, R_2Ph_2Sn (R_2 = 2 neopentyl, 2 trimethylsilyl, 2 neohexyl, 2 cyclohexyl, hexamethylene), in excellent yield when R is hindered but in lower yield when a ring is formed. Heating these compounds with chloroacetic acid cleaved the two phenyl groups in excellent yield to give crystalline bis(chloroacetates). The dialkyltin(IV) bis(chloroacetates) were converted to oxides by reaction with sodium hydroxide. The crystal structure of hexamethylenetin bis(chloroacetate) ($R = R_w = 0.0241$) demonstrated that it was a monomer with a C–Sn–C angle of 122.2(3)° having hexacoordinate tin bonded to anisobidentate chloroacetate groups. C–Sn–C bond angles for all compounds in solution were obtained from ${}^1J_{^{119}Sn,^{13}C}$ values. Literature Karplus-type equations for ${}^3J_{^{119}Sn,^{13}C}$ values in trimethyltin derivatives apply approximately to dialkyldiphenyltin derivatives but not to dialkyltin(IV) bis(chloroacetates).

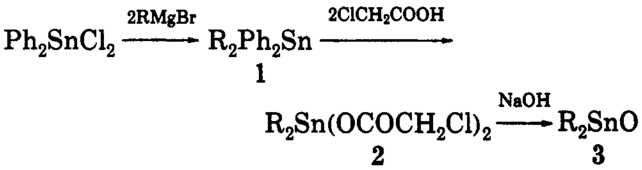
Introduction

Dibutylstannylene acetals are widely used intermediates for the regioselective monosubstitution of diol hydrogens by electrophiles.[1,2] The regioselectivity obtained ranges from poor to excellent, depending on the structure of the diol and the reaction conditions. It was postulated that good regioselectivity in the absence of added nucleophiles was obtained only when one of the three possible stannylene acetal dimers was dominant in solution.[2] Steric effects appear to be the major factor in determining which dimers are populated.[2] On this basis, it was thought that changing the sizes and shapes of the substituents on tin would alter the relative populations of the three dimers and hence modify the regioselectivity obtained in reactions with electrophiles. This hypothesis has proven to be valid.[3] Thus, a general synthetic procedure was required for dialkyltin oxides, the precursors of dialkylstannylene acetals.

Because electronegative substituents on dialkyltin(IV) derivatives can be converted easily into other substituents,[4] preparation of any such derivative provides a pathway to all. Most available methods have proceeded via the halides. Three techniques are commonly used: cleavage reactions of tetraalkyltin(IV) compounds, redistribution reactions of equimolar amounts of tetraalkyltin(IV) compounds and tin tetrahalides, and direct synthesis from alkyl halides and metallic tin. All of these methods yield equilibrium mixtures from which the major product, the dialkyltin(IV) dihalide, is separated by distillation.[4] The major products are pure enough to be adequate for most purposes if the alkyl group is primary and not hindered, but even then it is difficult to obtain absolutely pure products. However, as the alkyl groups become more complicated, difficulties arise in both preparation and purification. In this publication, we outline a general procedure for the preparation of dialkyltin(IV) derivatives that works efficiently for all compounds, including those containing bulky alkyl groups, and yields absolutely pure products.

Results and Discussion

Synthesis. The method reported here first involves formation of a dialkyldiphenyltin(IV) species and then cleavage of the two phenyl groups by chloroacetic acid, followed by conversion to the diorganotin(IV) oxide by reaction with sodium hydroxide:



$$Ph_2SnCl_2 \xrightarrow{2RMgBr} \underset{1}{R_2Ph_2Sn} \xrightarrow{2ClCH_2COOH} \underset{2}{R_2Sn(OCOCH_2Cl)_2} \xrightarrow{NaOH} \underset{3}{R_2SnO}$$

a, R = neopentyl; **b**, R = (trimethylsilyl)methyl; **c**, R = 3,3-dimethylbutyl; **d**, R = cyclohexyl; **e**, R_2 = hexamethylene

Dialkyldiphenyltin(IV) derivatives (1) are formed in excellent yield by reaction of diphenyltin dichloride with 2 equiv of an alkyl Grignard reagent, usually in tetrahydrofuran, as previously reported for compounds containing different large alkyl groups.[5] The yield of 1,1-diphenylstannacycloheptane (1e) obtained from the di-Grignard reagent derived from 1,6-dibromohexane was lower than the others but was similar to the yield obtained previously (26%).[6] Tin-119 NMR data for these compounds are listed in Table I and discussed later.

The key step in the procedure is the cleavage of the phenyl groups in the dialkyldiphenyltin derivatives (1). It is well-known that electrophiles such as halogens or acids cleave phenyl groups from tetraorganotin compounds more

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Table I. Tin-119 NMR Spectral Data

		coupling const to alkyl C and H (Hz)						
		^{1}J			$^{3}J_{Sn,C}$			
compd	chem shift (ppm)	^{119}Sn,C	^{117}Sn,C	$^{2}J_{Sn,C}$	measd[a]	$^{3}J_{^{119}Sn,C}$[b]	$^{2}J_{Sn,H}$	θ value from eq 1 (deg)
1a	−90.1	362.4	346.2	19.1	35.3	36.1	54.1	111
1b	−48.6	265.7	253.7	*c*	15.3	15.6	73.7	101
1c	−64.2	367.2	351.0	21.9	66.8	68.3	*d*	111
1d	−106.3	384.6	367.6	17.3	62.0, 59.2	62.0	*d*	113
1d[e]	*d*	386.9	369.6	16.7	64.9	66.4	*d*	113
1e	−58.5	360.0	343.8	11.4	21.5	22.0	*d*	111
2a	−113.3	507.4	484.5	31.5	63.4, 60.6	63.4	65.3	125
2b	−76.7	470.0	439.7	*c*	52.5	53.7	103.2, 98.9	122
2c	−120.1	553.2	528.4	39.1	109.7	112.2	*d*	130
2d	−186.3	488.8	467.3	21.4	104.2, 100.1	104.2	*d*	124
2e	−58.0	488.0	466.0	10.0	21.9	22.4	*d*	124

[a] Measured values. [b] Either measured value or, in the cases where only an average value was measured, calculated by multiplying the measured value by $2\gamma_{^{119}Sn}/(\gamma_{^{119}Sn} + \gamma_{^{117}Sn})$. [c] Not applicable. [d] Not measured. [e] Values measured for a solution in dichloromethane-d_2 at 203 K.

