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HYDROLYSIS PATHWAY LEADING TO THE FORMATION OF NOVEL OXO- AND HALO-BRIDGED TIN(IV) LADDER COMPOUNDS. THE MOLECULAR STRUCTURE OF THE DIMERIC DISTANNOXANES

$[\text{Ph}_2(\text{Cl})\text{SnOSnPh}_2(\text{OH})]_2 \cdot 2(\text{CH}_3)_2\text{CO}$ AND $[\text{Ph}_2(\text{Cl})\text{SnOSnPh}_2(\text{Cl})]_2$

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HYDROLYSIS PATHWAY LEADING TO THE FORMATION OF NOVEL OXO- AND HALO-BRIDGED TIN(IV) LADDER COMPOUNDS. THE MOLECULAR STRUCTURE OF THE DIMERIC DISTANNOXANES $[\text{Ph}_2(\text{Cl})\text{SnOSnPh}_2(\text{OH})]_2 \cdot 2(\text{CH}_3)_2\text{CO}$ AND $[\text{Ph}_2(\text{Cl})\text{SnOSnPh}_2(\text{Cl})]_2^{1,2}$

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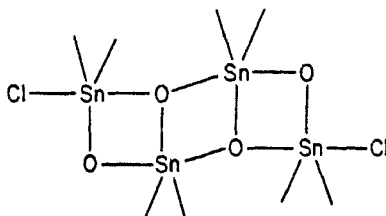
Acid–base adduct formation occurs in benzene solutions of Ph_2SnCl_2 with quinuclidine, Dabco, and acridine as ligands. By use of the latter base, the dichlorodistannoxane $[\text{Ph}_2\text{ClSnOSnPh}_2\text{Cl}]_2$ (**6**) also was isolated. In more polar solvents, hydrolysis reactions of Ph_2SnCl_2 occur more readily, leading to dimeric distannoxanes. The hydroxystannoxane $[\text{Ph}_2\text{ClSnOSnPh}_2\text{OH}]_2 \cdot 2(\text{CH}_3)_2\text{CO}$ (**5**) is isolated from the reaction of Ph_2SnCl_2 and quinuclidine in acetonitrile solution. It is also obtained by the analogous reaction of Dabco in acetone. Further characterized from these reactions were anionic complexes $[\text{Ph}_2\text{SnCl}_4][\text{base} \cdot \text{H}]_2$ (base = quinuclidine, Dabco, or acridine). The isolation and structural characterization of successive members in the hydrolysis lead to a mechanism of formation of the dimeric distannoxanes **5** and **6**. X-ray analysis shows they both possess “ladder” structures with tin atoms in trigonal-bipyramidal conformations. This is the first structural study of distannoxanes containing directly bonded aryl groups. **5** crystallizes in the monoclinic space group $P2_1/n$ with $a = 11.758$ (2) Å, $b = 19.327$ (3) Å, $c = 11.649$ (1) Å, $\beta = 92.87$ (1)°, and $Z = 2$. The structure was refined to $R = 0.028$ and $R_w = 0.039$. For **6**, the monoclinic space group $P2_1/c$ was obtained with $a = 10.284$ (2) Å, $b = 10.513$ (3) Å, $c = 22.143$ (4) Å, $\beta = 100.75$ (2)°, and $Z = 2$. The structure was refined to $R = 0.023$ and $R_w = 0.034$.

INTRODUCTION

Partial hydrolysis of diorganotin dihalides leads to interesting classes of tetraorganodistannoxanes, $\text{R}_2\text{XSnOSnR}_2\text{X}$ and $\text{R}_2\text{XSnOSnR}_2\text{OH}$.^{4–7} Solution work established dimeric formulations as early as 1939 for the halo derivatives $[\text{Et}_2\text{XSnOSnEt}_2(\text{OH})]_2$ ($\text{X} = \text{Br}, \text{I}$).⁸ Later work supported the dimeric nature of this class of substances for many of the members as well as the presence of the four-membered distannoxane ring.^{4–7}

More recently further detail was revealed from an X-ray diffraction study of $[\text{Me}_2\text{ClSnOSnMe}_2\text{Cl}]_2$ (**1**) and its ethyl homologue $[\text{Et}_2\text{ClSnOSnEt}_2\text{Cl}]_2$.⁹ In particular, the former substance showed a planar ladder arrangement with a distorted trigonal-bipyramidal arrangement about the tin atoms. This is analogous to the structure of $[(i\text{-Pr})_2\text{ClSnOSn}(i\text{-Pr})_2\text{Cl}]_2$ (**2**).¹⁰ Structures of related distannoxanes, determined earlier, have similar ladder structures, e.g., the isothiocyanato

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derivative $[\text{Me}_4\text{Sn}_2(\text{NCS})_2\text{O}]_2$,¹¹ although the trimethylsiloxy derivative, $[\text{Me}_4\text{Sn}_2(\text{OSiMe}_3)_2\text{O}]_2$ (**3**),^{12,13} is described more accurately as a “staircase.”

