PREPARATION AND PROPERTIES OF DIMERIC TETRA-ALKYLDISTANNOXANE DERIVATIVES: $XR_2SnOSnR_2OH$ and $XR_2SnOSnR_2OR'$

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Although many of the observed properties of the organometallic compounds of the fourth group elements (Si, Ge, Sn, Pb) are similar, there are certain unique properties of these compounds which are peculiar to a particular element. Many studies have been done on the organosilicon compounds, particularly on organosiloxanes, because they are associated with the industrially important silicones. Organosiloxane chemistry is unique in the sense that the Si–O–Si linkage has the peculiar $d\pi$–$p\pi$ bonding which distinguishes the silicon chemistry from that of carbon. We have little knowledge of the particular properties associated with the M–O–M bond in organogermoxanes and plumboxanes. Although many kinds of organostannoxanes have been reported[1], the characteristic properties due to the Sn–O–Sn bond have not been made clear. Recently, Okawara pointed out[2] that tetraalkyl-1,3-dichlorodistannoxanes, $ClR_2SnOSnR_2Cl$, and tetraalkyl-1,3-bis(trimethylsiloxy)distannoxanes, $Me_3SiOR_2SnOSnR_2OSiMe_3$, are dimeric in benzene solution, and suggested the presence of a four membered ring, due to the coordination from the oxygen atom between two tin atoms of one chain to a tin atom of the other chain (see structure (I)), taking account of the results of an X-ray analysis of tetramethyl-1,3-bis(trimethylsiloxy)distannoxane, which is in progress in this laboratory. Analogous structures were proposed later by Alleston *et al.*[3]

In this report, we wish to report on the preparation and properties of fairly stable compounds of the types $XR_2SnOSnR_2OH$ and $XR_2SnOSnR_2OR'$ ($X =$ halogen; $R =$ Me, Et, *n*-Pr or *n*-Bu; $R' =$ Me, Et) which can be derived from $XR_2SnOSnR_2X$ or R_2SnX_2. Some of these compounds are soluble in organic solvents and dimeric in benzene or in cyclohexane, and it is reasonable to assume that these compounds have also the similar type of dimerization. In the following paper[9], the results of the infrared spectra of these compounds are summarized and the characteristic absorptions associated with these compounds will be discussed.

Dimeric $XR_2SnOSnR_2X$

It has been made clear in several recent reports that the compounds of the type $R_2SnO \cdot R_2SnX_2$ are formulated as tetraalkyl-1,3-dihalodistannoxanes, $XR_2SnOSnR_2X$, which have an Sn–O–Sn linkage in the molecule. Okawara and Rochow[4] prepared the compound having the composition $Me_2SnO \cdot Me_2SnCl_2$ by the partial hydrolysis of $ClMe_2Sn(OOCH)$ or $ClMe_2Sn(OOCCH_3)$, or by the reaction of polymeric dimethyltin oxide suspended in methanol with aqueous HCl, and gave the distannoxane formula, $ClMe_2SnOSnMe_2Cl$, for it. Another support for this formulation is that this compound has an characteristic strong absorption associated with the Sn–O–Sn bond near 600 cm^{-1}, which is closely related to the absorption found in the infrared spectra of polymeric SnO_2, $MeSnO_{1.5}$ and Me_2SnO in this region[5]. Later, Gibbons *et al.*[6] mentioned that "$Bu_2SnO \cdot Bu_2SnCl_2$" should be represented as $ClBu_2SnOSnBu_2Cl$, because the compound can be obtained by adding water to the ethanol solution of Bu_2SnCl_2 or by the oxidation of tetra-*n*-butyl-1,2-dichloroditin, $ClBu_2SnSnBu_2Cl$, by oxygen.

In general, such compounds, which are known to be dimeric in solution, have been prepared by the partial hydrolysis of dialkyltin dihalides, R_2SnX_2, in a moist polar solvent, or by the reaction of an equivalent amount of the polymeric dialkyltin oxide, R_2SnO, and R_2SnX_2 in a wet solvent[1], or by the reaction of R_2SnO and aqueous HX. The compounds $(BrMe_2SnOSnMe_2Br)_2$ and $(IR_2SnOSnR_2I)_2$ (R = Me, Et, *n*-Pr or *n*-Bu) cannot be obtained by these methods rather the corresponding hydroxides $(XR_2SnOSnR_2OH)_2$ or alkoxides $(XR_2SnOSnR_2OR')_2$ (R′ = alkyl group of the alcohol used for the solvent) are isolated instead.