Table II. Fractional Atomic Positional Parameters and Equivalent Isotropic Temperature Factors (Å^2) for Hexamethylenetin Bis(chloroacetate) (2e)

	x/a	y/b	z/c	U_{eq}
Sn1	0.00581(4)	0.67456(2)	0.09638(6)	0.0450
Cl1	0.3946(2)	0.4870(1)	−0.0232(3)	0.0867
Cl2	0.0439(2)	0.8801(1)	0.5277(3)	0.0905
O1	0.1877(4)	0.6431(2)	0.1837(5)	0.0482
O2	0.1411(4)	0.5605(2)	−0.0153(7)	0.0614
O3	0.0259(5)	0.7553(2)	0.2864(6)	0.0600
O4	−0.1554(6)	0.7885(3)	0.1611(8)	0.0932
C1	0.2169(6)	0.5861(3)	0.0919(9)	0.0438
C2	0.3475(6)	0.5555(4)	0.1252(10)	0.0537
C3	−0.0757(8)	0.7979(4)	0.2737(10)	0.0646
C4	−0.0932(8)	0.8598(5)	0.4016(12)	0.0894
C5	0.0117(8)	0.7169(3)	−0.1580(8)	0.0689
C6	−0.1145(11)	0.6945(7)	−0.2506(17)	0.0668
C6*	−0.0604(13)	0.6708(9)	−0.2913(15)	0.0933
C7	−0.1498(12)	0.6121(7)	−0.2350(16)	0.0626
C7*	−0.1958(13)	0.6482(10)	−0.2487(22)	0.1108
C8	−0.2610(11)	0.6112(9)	−0.1035(16)	0.0709
C8*	−0.2104(19)	0.5813(9)	−0.1292(17)	0.1096
C9	−0.2262(15)	0.5633(7)	0.0506(16)	0.0879
C9*	−0.2515(12)	0.6027(11)	0.0526(16)	0.0939
C10	−0.1397(7)	0.6019(5)	0.1804(10)	0.0707

Table III. Selected Bond Distances (Å) and Angles (deg) for Hexamethylenetin Bis(chloroacetate) (2e)

Sn(1)–O(1)	2.089(5)	Sn(1)–O(2)	2.635(5)	Sn(1)–O(3)	2.079(5)
Sn(1)–O(4)	2.696(7)	Sn(1)–C(1)	2.712(7)	Sn(1)–C(3)	2.745(9)
Sn(1)–C(5)	2.115(8)	Sn(1)–C(10)	2.104(8)	Cl(1)–C(2)	1.756(8)
Cl(2)–C(4)	1.768(10)	O(1)–C(1)	1.284(8)	O(2)–C(1)	1.235(9)
O(3)–C(3)	1.310(10)	O(4)–C(3)	1.216(11)	C(1)–C(2)	1.490(10)
C(3)–C(4)	1.502(13)	C(5)–C(6)	1.551(15)	C(6)–C(7)	1.53(2)
C(7)–C(8)	1.54(2)	C(8)–C(9)	1.52(2)	C(9)–C(10)	1.52(2)
C(5)–C(6*)	1.52(2)	C(6*)–C(7*)	1.50(2)	C(7*)–C(8*)	1.53(2)
C(8*)–C(9*)	1.52(2)	C(9*)–C(10)	1.53(2)		

O(1)–Sn(1)–O(2)	53.9(2)	O(1)–Sn(1)–O(3)	82.4(2)
O(1)–Sn(1)–O(4)	135.2(2)	O(1)–Sn(1)–C(3)	109.7(2)
O(1)–Sn(1)–C(5)	111.9(2)	O(1)–Sn(1)–C(10)	112.6(3)
O(2)–Sn(1)–O(3)	136.3(2)	O(2)–Sn(1)–O(4)	170.3(2)
O(2)–Sn(1)–C(5)	87.6(2)	O(2)–Sn(1)–C(10)	90.1(3)
O(3)–Sn(1)–O(4)	53.1(2)	O(3)–Sn(1)–C(5)	113.9(3)
O(3)–Sn(1)–C(10)	106.7(3)	O(4)–Sn(1)–C(5)	85.3(2)
O(4)–Sn(1)–C(10)	88.1(3)	C(5)–Sn(1)–C(10)	122.2(3)
Sn(1)–C(5)–C(6)	108.3(6)	C(5)–C(6)–C(7)	114.7(10)
C(6)–C(7)–C(8)	104.0(10)	C(7)–C(8)–C(9)	110.3(11)
C(8)–C(9)–C(10)	113.8(11)	Sn(1)–C(10)–C(9)	120.4(7)
Sn(1)–C(5)–C(6*)	114.9(7)	C(5)–C(6*)–C(7*)	117.4(12)
C(6*)–C(7*)–C(8*)	116.1(14)	C(7*)–C(8*)–C(9*)	113.0(13)
C(8*)–C(9*)–C(10)	112.6(12)	Sn(1)–C(10)–C(9*)	110.0(7)

readily than alkyl groups.[7,8] Some time ago, Sasin *et al.* observed that gentle reflux of tetrapropyltin or tetraisopropyltin with 1 or 2 equiv of chloroacetic acid for 0.5 h yielded the crystalline mono- and bis(chloroacetates) in moderate yields, 35 and 47%, respectively.[9] It has been found in the present work that dialkyldiphenyltin compounds react with 2 equiv of chloroacetic acid to give the dialkyltin(IV) bis(chloroacetate) products in high yield. The reaction proceeds at 120 °C, but 20 min at 160 °C ensures completion. Isolation is particularly simple. All of the bis(chloroacetates) are crystalline and can be obtained conveniently in high purity by recrystallization.