Of interest is the course of the hydrolytic reaction by which these dimeric distannoxanes are formed from diorganotin dihalides. Monohydroxides $\text{R}_2\text{SnX}(\text{OH})$ have been implicated^{5,14} as initial products in the hydrolysis. Also prominent in the hydrolysis reactions, which are usually carried out in moist polar solvents,⁴ is the formation of dimeric hydroxydistannoxanes, $[\text{R}_2\text{XSnOSnR}_2(\text{OH})]_2$. These are the partial hydrolysis products of the dihalodistannoxanes. X-ray structural studies of two of these hydroxy derivatives have been reported, $[(i\text{-Pr})_2\text{ClSnOSn}(i\text{-Pr})_2\text{OH}]_2$ (**4a**)¹⁵ and $[(\text{Me}_3\text{SiCH}_2)_2\text{ClSnOSn}(\text{Me}_3\text{SiCH}_2)_2\text{OH}]$ (**4b**),¹⁵ as well as a rare example of a fully hydroxylated distannoxane, $[(\text{Me}_3\text{SiCH}_2)_2(\text{OH})\text{SnOSn}(\text{Me}_3\text{SiCH}_2)_2(\text{OH})_2]_2$ (**4c**).¹⁰ All of these structures, **4a–c**, have a planar ladder arrangement like **1** with pentacoordinated tin centers.

We have performed a variety of hydrolyses of Ph_2SnCl_2 for the purpose of isolating intermediates leading to the characterization of the possible mechanistic sequence in the formation of dimeric distannoxanes. In conducting these reactions, the chlorohydroxydistannoxane $[\text{Ph}_2(\text{Cl})\text{SnOSnPh}_2(\text{OH})]_2 \cdot 2(\text{CH}_3)_2\text{CO}$ (**5**), the dichlorodistannoxane $[\text{Ph}_2(\text{Cl})\text{SnOSnPh}_2(\text{Cl})]_2$ (**6**), and salts of the stannate anion $[\text{Ph}_3\text{SnCl}_4]$ were isolated. This report represents the first structural study of distannoxanes containing aryl substituents. The X-ray structures of **5** and **6** are reported here along with synthetic aspects. This information is used to formulate a reasonable scheme for the hydrolytic process.

EXPERIMENTAL

Synthesis. Formation of the 1:1 Adduct (7) of Diphenyltin(IV) Dichloride and Quinuclidine. Two grams (5.82 mmol) of diphenyltin dichloride was dissolved in 30 mL of dry benzene with stirring. To the solution was added 0.65 g (5.85 mmol) of quinuclidine, and immediately a white, insoluble product formed. The white powder was filtered off and washed with benzene; mp 186–188 °C (yield 1.42 g, 53.6%). Anal. Calcd for $\text{C}_{19}\text{H}_{23}\text{NCl}_2\text{Sn}$: C, 50.14; H, 5.05; N, 3.08; Cl, 15.62. Found: C, 49.31; H, 5.62; N, 3.55; Cl, 15.04.

Formation of the Diphenyltetrachlorostannate(IV)–Quinuclidinium Complex, $[\text{Ph}_2\text{SnCl}_4][\text{quinuclidine} \cdot \text{H}]_2$ (8**), from 7.** Solution of ~0.1 g of **7** in 75 mL of benzonitrile was effected by heating the mixture at 120 °C for 20 min. Upon cooling of the solution, small, white needle-like crystals of **8** formed; mp 230–236 °C dec. Anal. Calcd for $\text{C}_{26}\text{H}_{38}\text{N}_2\text{Cl}_4\text{Sn}$: C, 48.84; H, 5.98; N, 4.38; Cl, 22.23. Found: C, 49.06; H, 6.04; N, 4.31; Cl, 21.67.

Reaction of Diphenyltin(IV) Dichloride with Quinuclidine in Acetonitrile Leading to $[\text{Ph}_2\text{SnCl}_4][\text{quinuclidine} \cdot \text{H}]_2$ (8**) and $\text{Ph}_2\text{ClSnOSnPh}_2\text{OH}$ (**5**).** To 0.50 g (1.45 mmol) of diphenyltin dichloride dissolved in 100 mL of freshly distilled acetonitrile was added 0.16 g (1.45 mmol) of quinuclidine. A small amount (~0.08 g) of white solid formed and was filtered off. The analysis of the white microcrystalline solid is consistent with the formation of $[\text{Ph}_2\text{SnCl}_4][\text{quinuclidine} \cdot \text{H}]_2$ (**8**). Anal. Found: C, 48.54; H, 5.98; N, 4.26; Cl, 21.00.

On standing, a white powdery solid formed from the filtrate, mp 192–193 °C, corresponding to the hydroxydistannoxane $\text{Ph}_2\text{ClSnOSnPh}_2\text{OH}$, (**5**). Anal. Calcd for $\text{C}_{24}\text{H}_{21}\text{ClO}_2\text{Sn}_2$: C, 46.91; H, 3.42; Cl, 5.77. Found: C, 47.07; H, 3.44; Cl, 5.98.

Synthesis of the 1:1 Adduct (9) of Diphenyltin(IV) Dichloride and 1,4-Diazabicyclo[2.2.2]octane (Dabco). One gram (2.90 mmol) of diphenyltin dichloride was dissolved with stirring in 30 mL of benzene. To the solution was added 0.33 g (2.90 mmol) of 1,4-diazabicyclo[2.2.2]octane (Dabco). Immediately, a white powdery precipitate formed which was filtered and air-dried (yield 0.91 g, 68.2%). Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{Cl}_2\text{N}_2\text{Sn}$: C, 47.40; H, 4.83; N, 6.14; Cl, 15.58. Found: C, 46.77; H, 4.97; N, 6.36; Cl, 16.00.