Dimeric $XR_2SnOSnR_2OH$

It is found that dimeric $XR_2SnOSnR_2X$ in ether gives also dimeric $XR_2SnOSnR_2OH$ with an equivalent amount of dilute NaOH, or more conveniently with an organic base, such as pyridine, which substitutes selectively two of the four chlorine atoms of the starting material. The properties and the infrared spectra of such compounds, $(XR_2SnOSnR_2OH)_2$, are identical with those of the compounds reported as $H(R_2SnO)_2OH \cdot R_2SnX_2$[1] by Harada (see Table 2), which were prepared by refluxing R_2SnX_2 and polymeric R_2SnO in 1:3 mole ratio in a wet organic solvent. The inconsistency of the reported[7] melting point (140–1°C) of $Et_2SnO \cdot Et_2SnI(OH)$ with our result for dimeric $IEt_2SnOSnEt_2OH$ might have come from the misobservation of the melting point of $IEt_2SnOSnEt_2OEt$ for that of hydroxide, as can be understood from the fact that this alkoxide changes easily to the hydroxide. This change, accompanied by the elevation of the melting point and tin content, was also traced with reference to the infrared spectra. As is seen in Table 2, these compounds show a wide range of melting point, even after several recrystallizations, in contrast to the compounds shown in Table 1, and seem to decompose at their melting point. The intensity of the infrared absorption due to the SnO–H stretching vibration does not change even if the samples are kept for a long time below the melting point, decreases once the sample has melted. These hydroxides do not react with carbon dioxide in a wet or dry solvent. It is worth noting that only one compound, trimethyltin hydroxide, has been known to have properties similar to those of these hydroxides; it is stable against condensation, and carbon dioxide does not react with it to form the carbonate in a dry solvent.

Dimeric $XR_2SnOSnR_2OR'$

This type of compound is easily prepared by the partial alcoholysis of $XR_2SnOSnR_2X$, or by the recrystallization of the hydroxide in an alcohol:

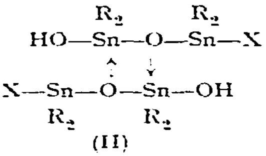
$$(XR_2SnOSnR_2OH)_2 \underset{H_2O}{\overset{R'OH}{\rightleftharpoons}} (XR_2SnOSnR_2OR')_2$$

The reaction seems to be reversible, for the reverse reaction can be carried out by recrystallization in moist acetone or by exposing the alkoxide to moist air for a few days. The stability of the alkoxides seems to be related to the kind of alkyl group present: the longer the alkyl groups attached to the tin atom or the oxygen atom, the less stable is the alkoxide. The melting points of the fairly stable alkoxides, which are listed in Table 3, seem to be the beginning point of decomposition, as is in the case of $(XR_2SnOSnR_2OH)_2$. These alkoxides may also be understood to be identical with the compounds reported as $R'(R_2SnO)_3OR' \cdot R_2SnX_2$[1].

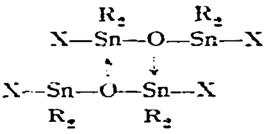
Dimerisation by coordination of distannoxanes

As shown in Fig. 1, the soluble compounds of the types $XR_2SnOSnR_2X$, $XR_2SnOSnR_2OH$ and $Me_3SiOR_2SnOSnR_2OSiMe_3$ are dimeric in benzene or cyclohexane, but R_2SnX_2[1], $Me_3SiOSnR_3$[8] and $R_3SnOSnR_3$ are monomeric in benzene. It can be concluded from these facts that the dimerisation of distannoxanes is closely associated with the presence of the Sn–O–Sn linkage, and further, it seems to be an important factor in the dimerization that one electronegative element, halogen or oxygen, is attached to each tin atom.

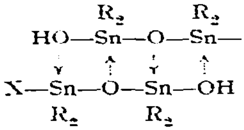
If the dimeric distannoxane of the simplest type has the structure (I), there are two kinds of tin atoms; the tetra-coordinated and the penta-coordinated, as was confirmed by the ^{119}Sn NMR spectra of such compounds by Alleston *et al.*[3]. Thus there are two different kinds of X substituents on tin, which differ in reactivity as is indicated by the existence of the fairly stable derivatives, $(XR_2SnOSnR_2OH)_2$ or $(XR_2SnOSnR_2OR')_2$. For these compounds there is a possibility for the existence of at least two isomers (II) and (II'), because we can find only one kind of absorption associated with Sn–OH or Sn–OR', as shown in the following paper[9].