The crystal structure of **2e** was determined to confirm the structure assigned and to determine the geometry about tin. Atomic coordinates and selected bond lengths and bond angles are given in Tables II and III. Compound **2e** is present as a monomer with no intermolecular Sn–O contacts less than 4.0 Å (see Figure 1). The hexacoordinate tin atom forms two bonds to each of the two anisobidentate carboxylate groups. The Sn–O bond lengths to each group are very different: 2.089(5) and 2.635(5) Å for one, 2.079(5) and 2.696(7) Å for the other. The four carbon atoms in the stannacycloheptane ring that are not attached to tin are 50% disordered. The ring adopts the lowest energy cycloheptane conformation, an approximately C_2-symmetric twist chair with the tin atom on the axis. In comparison to cycloheptane,[10] the conformation is flattened about the tin atom and more puckered at the other end. The disorder arises because the ring is twisted but has no preference for the direction of twist.

The crystal structures of a number of dialkyltin dicarboxylates have appeared in the last few years. The crystal structures can be classified into three types: polymers with bridging ester groups,[11] loosely associated dimers,[12,13] and monomers.[12,14] In dimers, the C–Sn–C bond angles range from about 140 to 159°.[12,13] In monomers, the bond angle is smaller, ranging from 130.6 to 140.7°.[12,14]

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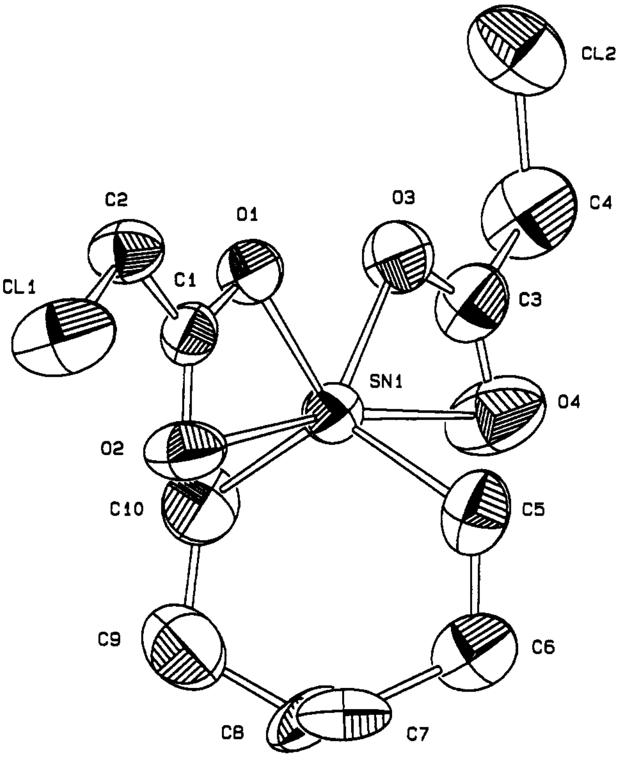

Figure 1. ORTEP plot of hexamethylenetin bis(chloroacetate) (**2e**) with thermal ellipsoids at the 50% probability level. Only one position of the disordered atoms is shown.

The structure of **2e** is very similar to the monomeric structures described earlier,[12,14] having hexacoordinate tin atoms coordinated to anisobidentate carboxylate groups. The most marked difference is in the C–Sn–C angle, being 122.2(3)° here as a result of ring formation. This bond angle is considerably smaller than any previously reported for diorganotin(IV) dicarboxylates. Perhaps as a result of the small bond angle, the carboxylate groups in **2e** are slightly more anisobidentate than any previously examined,[11-14] having both among the shortest Sn–O bonds and the longest Sn–O bond, 2.696(7) Å.

For compound **2e**, the ^{119}Sn NMR chemical shift measured in chloroform-*d*, −58.0 ppm, was very similar to that obtained from the CP/MAS spectrum of **2e** in the solid state, −61.8 ppm. If compound **2e** had a different structure in solution than in the solid state, quite different chemical shifts would be expected.

The dialkyltin bis(chloroacetates) (**2**) were transformed into dialkyltin oxides (**3**) by treatment of solutions in organic solvents with aqueous sodium hydroxide solutions for times ranging up to 1 h.