Reaction of Diphenyltin(IV) Dichloride with Dabco in Acetone. Two grams (5.81 mmol) of diphenyltin dichloride was dissolved in 50 mL of acetone. With stirring, 0.65 g (5.81 mmol) of Dabco were added. A whitish microcrystalline product formed (Yield 1.13 g, 42.6%). Recrystallization from dimethyl sulfoxide resulted in the formation of $[\text{Ph}_2\text{SnCl}_4][\text{Dabco} \cdot \text{H}]_2$ (**10**) as shown by an X-ray study.¹⁶

Upon standing, crystals formed in the acetone filtrate. Upon drying, the crystals changed to a white powder, mp 192–193 °C, corresponding to the hydroxydistannoxane $\text{Ph}_2\text{ClSnOSnPh}_2\text{OH}$ (**5**). Anal. Calcd for $\text{C}_{24}\text{H}_{21}\text{O}_2\text{ClSn}_2$: C, 46.91; H, 3.42. Found: C, 46.72; H, 3.45.

*Reaction of Diphenyltin(IV) Dichloride with Acridine, Formation of the 1:1 Adduct, $\text{Ph}_2\text{SnCl}_2 \cdot \text{Acridine}$ (**11**), the Dichlorodistannoxane **6**, and the Acridine Complex $[\text{Ph}_2\text{SnCl}_4][\text{acridine} \cdot \text{H}]_2$ (**12**).* One gram (2.90 mmol) of diphenyltin dichloride was dissolved in 150 mL of benzene. To this solution was added 0.52 g (2.90 mmol) of acridine. An immediate mustard colored precipitate of **11** formed. The precipitate was filtered off and washed with benzene; mp 125–127 °C, yield 0.46 g, 30.2%). The solid turned red upon melting. Anal. Calcd for $\text{C}_{25}\text{H}_{19}\text{Cl}_2\text{NSn}$: C, 57.40; H, 3.63; N, 2.68; Cl, 13.59. Found: C, 58.37; H, 4.04; N, 2.81; Cl, 15.00.

On standing, large colorless crystals of the dichlorodistannoxane **6** formed from the filtrate; mp 194–196 °C. Anal. Calcd for $\text{C}_{24}\text{H}_{21}\text{Cl}_2\text{OSn}_2$: C, 45.54; H, 3.16; Cl, 11.23. Found: C, 45.77; H, 3.11; Cl, 10.78. In addition, yellow-orange crystals of **12** also formed; mp 177–179 °C. The latter turned red on melting.

This same substance was obtained by partially hydrolyzing the mustard colored adduct $\text{Ph}_2\text{SnCl}_2 \cdot \text{acridine}$ (**11**). This was accomplished by heating a methylene chloride solution of **11** at 50 °C for a few minutes with stirring, after which time an orange powder appeared; mp 178–179 °C. The analysis revealed the yellow-orange powder to contain the diphenyltetrachlorostannate(IV) anion, $[\text{Ph}_2\text{SnCl}_4][\text{acridine} \cdot \text{H}]_2$ (**12**). Anal. Calcd for $\text{C}_{38}\text{H}_{28}\text{N}_2\text{Cl}_4\text{Sn}$: C, 59.01; H, 3.62; N, 3.62; Cl, 18.38. Found: C, 58.51; H, 3.93; N, 3.51; Cl, 18.24.

Crystallography. All X-ray crystallographic studies were done by using an Enraf-Nonius CAD4 diffractometer and graphite monochromated molybdenum radiation ($\lambda(\text{K}\alpha_1) = 0.709\,30\,\text{\AA}$, $\lambda(\text{K}\alpha_2) = 0.713\,59\,\text{\AA}$) at an ambient temperature of $23 \pm 2\text{ }^\circ\text{C}$. Details of the experimental and computational procedures have been described previously.¹⁷

Colorless crystals of **5**, grown from acetone, degrade rapidly when exposed to ambient conditions, a behavior which is most probably due to loss of acetone of solvation. A crystal of **5** ($0.25 \times 0.35 \times 0.38\text{ mm}$) which was mounted inside of a sealed thin-walled glass capillary proved to be stable and was used for the X-ray studies.

*Crystal data for $(\text{Ph}_2\text{Sn}_2\text{ClO}_2\text{H})_2 \cdot 2(\text{CH}_3)_2\text{CO}$ (**5**):* uniquely determined space group $P2_1/n$ (alternate setting of $P2_1/c$ [C_{2h}^2 , No. 14]¹⁸), $a = 11.758\,(2)\,\text{\AA}$, $b = 19.327\,(3)\,\text{\AA}$, $c = 11.649\,(1)\,\text{\AA}$, $\beta = 92.87\,(1)^\circ$, $Z = 2$, and $\mu(\text{Mo K}\alpha) = 2.027\text{ mm}^{-1}$; 4609 independent reflections ($+h, +k, \pm l$) were measured by using the θ - 2θ scan mode for $2^\circ \leq 2\theta(\text{Mo K}\alpha) \leq 50^\circ$. No corrections were made for absorption.

The structure was solved by using standard Patterson and difference Fourier techniques and was refined by full-matrix least-squares.¹⁹ The 33 independent non-hydrogen atoms (29 for half the dimer about an inversion center, four for acetone in general positions) were refined anisotropically. Coordinates for the 20 independent phenyl hydrogen atoms were calculated, and these atoms were included in the refinement as fixed isotropic scatterers whose coordinates were updated as refinement converged so that the final C—H bond lengths were 0.98 Å. Coordinates for the hydrogen atom of the hydroxide moiety were obtained from the strongest peak (0.513 e/\AA^3) on a difference Fourier which was based on the aforementioned 53 atoms. This atom was also included in the refinement as a fixed isotropic scatterer. Hydrogen atoms of the acetone molecule were omitted. The final agreement factors²⁰ were $R = 0.028$ and $R_w = 0.039$ for the 3856 reflections having $I \geq 2\sigma_I$.