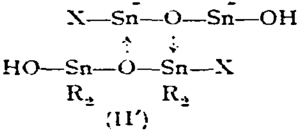
(II)



(I)



(III)



(II')

If the substitution reaction proceeds without serious changes in the skeletal structure shown in (I), it is likely to assign structure (II) to these compounds, because the tin atom which more easily undergoes substitution would be the penta-coordinated one. However, we could obtain only one uniform product in our experiments, never two isomers. This suggests that either one of the isomers is unstable, or structures (II) and (II') should be replaced by another reasonable structure.

Additional intra- and inter-molecular coordination in the dimeric distannoxanes

If we assume an additional weak intramolecular coordination from the hydroxyl oxygen to the four coordinated tin atom in the dimeric distannoxane, similar to that occurring in dimeric trimethyltin hydroxide[10] in solution, we obtain structure (III), in which each tin atom is penta-coordinated. We can predict from this structure: (i) the presence of only one compound, but not of isomers in (XR$_2$SnOSnR$_2$OH)$_2$ or its alkoxides, (ii) the same position at 3658–3660 cm^{-1} of the infrared absorption associated with the OH stretching vibration of this compound and trimethyltin hydroxide in carbon tetrachloride, (iii) the similarity in the chemical properties of both compounds described above, such as stability toward condensation or reaction with carbon dioxide. In the solid state, this weak intramolecular coordination might be changed to the intermolecular one with an accompanying shift of OH absorption[9] as in the case of trimethyltin hydroxide.

EXPERIMENTAL

Starting materials

Dialkyltin dichlorides and di-*n*-butyltin oxide were supplied from the Nitto Chemical Co. Dimethyl-, diethyl- and di-*n*-propyltin oxides were prepared by the hydrolysis of dialkyltin dichloride in methanol or acetone with aqueous ammonia, and all the oxides were purified by washing several times with aqueous ammonia or acetone until the filtrate showed no reaction with silver nitrate. Dialkyltin dibromides were prepared by the reaction of the corresponding dialkyltin oxide with hydrobromic acid. Dialkyltin diiodides were kindly supplied by Dr. Matsuda[11]. All the halides were purified by sublimation, recrystallization or distillation and identified by their melting points or refractive indices.

Preparation of XR$_2$SnOSnR$_2$X

ClR$_2$SnOSnR$_2$Cl (R = Et, *n*-Pr, *n*-Bu). Diethyltin dichloride (2.0 g) was dissolved in 15 ml ethanol, an equivalent amount of 0.64 g pyridine in 6 ml ethanol being added. Addition of a few drops of water to the solution caused formation of a white precipitate (probably the pyridine complex) which dissolved on heating for a short time on a water bath. The clear solution gave crystals of ClEt$_2$SnOSnEt$_2$Cl; yield 1.0 g. The observed melting point, shown in Table 1, agreed well with that of the complex compound reported as Et$_2$SnO·Et$_2$SnCl$_2$[1], and the mixed melting point of both compounds showed no depression.

ClMe$_2$SnOSnMe$_2$Cl. The following procedure is preferred to obtain this compound with good yield. Dimethyltin dichloride (11 g) was dissolved in 80 ml water, and an equivalent amount of 3.9 g pyridine in 30 ml ethanol was added slowly with stirring; the white precipitate produced immediately was washed with ethanol repeatedly, and dried at 105°; yield 5.7 g.

BrR$_2$SnOSnR$_2$Br (R = Et, *n*-Pr, *n*-Bu). Diethyltin dibromide (0.5 g) was dissolved in 5 ml ethanol, then 2 ml water was added, followed by refluxing for 30 min. The solution was left at room temperature overnight; white crystals of

$BrEt_2SnOSnEt_2Br$ formed during this time; yield 0.2 g. However, partial hydrolysis with pyridine in this case gave the hydroxy derivative. These compounds were also obtained together with the dialkyltin dibromide by the reaction of dialkyltin oxide and concentrated hydrobromic acid, with a large amount of ligroin.