Other Preparations. Zimmer *et al.* reported that dibutyldineopentyltin reacted with 2 equiv of bromine at reflux in carbon tetrachloride to yield only dineopentyltin dibromide (**4**), the product of selective cleavage of the less hindered butyl group.[15] Repetition of this work revealed that the cleavage process was not as selective as had been reported; the product obtained was a 3:2 mixture of **4** and butylneopentyltin dibromide (**5**), as determined by ^{119}Sn and ^{13}C NMR spectroscopy (see Experimental Section). The original characterization of the product mixture had been performed only by analysis, and a 3:2 mixture of **4** and **5** fits the analytical data better than pure **4**. Iodinolysis of mixed tetraalkyltin compounds also gave mixtures of products.[16]

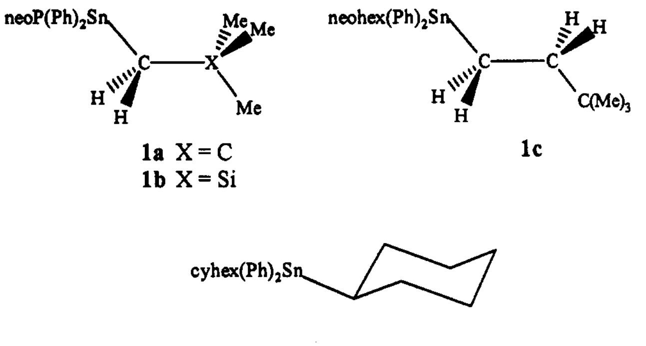

Figure 2. Representations of the favored geometries of compounds **1a**–**1d**.

Geometry and ^{119}Sn NMR Parameters. The $^{1}J_{^{119}\mathrm{Sn},^{13}\mathrm{C}}$ values yield interesting geometrical information. These have been related to C–Sn–C bond angles by the relationship

$$^{1}J_{^{119}\mathrm{Sn},^{13}\mathrm{C}} = 9.99\theta - 746\ \mathrm{Hz} \qquad (1)$$

for dibutyltin(IV) compounds,[17] and a similar relationship was developed for dimethyltin(IV) compounds.[18] The two equations give fairly similar θ values for compounds **1a**–**1e**, but the values from the dimethyltin(IV) equation are 3–6° less than those from eq 1. The values calculated using eq 1 are listed in Table I and seem reasonable, except for that for **1b**. The geometry of compound **1b** should not be markedly different than that of **1a**, but the electronic effects of the geminal silicon atoms presumably alter the $^{1}J_{\mathrm{Sn,C}}$ value.

Geometrical information can also be obtained from $^{3}J_{^{119}\mathrm{Sn},^{13}\mathrm{C}}$ values.[19,20] The following Karplus-type relationship has been developed for organotrimethyltin(IV) compounds:[19]

$$^{3}J_{^{119}\mathrm{Sn},^{13}\mathrm{C}} = 30.4 - 7.6 \cos\theta + 25.2 \cos 2\theta \qquad (2)$$

Many of the compounds used to develop the relationship were strained compounds, e.g. norbornyl derivatives. The compounds here provide an interesting test to determine whether this relationship applies to all tin compounds for several reasons: most of the geometries are reasonably well defined (see the following), the three methyl groups on tin are replaced by varying organic groups, and all compounds are relatively unstrained. When only average $^{3}J_{^{119}\mathrm{Sn},^{13}\mathrm{C}}$ and $^{3}J_{^{117}\mathrm{Sn},^{13}\mathrm{C}}$ values were obtained, the measured values were converted to $^{3}J_{^{119}\mathrm{Sn},^{13}\mathrm{C}}$ values, as detailed in a footnote in Table I.

The favored geometries of the compounds discussed in the following are shown in Figure 2. In compounds **1a** and **1b**, the tin atom is *gauche* to two methyl groups and *anti* to the other; the observed coupling constant will be an average of the values for the two *gauche* relationships

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and the one *anti* relationship. For compound **1c**, the vicinal coupling constants in the CH_2CH_2 unit were obtained by simulation of the AA′BB′ pattern and values of 14.4 and 4.1 Hz were obtained. The very different magnitudes of these values and the very large size of the value for the protons having *anti* relationships indicate that **1c** is close to being conformationally homogeneous in a conformation where the Sn–C–C–C torsional angle is close to 180°. In compound **1d**, the Sn atom is *anti* to C-3 and C-5 in the cyclohexane ring, if the Sn-bearing substituent is equatorial. A solution of **1d** in CD_2Cl_2 was examined by ^{13}C NMR spectroscopy as a function of temperature. Coalescence was observed for the signals of several cyclohexane carbons at about −30 °C. The $^{3}J_{^{119}Sn,^{13}C}$ values obtained were 62.1 Hz at 25 °C and 66.4 Hz for the major species at −70 °C, indicating that the 25 °C spectra arise from a conformational mixture. The signals of the minor species present at −70 °C were too small for coupling constants to be obtained. The actual Sn–C–C–C torsional angle in the equatorial conformation of **1d** is probably about 175°, because cyclohexane rings are normally flattened by about 5°.[21] In compound **1e**, the Sn–C–C–C torsional angle is approximately *gauche*. The values calculated by means of eq 2 are in the right order but are slightly small. For instance, for the compounds best defined geometrically, **1a**, **1c**, and **1d**, values of 30.4, 63.2, and 62.8 Hz were calculated, whereas 36.1, 68.3, and 66.4 Hz were observed. Adjusting eq 2 to the following fits these values (±1.5 Hz):

$$^{3}J_{^{119}Sn,^{13}C} = 36.1 - 7.3 \cos\theta + 24.9 \cos 2\theta \qquad (3)$$

Equation 2 gives an Sn–C–C–C value for **1e** of 49°, whereas eq 3 gives 57°. Both values are within the range of torsional angles expected for **1e**.

The series of bis(chloroacetates) can be considered in the same way. The C–Sn–C bond angles calculated for compounds **2a**, **2c**, and **2d** by means of eq 1 (see Table I) are slightly smaller than those previously determined from X-ray structures of compounds found to be monomers, 130.6–140.7°.[12,14] However, that calculated for **2e**, 123.5°, is almost the same as the value obtained in the X-ray structure determination (1.3° larger). Thus, the calculated bond angles probably are quite close to actual values.

Attempts made to fit $^{3}J_{^{119}Sn,^{13}C}$ values for compounds **2a**–**2e** to Karplus-type equations were unsuccessful, even though it is apparent that the sizes of the torsional angles involved are the most significant factors in determining the magnitudes of the coupling constants.