A colorless crystal **6** ($0.23 \times 0.33 \times 0.35\text{ mm}$) which was grown from benzene solution and mounted inside a sealed thin-walled glass capillary was used for the X-ray studies.

Crystal data for $(\text{Ph}_2\text{Sn}_2\text{ClO})_2 \cdot 2(\text{CH}_3)_2\text{CO}$ (**5**): uniquely determined space group $P2_1/c$,¹⁸ $a = 10.284(2) \text{ \AA}$, $b = 10.513(3) \text{ \AA}$, $c = 22.143(4) \text{ \AA}$, $\beta = 100.75(2)^\circ$, $Z = 2$, and $\mu(\text{Mo K}\alpha) = 2.372 \text{ mm}^{-1}$; 2690 independent reflections ($+h, +k, \pm l$) were measured by using the θ - 2θ scan mode for $2^\circ \leq 2\theta(\text{Mo K}\alpha) \leq 43^\circ$. No corrections were made for absorption.

The structure was solved and refined as for **5** (29 anisotropic non-hydrogen atoms, 20 fixed isotropic hydrogen atoms). The final agreement factors were $R = 0.023$ and $R_w = 0.034$ for the 2387 reflections having $I \geq 2\sigma_I$.

RESULTS

The atom labeling scheme for **5** is given in the ORTEP plot of Figure 1, while atomic coordinates are given in Table I. The corresponding information for **6** is given in Figure 2 and in Table II. For both compounds, selected bond lengths and angles are given in Table III. Anisotropic thermal parameters, fixed parameters for hydrogen atoms, additional bond lengths and angles, and deviations from some least-squares mean planes are provided as supplementary material.

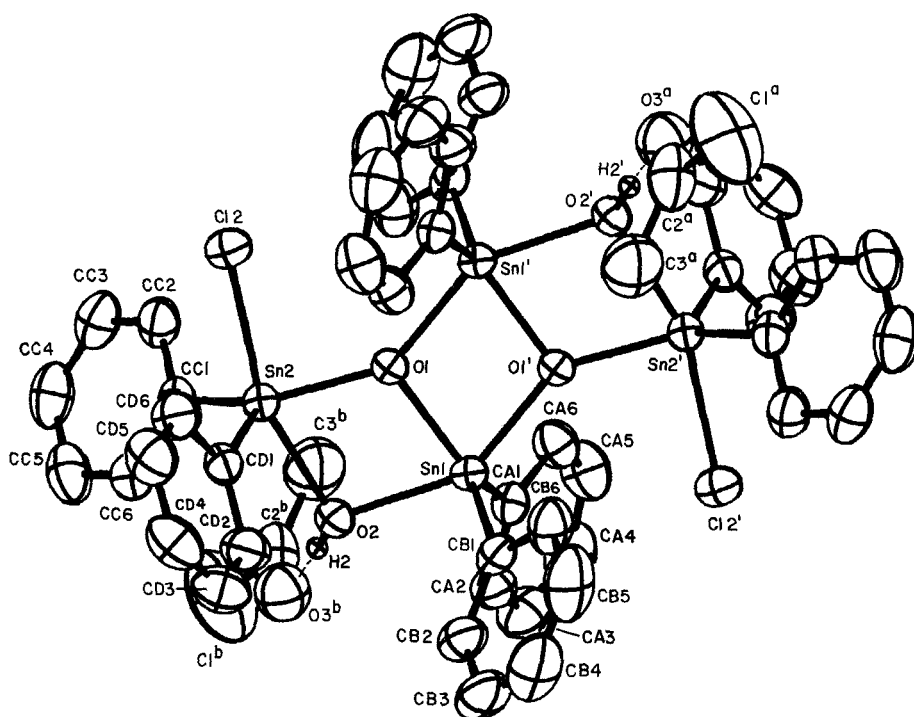


FIGURE 1 ORTEP plot of $(\text{Ph}_2\text{Sn}_2\text{ClO}_2\text{H})_2 \cdot 2(\text{CH}_3)_2\text{CO}$ (**5**) with thermal ellipsoids at the 50% probability level. Phenyl hydrogen atoms have been omitted for purposes of clarity. Primed atoms are generated from unprimed ones by $-x, -y, -z$. Acetone molecules shown are related to those in the coordinate list by $b = \frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$ and $a = x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$.

TABLE I
Atomic coordinates in crystalline $(\text{Ph}_2\text{Sn}_2\text{ClO}_2\text{H}) \cdot 2(\text{CH}_3)_2\text{CO}$ (5)^a

atom type ^b	10 ⁴ x	10 ⁴ y	10 ⁴ z
Sn1	1040.8 (2)	-524.8 (1)	502.6 (2)
Sn2	1990.5 (2)	1113.5 (1)	706.9 (2)
O2	2489 (2)	48 (1)	1212 (2)
O1	636 (2)	505 (1)	271 (2)
Cl2	780 (1)	2106 (1)	121 (1)
CA1	723 (4)	-1063 (2)	2044 (3)
CA2	1636 (4)	-1408 (2)	2595 (4)
CA3	1461 (5)	-1802 (3)	3586 (4)
CA4	392 (6)	-1849 (3)	3997 (4)
CA5	-501 (5)	-1504 (3)	3454 (4)
CA6	-348 (4)	-1104 (2)	2476 (4)
CB1	1911 (4)	-964 (2)	-876 (4)
CB2	3034 (4)	-1169 (2)	-679 (4)
CB3	3605 (5)	-1490 (3)	-1551 (6)
CB4	3080 (6)	-1592 (3)	-2602 (6)
CB5	1966 (6)	-1394 (4)	-2801 (5)
CB6	1364 (5)	-1074 (3)	-1943 (4)
CC1	2364 (4)	1512 (2)	2390 (4)
CC2	1610 (4)	1950 (2)	2927 (4)
CC3	1910 (5)	2258 (3)	3962 (4)
CC4	2971 (5)	2148 (3)	4480 (4)
CC5	3735 (5)	1710 (3)	3969 (5)
CC6	3431 (4)	1392 (2)	2915 (4)
CD1	3185 (3)	1173 (2)	-612 (3)
CD2	3934 (4)	638 (3)	-804 (4)
CD3	4706 (4)	679 (3)	-1662 (5)
CD4	4732 (4)	1258 (3)	-2339 (4)
CD5	4010 (5)	1799 (3)	-2166 (5)
CD6	3215 (4)	1760 (3)	-1311 (4)
C1	1568 (8)	5014 (6)	-641 (6)
C2	2211 (6)	4962 (3)	529 (5)
C3	3452 (6)	5133 (4)	556 (6)
O3	1740 (3)	4817 (2)	1402 (3)
H2	2800	-50	2000

^a Numbers in parentheses are estimated standard deviations. ^b Atoms are labeled to agree with Figure 1.

DISCUSSION

Structures

Both the halohydroxydistannoxane $[\text{Ph}_2\text{ClSnOSnPh}_2\text{OH}]_2 \cdot 2(\text{CH}_3)_2\text{CO}$ (5) and the dichlorodistannoxane $[\text{Ph}_2\text{ClSnOSnPh}_2\text{Cl}]_2$ (6) have dimeric formulations. They exist as ladder compounds that contain pentacoordinated tin atoms.

Both compounds 5 and 6 can be viewed as centrosymmetric dimers, where one half of the molecule comprises the crystallographic asymmetric unit and other half is generated by an inversion center.

The two independent tin atoms in each molecule are pentacoordinated with geometries about the Sn atoms that can be described as distorted trigonal bipyramids, having two phenyl groups and O1 in equatorial positions. The distortions away from ideal trigonal-bipyramidal geometry are not along the Berry coordinate²¹

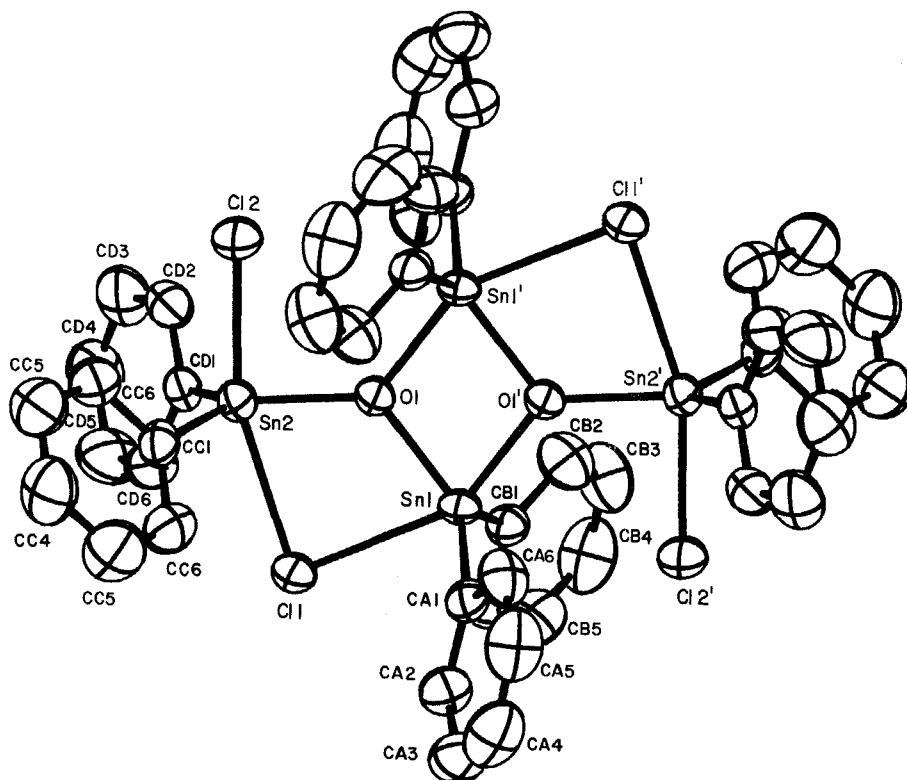


FIGURE 2 ORTEP plot of $(\text{Ph}_3\text{Sn}_2\text{Cl}_2\text{O})_2$ (**6**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for purposes of clarity. Primed atoms are generated from unprimed ones by $-x$, $-y$, $-z$.

but rather seem to be due to the constraints imposed by the fused ring systems as well as weak interactions between Cl2 and Sn1'. These constraints cause the "axial" atoms, O2 (Cl1) and O1' for Sn1, O2 (Cl1) and Cl2 for Sn2 for **5** (**6**), to be bent toward what would be the "pivotal" atom (O1) in the formal Berry process.