Experimental Section

General Methods. Melting points were determined using a Fisher–Johns melting point apparatus and are uncorrected. Dry column chromatography was done using TLC grade silica gel (60 PF-254, Merck). NMR spectra were recorded on Bruker AC 250F or AMX 400 spectrometers at 20 °C for solutions in $CDCl_3$ unless otherwise specified; ^{1}H and ^{13}C NMR spectra were referenced to internal TMS or for ^{13}C to chloroform-*d* as 77.0 ppm; ^{119}Sn NMR spectra were referenced to external tetramethyltin. The ^{119}Sn CP/MAS spectrum was recorded on the Bruker AMX 400 spectrometer, in a 4 mm rotor spun at rates of 7–9 kHz. Shifts were referenced to tetracyclohexyltin, which has a chemical shift of −97.35 ppm relative to tetramethyltin.[22] AA′BB′ ^{1}H NMR patterns were analyzed using the iterative fitting program LAME8.[23] Mass spectra were measured on a Du Pont-CEC 21-104 mass spectrometer at 70-eV ionization and a source temperature of 105 °C, using a glass, direct-insertion probe. Microanalyses were performed by Canadian Microanalytical Service Ltd., Vancouver, BC, Canada.

General Method for Preparation of Dialkyldiphenyltin Compounds. The corresponding Grignard reagent was prepared by adding an alkyl chloride or bromide (0.16 mol) dropwise to magnesium turnings (0.15 mol) in dry THF (100 mL), and then refluxing the mixture overnight under a nitrogen atmosphere. The heat source was removed, and a solution of diphenyltin dichloride (20.6 g, 0.06 mol) in THF (35 mL) was added in dropwise fashion at a rate that maintained reflux (about 30 min). The mixture was refluxed overnight under nitrogen and then cooled to room temperature. Excess Grignard reagent was hydrolyzed with saturated ammonium chloride solution (30 mL). The organic layer was filtered, and the residue was washed with ether (3 × 30 mL). The filtrate and washings were combined, and the solvents were removed on a rotary evaporator. The residue was taken up in ether (100 mL), and the resulting solution was washed with 10% KF solution (30 mL) and then with water (2 × 25 mL). The ether solution was dried over sodium sulfate. Removal of solvent afforded the desired compound.

Dineopentyldiphenyltin (1a). Preparation using the general method gave compound **1a**: yield 24.4 g, 98%. Recrystallization was performed from hexane: mp 43–44 °C; ^{1}H NMR δ 7.65–7.20 (m, 10H, Ar H), 1.51 (s, 4H, CH_2), 0.96 (s, 18H, CH_3); ^{13}C NMR δ 142.4 (s, C_{arom}, $J_{Sn,C}$ = 430.1, 412.0 Hz), 137.1 (d, $C_{Ar\text{-}ortho}$, $J_{Sn,C}$ = 33.4 Hz), 128.3 (d, $C_{Ar\text{-}meta}$, $J_{Sn,C}$ = 43.9 Hz), 128.2 (d, $C_{Ar\text{-}para}$), 33.6 (q, CH_3), 32.11 (s, C_q), 32.08 (t, CH_2); ^{119}Sn NMR (pentane) δ −90.1. Anal. Calcd: C, 63.64; H, 7.77. Found: C, 63.67; H, 7.61.

Bis((trimethylsilyl)methyl)diphenyltin (1b). Preparation using the general method gave compound **1b**: yield 26.2 g, 97%; bp 131–134 °C/0.18 Torr, lit.[8] bp 130–132 °C/0.2 Torr; ^{1}H NMR δ 7.7–7.2 (m, 10H, Ar H), 0.26, (s, 4H, CH_2), −0.04 (s, 18H, CH_3); ^{13}C NMR δ 141.6 (s, C_{Ar}, $J_{Sn,C}$ = 475.9, 454.9 Hz), 136.6 (d, $C_{Ar\text{-}ortho}$, $J_{Sn,C}$ = 37.2 Hz), 128.4 (d, $C_{Ar\text{-}meta}$, $J_{Sn,C}$ = 47.7 Hz), 128.2 (d, $C_{Ar\text{-}para}$), 1.6 (q, CH_3), −3.6 (t, CH_2); ^{119}Sn NMR (neat) δ −48.6.

Dineohexyldiphenyltin (1c). Preparation using the general method gave compound **1c**: yield 26.0 g, 98%; bp 150 °C/0.18 Torr; ^{1}H NMR δ 7.6–7.3 (m, 10H, Ar H), 1.304, 1.567 (2 AA′BB′ patterns, 8H, $J_{AA'}$ = −13.63 Hz, $J_{BB'}$ = −12.62 Hz, J_{AB} = 14.37 Hz, $J_{AB'}$ = 4.07 Hz, from simulation, rms standard deviation 0.053 Hz, 2 CH_2CH_2), 0.97 (s, 18H, CH_3); ^{13}C NMR δ 140.2 (s, C_{Ar}, $J_{Sn,C}$ = 434.9 Hz and 415.8 Hz), 136.9 (d, $C_{Ar\text{-}ortho}$, $J_{Sn,C}$ = 32.4 Hz), 128.3 (d, $C_{Ar\text{-}meta}$, $J_{Sn,C}$ = 23.9 Hz), 128.6 (d, $C_{Ar\text{-}para}$), 40.6 (t, CH_2), 32.2 (s, C_q), 28.7 (q, CH_3), 4.2 (t, CH_2Sn); ^{119}Sn NMR (neat) δ −64.2. Anal. Calcd: C, 65.03; H, 8.19. Found: C, 64.81; H, 8.08.