Both compounds have "ladder" structures rather than "staircase" arrangements, as evidenced by the near coplanarity of the atoms comprising the fused ring systems. For **5**, the atoms Sn1, Sn2, O1, O2, Sn1', Sn2', O1', and O2' are coplanar to within ± 0.07 Å, while for **6** the corresponding atoms Sn1, Sn2, O1, Cl1, Sn1', Sn2', O1', and Cl1' are coplanar to within ± 0.03 Å. This near coplanarity is also seen in the dihedral angle between the planes defined by the central and terminal four-atom rings. For **5**, the dihedral angle between the least-squares mean plane defined by atoms Sn1, Sn2, O1, and O2 (coplanar to within ± 0.06 Å), plane 6 of Table G (supplementary material), and atoms Sn1, O1, Sn1', and O1' (required by symmetry to be coplanar), plane 5 of Table G, is 3.4° . For **6** the corresponding values (substituting Cl1 for O2) are ± 0.01 Å and 1.8° (Table H), supplementary material.

For Sn1, in both compounds, there is close intramolecular contact with Cl2', which may be viewed as a weak bonding interaction. The Sn1–Cl2' distances are 3.780 (1) and 3.355 (2) Å for **5** and **6**, respectively, compared to the van der Waals'

TABLE II
 Atomic coordinates in crystalline $(\text{Ph}_4\text{Sn}_2\text{Cl}_2\text{O})_2$ (6)^a

atom type ^b	10 ⁴ x	10 ⁴ y	10 ⁴ z
Sn1	1432.9 (3)	-108.1 (3)	-234.5 (2)
Sn2	1718.9 (3)	881.5 (3)	1343.0 (2)
Cl1	3542 (1)	499 (1)	630 (1)
Cl2	-368 (1)	935 (1)	1707 (1)
O1	628 (3)	312 (3)	522 (1)
CA1	1886 (5)	1431 (5)	-776 (2)
CA2	3172 (6)	1566 (5)	-862 (3)
CA3	3510 (7)	2464 (6)	-1263 (3)
CA4	2545 (8)	3237 (6)	-1588 (3)
CA5	1268 (7)	3131 (6)	-1502 (3)
CA6	923 (6)	2217 (6)	-1109 (3)
CB1	2051 (5)	-2018 (5)	-258 (2)
CB2	3351 (7)	-2301 (6)	-271 (3)
CB3	3705 (7)	-3576 (7)	-360 (3)
CB4	2787 (9)	-4532 (6)	-417 (3)
CB5	1510 (7)	-4243 (6)	-408 (3)
CB6	1121 (6)	-2997 (6)	-329 (3)
CC1	2110 (5)	2883 (5)	1419 (2)
CC2	2808 (6)	3543 (6)	1037 (3)
CC3	3061 (9)	4825 (6)	1137 (4)
CC4	2614 (8)	5464 (6)	1599 (3)
CC5	1927 (7)	4821 (6)	1978 (3)
CC6	1655 (6)	3533 (6)	1888 (3)
CD1	2673 (5)	-499 (5)	1987 (2)
CD2	1977 (5)	-1089 (6)	2377 (3)
CD3	2638 (7)	-1875 (6)	2854 (3)
CD4	3967 (7)	-2073 (7)	2911 (3)
CD5	4651 (6)	-1492 (7)	2517 (3)
CD6	4020 (5)	-687 (6)	2062 (3)

^a Numbers in parentheses are estimated standard deviations. ^b Atoms are labeled to agree with Figure 2.

 TABLE III
 Selected bond lengths (Å) and bond angles (deg) for $(\text{Ph}_4\text{Sn}_2\text{ClO}_2\text{H})_2 \cdot 2(\text{CH}_3)_2\text{CO}$ (5) and $(\text{Ph}_4\text{Sn}_2\text{Cl}_2\text{O})_2$ (6)^a

bond length type ^b	compound		bond length type	compound	
	5	6		5	6
Sn1-O1	2.061 (3)	2.050 (3)	Sn2-O1	2.024 (3)	2.040 (3)
Sn1-O1'	2.127 (3)	2.107 (3)	Sn2-Cl2	2.465 (1)	2.430 (1)
Sn1-O2(Cl1)	2.160 (3)	2.668 (1)	Sn2-O2(Cl1)	2.212 (3)	2.697 (1)
Sn1-CA1	2.124 (4)	2.117 (5)	Sn2-CC1	2.131 (4)	2.144 (5)
Sn1-CB1	2.124 (4)	2.109 (6)	Sn2-CD1	2.135 (4)	2.141 (5)
Sn1'-Cl2	3.780 (1)	3.365 (2)			
bond angle type	compound		bond angle type	compound	
	5	6		5	6
O2(Cl1)-Sn1-O1'	148.1 (1)	150.7 (1)	O2(Cl1)-Sn2-Cl2	160.0 (1)	162.0 (1)
O2(Cl1)-Sn1-O1	74.2 (1)	76.2 (1)	O2(Cl1)-Sn2-O1	73.8 (1)	76.2 (1)
O2(Cl1)-Sn1-CA1	95.5 (1)	89.4 (1)	O2(Cl1)-Sn2-CC1	93.0 (1)	93.0 (1)
O2(Cl1)-Sn1-CB1	95.4 (1)	92.1 (1)	O2(Cl1)-Sn2-CD1	93.8 (1)	90.4 (1)
O1'-Sn1-O1	74.0 (1)	74.5 (1)	Cl2-Sn2-O1	86.9 (1)	86.0 (1)
O1'-Sn1-CA1	99.7 (1)	102.8 (2)	Cl2-Sn2-CC1	93.6 (1)	95.6 (1)
O1'-Sn1-CB1	99.1 (1)	100.8 (2)	Cl2-Sn2-CD1	98.6 (1)	96.8 (1)
O1-Sn1-CA1	122.3 (1)	117.6 (2)	O1-Sn2-CC1	124.3 (1)	115.0 (2)
O1-Sn1-CB1	113.8 (1)	113.2 (2)	O1-Sn2-CD1	112.8 (1)	120.2 (2)
CA1-Sn1-CB1	123.7 (2)	127.9 (2)	CC1-Sn2-CD1	122.0 (2)	123.9 (2)
Sn1-O1-Sn2	110.8 (1)	123.6 (2)	Sn1'-O1-Sn2	142.9 (1)	130.8 (2)
Sn1-O1-Sn1'	106.0 (1)	105.5 (1)	Sn1-O2(Cl1)-Sn2	100.5 (1)	84.00 (4)

^a Numbers in parentheses are estimated standard deviations. ^b Atoms are labeled to agree with Figures 1 and 2, where atom names given in parentheses apply to compound 6.

sum of 4.0 Å.²² The approach of Cl2' to Sn1 might account for the fact that the CA1—Sn1—CB1 angle is slightly larger than the ideal value of 120° for the TBP. These angles have values of 123.7 (2)° and 127.9 (2)° for **5** and **6**, respectively, and increase as the Sn1—Cl2' distance decreases.

In **5**, the hydrogen atom of the bridging hydroxide enters into a hydrogen-bonding interaction with the O atom of the acetone of solvation. This interaction is evidenced by the O2—O3 and H2—O3 distances which are 2.914 (5) and 1.929 Å, respectively. The H bond is nearly linear with an O2—H2—O3 angle of 173.4°. Concomitant with this interaction, H2 is tipped 0.734 Å out of the plane of the “ladder” backbone in a direction toward O3.

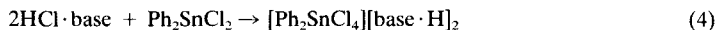
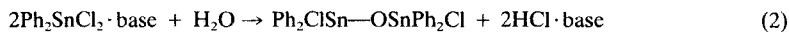
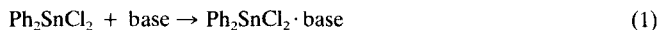
The ladder structures of **5** and **6** contrast with the staircase structure of [Me₄Sn₂(OSiMe₃)₂O]₂ (**3**),^{12,13} but they are similar to the other chlorodistannoxanes studied by X-ray diffraction in the appearance of a planar arrangement of the atoms comprising the ladder unit.^{9,10,15} In the case of the dichlorodistannoxane **6**, it is also similar to **1** in that they both contain one longer and one shorter axial Sn—O bond length. For **6**, these are 2.430 (1) Å for Sn2—Cl2 and 2.697 (1) Å for Sn2—Cl1. The comparable Sn—Cl bonds in **1**⁹ are 2.438 (4) Å and 2.788 (5) Å. The major difference between the structures of **1** and **6** is found in a weak Sn—Cl interaction (3.348 (5) Å) for **1** which links adjacent “ladders” by bisecting the “equatorial” Me—Sn—Me bond, causing the structure to be more distorted from trigonal bipyramidal than **6**. The equatorial angle C—Sn—C for **1**⁹ is 140.6 (9)° whereas the same angle in both **6** (CA1—Sn1—CB1) (127.9 (2)°) and **5** (123.7 (2)°) is much smaller. Actually, the structures of **5** and **6** are closer in detail to the structures of the more shielded distannoxanes, **2**,¹⁰ **4a–b**,¹⁵ and **4c**.¹⁰

Synthetic Aspects

Our approach in studying the base-catalyzed hydrolysis of Ph₂SnCl₂ was to isolate and structurally characterize successive products in the hydrolysis reaction so that a mechanistic sequence leading to the formation of the hydroxydistannoxane may become reasonably apparent.

An initiating feature appears to be the formation of a 1:1 acid–base adduct. In this study, three of these adducts have been prepared as insoluble powders by using nitrogen donors: Ph₂SnCl₂·quinuclidine (**7**), Ph₂SnCl₂·Dabco (**9**), and Ph₂SnCl₂·acridine (**11**). The largest yields for these adducts were obtained by reacting the starting materials in benzene. When more polar solvents were used, additional products formed. For example, the reaction of Ph₂SnCl₂ and quinuclidine in acetonitrile led to the formation of the white crystalline complex, [Ph₂SnCl₄][quinuclidine·H]₂ (**8**).²³ From the filtrate, the chlorohydroxydistannoxane [Ph₂ClSnOSnPh₂OH]₂ (**5**) was isolated.

This type of reaction producing a tin–ether species is not novel to 1:1 adduct reactions used in this study. Harrison and Molloy²⁴ discuss the reaction of diphenyltin chloride with 1-aminobenzothiazole. In benzene, a 1:1 adduct is formed, which upon recrystallization in ethanol leads to the 2-aminobenzothiazole hydrochloride



SCHEME I

salt. Conducting the reaction of diphenyltin dichloride with 2-aminobenzothiazole in acetone gives the dichlorodistannoxane $[\text{Ph}_2\text{ClSnOSnPh}_2\text{Cl}]_2$ (**6**).