Dicyclohexyldiphenyltin (1d). Preparation using the general method gave compound **1d**: yield 23.2 g, 88%; mp 122–123 °C, lit.[24] mp 119–120 °C; ^{1}H NMR δ 7.6–7.2 (m, 10H, Ar H), 2.1–1.8 (m, 3H, H-1, H-2e, H-6e), 1.8–1.6 (m, 5H, H-2a, H-3e, H-4e, H-5e, H-6a), 1.35–1.30 (m, 3H, H-3a, H-4a, H-5a); ^{13}C NMR δ 139.9 (s, C_{Ar}, $J_{Sn,C}$ = 389.9, 371.9 Hz), 137.5 (d, $C_{Ar\text{-}ortho}$, $J_{Sn,C}$ = 29.3 Hz), 128.2 (d, $C_{Ar\text{-}meta}$, $J_{Sn,C}$ = 41.5, 39.6 Hz), 128.3 (d, $C_{Ar\text{-}para}$), 32.0 (t, CH_2-2,6), 29.1 (t, CH_2-3,5), 27.8 (d, CH), 27.0 (t, CH_2-4); ^{119}Sn NMR δ −106.3, lit.[25] −106.5 (chloroform).

1,1-Diphenylstannacycloheptane (1e). Compound **1e** was prepared by a modification of Zimmer's method.[6] The Grignard reagent was prepared by stirring a mixture of 1,6-dibromohexane (29 g, 0.118 mol) and magnesium turnings (5.75 g, 0.236 mol) in anhydrous ether (100 mL) at reflux for 12 h and then cooling and diluting with anhydrous ether (900 mL). A solution of diphenyltin dichloride (33.4 g, 0.100 mol) in anhydrous THF (500 mL) was quickly added to the cloudy Grignard reagent mixture. The reaction mixture was refluxed 12 h and then cooled to room

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temperature. Water (50 mL) was added slowly. The precipitate was removed by filtration and then washed with pentane (2 × 100 mL). The combined filtrate and washings were concentrated on a rotary evaporator. The residue was taken up in hexane (300 mL). The solution was dried (Na_2SO_4) and concentrated. Column separation of the residue (hexane as eluent) afforded the title compound: yield 10.7 g, 30%; bp 146 °C/0.08 Torr, lit.[6] bp 140 °C/0.07 Torr; ^1H NMR δ 7.6–7.2 (m, 10H, Ar H), 1.95 (m, 4H, H_β), 1.64 (m, 4H, H_γ), 1.41 (m, 4H, H_α); ^{13}C NMR δ 141.1 (s, C_{Ar}, $J_{Sn,C}$ = 434.9, 414.9 Hz), 136.7 (d, $C_{Ar\text{-}ortho}$, $J_{Sn,C}$ = 33.4 Hz), 128.4 (d, $C_{Ar\text{-}meta}$, $J_{Sn,C}$ = 43.8 Hz), 128.5 (d, $C_{Ar\text{-}para}$, $J_{Sn,C}$ = 10.5 Hz), 31.4 (d, C_β), 25.4 (d, C_γ), 11.2 (d, C_α); ^{119}Sn NMR δ −58.5; MS *m/z* 358 (8%, $M^{\cdot+}$ 281 [25%, $PhSn(CH_2)_6^+$], 280 (51%, $M^{\cdot+}$ −PhH), 274 (20%, $Ph_2Sn^{\cdot+}$), 197 (84%, $PhSn^+$), 120 (100%, $Sn^{\cdot+}$), m* 215–224 [$(280)^2/358 = 219.0$, $(281)^2/358 = 220.6$], 135–143 [$(197)^2/280 = 138.6$].

General Method for Preparation of Dialkyltin Bis(chloroacetates). The corresponding dialkyldiphenyltin compound (0.02 mol) and chloroacetic acid (0.04 mol) were gradually heated in a oil bath to 160 °C. The temperature was maintained at 160 °C for 20 min. After the reaction mixture had cooled to room temperature, hexane (50 mL) was added and the mixture was refluxed until crystalline material dissolved. Cooling the filtered solution to room temperature gave colorless crystals that were washed with hexane (3 × 3 mL). The analytical samples were recrystallized again from hexane.

Dineopentyltin Bis(chloroacetate) (2a). Preparation using the general method gave compound **2a**: yield 8.0 g, 90%; mp 75–76 °C; ^1H NMR δ 4.10 (s, 4H, CH_2Cl), 1.91 (s, 4H, CH_2Sn), 1.08 (s, 18H, CH_3); ^{13}C NMR δ 176.0 (s, C=O), 45.3 (t, CH_2Sn), 41.2 (t, CH_2Cl), 32.3 (q, CH_3), 32.7 (s, C_q); ^{119}Sn NMR (neat) δ −113.3. Anal. Calcd: C, 37.54; H, 5.85; Cl, 15.83; Found: C 37.54; H, 5.84; Cl, 15.90.

Bis((trimethylsilyl)methyl)tin Bis(chloroacetate) (2b). Preparation using the general method gave compound **2b**, yield 9.4 g, 98%; mp 104–106 °C; ^1H NMR δ 4.10 (s, 4H, CH_2Cl), 0.76 (s, 4H, CH_2Sn), 0.11 (s, 18H, CH_3); ^{13}C NMR δ 176.3 (s, C=O), 41.1 (t, CH_2Cl), 10.2 (t, CH_2Sn), 0.8 (q, CH_3); ^{119}Sn NMR (neat) δ −76.7. Anal. Calcd: C, 30.02; H, 5.46. Found: C, 29.95; H, 5.45.

Dineohexyltin Bis(chloroacetate) (2c). Preparation using the general method gave compound **2c**, yield 9.14 g, 96%; mp 94–96 °C; ^1H NMR δ 4.15 (s, 4H, CH_2Cl), 1.698, 1.529 (2 AA′BB′ patterns, 8H, $J_{AA'}$ = −12.40 Hz, $J_{BB'}$ = −13.61 Hz, J_{AB}= 13.49 Hz, $J_{AB'}$ = 4.56 Hz, analyzed by simulation, rms standard deviation 0.039 Hz, 2 CH_2CH_2), 0.88 (s, 18 H, CH_3); ^{13}C NMR δ 176.7 (s, C=O), 40.91 (t, CH_2Cl), 37.3 (t, CH_2), 32.0 (s, C_q), 28.5 (q, CH_3), 20.6 (t, CH_2Sn); ^{119}Sn NMR (neat) δ −120.1. Anal. Calcd: C, 40.37; H, 6.35; Cl, 14.90. Found: C, 39.88; H, 6.20; Cl, 15.26.

Dicyclohexyltin Bis(chloroacetate) (2d). Preparation using the general method gave compound **2d**, yield 9.16 g, 97%; mp 102–103 °C; ^1H NMR δ 4.13 (s, 4H, CH_2Cl), 2.34 (m, 1H, H-1), 1.94 (m, 2H, H-2e,6e), 1.77–1.57 (m, 5H, H-2a,6a,3e,4e,5e), 1.31 (m, 3H, H-3a,4a,5a); ^{13}C NMR δ 176.4 (s, C=O), 44.4 (d, C-1), 40.9 (t, CH_2Cl), 29.5 (t, C-2,6), 28.3 (t, C-3,5), 26.1 (t, C-4, $J_{Sn,C}$ = 12 Hz); ^{119}Sn NMR δ −186.3. Anal. Calcd: C, 40.72; H, 5.55; Cl, 15.02. Found: C, 40.78; H, 5.51; Cl, 14.86.

Hexamethylenetin Bis(chloroacetate) (2e). Preparation using the general method gave compound **2e**, yield 7.30 g, 96%; mp 96–98 °C; ^1H NMR δ 4.13 (s, 4H, CH_2Cl), 1.94 (m, 4H, H_β), 1.75–1.68 (m, 8H, $H_\alpha + H_\gamma$); ^{13}C NMR δ 175.8 (s, C=O), 40.9 (t, CH_2Cl), 30.3 (t, C_γ), 25.3 (t, C_α), 23.2 (t, C_β); ^{119}Sn NMR δ −58.0.

Dineopentyltin Oxide (3a). Dineopentyltin bis(chloroacetate) (11.2 g, 0.025 mol) in ether (80 mL) was shaken with an aqueous sodium hydroxide solution (2.5 g, 0.062 mol in 25 mL) in a separatory funnel. Hexane (50 mL) was added, and the organic layer was separated and dried over anhydrous sodium sulfate. Removal of solvents gave a colorless powder (6.6 g, 92%). The analytical sample was recrystallized from hexane: mp 202–204 °C; ^1H NMR δ 1.40 (s, 4H, $J_{Sn,H}$ = 62.6 Hz, CH_2), 1.10 (s, 18H, $J_{Sn,H}$ = 31.7 Hz, CH_3); ^{13}C NMR δ 43.0 (t, $^1J_{Sn,C}$ = 501.5, and 460.6 Hz, CH_2), 33.6 (q, $^3J_{Sn,C}$ = 49.6 Hz, CH_3), 31.8 (s, $^2J_{Sn,C}$ = 23.4 Hz, C_q); ^{119}Sn NMR δ 15.3. Anal. Calcd: C, 43.36; H, 8.01. Found: C, 42.96; H, 7.85.

Bis((trimethylsilyl)methyl)tin Oxide (3b). A solution of bis((trimethylsilyl)methyl)tin bis(chloroacetate) (9.60 g, 0.020 mol) in ether (100 mL) was shaken with an aqueous sodium hydroxide solution (2.0 g, 0.050 mol in 20 mL) in a separatory funnel. Hexane (50 mL) was added, and the organic layer was separated and dried over anhydrous sodium sulfate. Removal of solvents gave a colorless powder (6.1 g, 98%). The analytical sample was recrystallized from ethyl acetate; mp 152 °C, lit.[8] softens and melts over the range 145–160 °C; ^1H NMR δ 0.24 (s, 4H, CH_2), 0.11 (s, 18H, CH_3); ^{13}C NMR δ 8.9 (t, $^1J_{Sn,C}$ = 348 Hz, CH_2), 1.7 (q, $^3J_{Sn,C}$ = 21.9 Hz, CH_3); ^{119}Sn NMR δ 50.0.

Dineohexyltin Oxide (3c). A solution of dineohexyltin bis(chloroacetate) (9.52 g, 0.020 mol) in ether (75 mL) was stirred with an aqueous solution of sodium hydroxide (2.0 g, 0.050 mol in 25 mL) for 0.5 h. The resulting precipitate was collected and washed with water (3 × 10 mL). The colorless powder was refluxed in 100 mL of toluene overnight with azeotropic removal of water. Filtration gave a white amorphous solid (5.7 g, 93%), which is polymeric **3c**: mp >300 °C. Anal. Calcd: C, 47.25; H, 8.59. Found: C, 46.99; H, 8.49.

Dicyclohexyltin Oxide (3d). A solution of dicyclohexyltin bis(chloroacetate) (9.44 g, 0.020 mol) in ether (140 mL) was stirred with an aqueous sodium hydroxide solution (2.0 g, 0.050 mol in 25 mL) for 1 h. The resulting precipitate was collected and washed with water (5 × 10 mL) and acetone (3 × 20 mL). The colorless powder was dried under vacuum at 100 °C overnight. A white amorphous solid was obtained (5.93 g, 98%), which is polymeric **3d**: decomposes over the range 283–290 °C, lit.[26] dec pt ca. 285 °C.