The same type of reaction sequence occurs when Ph_2SnCl_2 and Dabco were reacted. The 1:1 adduct **9** forms in benzene. In acetone, the reaction produces the white powdery complex, $[\text{Ph}_2\text{SnCl}_4][\text{Dabco} \cdot \text{H}]_2$ (**10**), and from the filtrate, crystals of the hydroxydistannoxane $[\text{Ph}_2\text{ClSnOSnPh}_2\text{OH}]_2$ (**5**) are obtained.

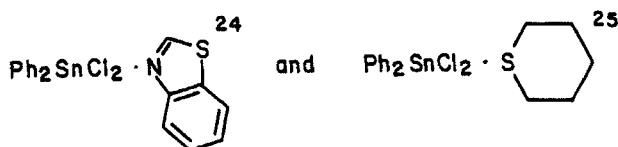
In the case of the reaction of Ph_2SnCl_2 with acridine in benzene, some differences were noted. Here it was possible to form the solid 1:1 adduct, $\text{Ph}_2\text{SnCl}_2 \cdot \text{acridine}$ (**11**), and from the filtrate, to obtain both colorless crystals of the dichlorodistannoxane **6** and a yellow-orange solid which proved to be the complex $[\text{Ph}_2\text{SnCl}_4][\text{acridine} \cdot \text{H}]_2$ (**12**). These solids could be mechanically separated. The latter, **12**, also was obtained from the recrystallization of the acridine adduct **11** in methylene chloride.

The above reactions involving the pickup of moisture, leading to the distannoxane dimer formulations **5** and **6**, are not unique but are representative of the way this class of compounds has been formed in the past. For example, the analogous dichlorodistannoxane **1** was isolated from the filtrate resulting from the reaction of Me_2SnCl_2 and 2-aminobenzothiazole in acetone solution.⁹ A white solid was also formed but not identified. Okawara and Wada^{4,7} earlier prepared a series of $[\text{R}_2\text{XSnOSnR}_2\text{X}]_2$ compounds by related reactions using R_2SnCl_2 with a nitrogen base in moist ethanol. They were able to form the hydroxydistannoxane from the chlorostannoxanes in moist methanol.⁴

In view of the results of our present findings and those of earlier workers,^{4,7,9} the mechanism shown in Scheme I leading to the formation of these two classes of dimeric distannoxanes seems plausible. All products isolated in this study are underlined. Of those isolated, we have determined the X-ray structure of at least one member in each case.^{23,25}

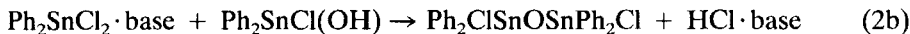
Initial acid–base adduct formation (eq 1) is followed by partial hydrolysis (eq 2) to give the dichlorostannoxane **6** and the base hydrochloride. Structural studies on the 1:1 acid–base adducts show that the base and one of the chlorine atoms occupy the weaker axial positions of a trigonal bipyramid. The base hydrochloride has been isolated in the analogous reaction of Harrison and Molloy.²⁴

It is expected that the longer and presumably weaker axial tin–chlorine bond length (Sn2—Cl1) in **6** is responsible for the hydrolysis in eq 3 leading to the hydroxydistannoxane **5**. The remaining tin–chlorine bond length (Sn2—Cl1) in **5** has increased only slightly in length (0.035 Å) compared to this bond in **6**. This may partially account for the lack of further hydrolysis under the mild conditions



reported here which would give a dihydroxydistannoxane. The only example structurally characterized by X-ray diffraction was a low-temperature study of **4c**¹⁰ which contains the relatively large protecting groups, Me_3SiCH_2 , formed by hydrolysis of the corresponding diorganotin dichloride with aqueous KOH in hot toluene. Finally, the formation of the diphenyltetrachlorostannate(IV) anion²³ may competitively occur by reaction of the base–hydrochloride and Ph_2SnCl_2 (eq 4).

This scheme is similar to the sequence formulated by Mufti and Poller²⁶ in their study of the hydrolysis of diisocyanates $\text{R}_2\text{Sn}(\text{NCO})_2$ leading to polymeric tin oxides. In addition, the hydroxyhalide species $\text{R}_2\text{SnX}(\text{OH})$ was postulated as a precursor to the formation of the dihalodistannoxane $\text{R}_2\text{XSnOSnR}_2\text{X}$. Although we found no evidence for the presence of $\text{Ph}_2\text{SnCl}(\text{OH})$, considering the lability of this class of substances,²⁷ its formation as a transient species could take part in eq 2.



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Registry No. **5**, 89462-21-5; **6**, 89462-22-6; **7**, 89462-19-1; **8**, 89462-23-7; **9**, 89462-24-8; **10**, 89462-25-9; **11**, 89462-26-0; **12**, 89462-27-1; Ph_2SnCl_2 , 1135-99-5.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes for **5** and **6**, anisotropic thermal parameters for **5** (Table A), hydrogen atom parameters for **5** (Table B), anisotropic thermal parameters for **6** (Table C), hydrogen atom parameters for **6** (Table D), additional bond lengths and angles for **5** (Table E) and **6** (Table F), and deviations from least-squares mean planes for **5** (Table G) and **6** (Table H) (32 pages). Ordering information is given on any current masthead page.

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