Hexamethylenetin Oxide (3e). To a solution of 1,1-stannacycloheptane bis(chloroacetate) (3.8 g, 0.010 mol) in dichloromethane (20 mL) was added an aqueous sodium hydroxide solution (0.9 g in 20 mL). The mixture was stirred for 0.5 h, and the resulting solid was filtered, washed with H_2O (6 × 10 mL), acetone (3 × 10 mL), and ether (3 × 10 mL) in sequence, and then dried under reduced pressure at 100 °C. The title oxide was obtained quantitatively as a colorless powder, polymeric **3e**: decomposes over the range 200–220 °C. Anal. Calcd: C, 32.93; H, 5.53. Found: C, 32.92; H, 5.47.

Attempted Preparation of Dineopentyltin Dibromide (4). Dibutyldineopentyltin (^{119}Sn NMR δ −31.4 ppm; 25.7 g, 0.068 mol) was dissolved in dry carbon tetrachloride (25 mL). A solution of bromine (22.0 g) in dry carbon tetrachloride (25 mL) was added dropwise to this solution at the boiling point. After completion of the addition, the mixture was refluxed for an additional 2 h. The solvent was removed under reduced pressure, and the residue was fractionally distilled using a concentric tube column at a pressure of 0.25 Torr. Three fractions were collected: 2, 5, and 20 g. The ^{119}Sn NMR spectra of all fractions were very similar, each containing two peaks at 114.3 and 103.4 ppm, having ratios of the integrals of 2:3, respectively. The former peak was assigned to butylneopentyltin dibromide (**5**) and the latter to **4**. The ^{13}C NMR spectrum contained two sets of peaks: one set at 47.2, 32.9, and 32.6 ppm (CH_2, CH_3, and C_q of neopentyl, respectively) assigned to **4** and another set having approximately one-third the intensity of those assigned to **4** at 46.7, 33.0, and 32.7 ppm (CH_2, CH_3, and C_q of neopentyl, respectively) and at 27.7, 26.8, 26.1 and 13.4 ppm (3 CH_2 and CH_3 of Bu, respectively), which were assigned to **5**. The ^{13}C NMR spectrum of dibutyltin dibromide contained peaks at 27.0 ($J_{^{119}Sn,^{13}C}$ = 389.1 Hz, C_α), 27.6 ($J_{Sn,^{13}C}$ = 33.4 Hz, C_β), 26.0 ($J_{Sn,^{13}C}$ = 83.9 Hz, C_γ), and 13.5 (C_δ) ppm, consistent with the above spectrum of **5**.

Crystal Structure of Hexamethylenetin Bis(chloroacetate) (2e). A colorless hexagonal prismatic crystal of **2e** was mounted in a glass capillary on a Rigaku AFC5R diffractometer as summarized in Table IV. Cell constants and an orientation matrix for data collection were obtained from a least-squares

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Table IV. Summary of Crystallographic Data for Hexamethylenetin Bis(chloroacetate) (2e)

mol formula	$C_{10}H_{16}O_4Cl_2Sn$
fw	389.83
cryst color, habit	colorless, hexagonal prism
cryst dimens, mm	0.45 × 0.40 × 0.35
cryst syst	orthorhombic
space group	$P2_12_12_1$
a, Å	10.405(2)
b, Å	17.990(2)
c, Å	7.752(2)
V, Å^3	1451.2(5)
Z	4
D(calcd), g/cm^3	1.784
F(000)	768
diffractometer	Rigaku AFC5R
monochromator	graphite
temp, °C	18
radiation	Mo Kα (λ = 0.710 69 Å)
μ, cm^{-1}	21.37
scan type	ω–2θ
scan rate, deg/min	8.0 (in ω)
2θ limit, deg	50
scan width, deg	1.78 + 0.35 tan θ
no. of unique rflns measd	1516
no. of obsd data ($I > 3.00\sigma(I)$)	1134
no. of variables	218
$R = \Sigma\|F_o\| - \|F_c\|/\Sigma\|F_o\|$	0.0241
$R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma wF_o^2]^{1/2}$	0.0241
goodness of fit	1.132
max and min peaks in final diff map, e/Å^3	0.305, –0.323

refinement using the setting angles of 19 carefully centered reflections in the range 40.33 < 2θ < 44.38°. On the basis of the systematic absences $h00$ ($h \neq 2$), $0k0$ ($k \neq 2n$), and $00l$ ($l \neq 2n$) and the successful solution and refinement of the structure, the space group was determined to be $P2_12_12_1$. Of the 1517 reflections that were collected, 1516 were unique (R_{int} = 0.056). Lorentz, polarization, empirical absorption,[27] and linear decay (27.0%) corrections were applied to the data. The structure was solved by direct methods.[28] The non-hydrogen atoms were refined anisotropically. Four carbon atoms of the seven membered ring are disordered; two positions of each (C6 and C6*, C7 and C7*, C8 and C8*, and C9 and C9*) were located and refined with occupation factors of 0.5. The hydrogen atoms were placed in their geometrically calculated positions with a C–H distance of 1.08 Å; their positions and their temperature factors were refined isotropically. Neutral atom scattering factors were taken from Cromer and Waber.[29] Anomalous dispersion effects were included in F_c;[30] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[31] All calculations were performed using SHELX 76.[32]

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Supplementary Material Available: Tables of hydrogen atom positional parameters and thermal parameters and complete tables of bond angles and torsional angles (5 pages). Ordering information is given on any current masthead page.

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