TABLE 1

PROPERTIES OF $XR_2SnOSnR_2X$

X	*R*	*M.p. (°C)*		*% Sn*	
		Found	*(Reported)*	*Found*	*(Calculated)*
Cl	Me	> 200	(– – –)[a]	61.69	(61.75)
	Et	175.5–6.5	(175.5)[b]	53.99	(53.89)
	n-Pr	121–2	(122)[b]	47.53	(47.80)
	n-Bu	110–12	(111–12)[c]	42.90	(42.95)
Br	Et	172–3	(170–1)[b]	44.84	(44.84)
	n-Pr	107–8	(108)[b]	40.50	(40.54)
	n-Bu	107–8	(108)[c]	36.93	(37.00)

[a] Ref. 2.
[b] Summarized in Ref. 1.
[c] Ref. 6.

All the compounds shown in Table 1 are insoluble in water, but soluble in most common organic solvents, with the exception of $ClMe_2SnOSnMe_2Cl$. The latter can be dissolved in water (ca. 1 g/100 ml) with stirring for a few hours; it is sparingly soluble in hot methanol and in hot benzene, but insoluble in other common organic solvents.

Preparation of $XR_2SnOSnR_2OH$ *and* $XR_2SnOSnR_2OR'$ *from* $XR_2SnOSnR_2X$

$XR_2SnOSnR_2OH$ ($X = Cl$, Br; $R = Et$, *n*-Pr, *n*-Bu). $ClEt_2SnOSnEt_2Cl$ (5 g) was dissolved in 60 ml moist methanol, and an excess of 3.6 ml pyridine was added. The mixture was heated on a water bath for a short time. The crystals were separated from the solution during a few days, and were washed with a small amount of methanol to give crystals with m.p. 214°–217°. These were found to be a mixture of hydroxy and methoxy compounds, but recrystallization from aqueous acetone gave the pure hydroxy compound, as shown in Table 2. Only $ClBu_2SnOSnBu_2OH$ could not be obtained by this procedure, even by prolonged refluxing, but it was obtained by the use of an equivalent amount of dilute NaOH instead of pyridine.

$ClMe_2SnOSnMe_2OR'$ ($R = H$, Me). These two new compounds could be obtained as follows. A solution of 3.8 g $ClMe_2SnOSnMe_2Cl$ and 2.5 ml pyridine in 400 ml hot methanol was refluxed for two hours. Methanol was distilled off under reduced pressure, and the product was recrystallized again from methanol, yielding 2.4 g (rhombic crystals) of $ClMe_2SnOSnMe_2OMe$. The crushed powder of this compound, after standing for a few days at room temperature, gradually changed into $ClMe_2SnOSnMe_2OH$, which was obtained only by this procedure.

Preparation of $IR_2SnOSnR_2OH$ *and* $IR_2SnOSnR_2OR'$ *from* R_2SnI_2 *(K. Taniguchi)*

The iodides shown in Tables 2 and 3 can be prepared conveniently from dialkyltin diiodide. The following procedure is also useful to prepare $BrMe_2SnOSnMe_2OR'$

($R = H, Me$) from dimethyltin dibromide. The solution of 2.0 g diethyltin diiodide and 0.6 g pyridine in 15 ml moist ethanol (or methanol) was heated below its boiling point for a short time. The solution yielded crystals in a few days. Recrystallization from ethanol (or methanol) gave $IEt_2SnOSnEt_2OEt$ (or $IEt_2SnOSnEt_2OMe$) shown in Table 3. The crushed powder of these compounds on exposure to the air for a few days at room temperature, changed into the hydroxide, which was characterized

TABLE 2

PROPERTIES OF $XR_2SnOSnR_2OH$

X	*R*	*M.p. (°C) Found (Reported)**	*% Sn Found (Calculated)*	*% C Found (Calculated)*	*% H Found (Calculated)*
Cl	Me	> 220	64.76 (64.86)	13.06 (13.13)	3.50 (3.58)
	Et	218– (215–17)	56.17 (56.24)	22.50 (22.76)	5.14 (5.02)
	n-Pr	175–94	49.62 (49.64)	29.79 (30.14)	5.13 (6.11)
	n-Bu	109–21	44.33 (44.43)	36.33 (35.97)	7.03 (6.98)
Br	Me	> 220 (– – –)	57.69 (57.84)		
	Et	204–12 (206–18)	50.88 (50.88)		
	n-Pr	172–88	45.39 (45.42)		
	n-Bu	114–28	40.95 (41.02)		
I	Me	> 220 (– – –)	51.98 (51.90)	10.67 (10.50)	2.92 (2.80)
	Et	195–208 (205–13)	46.25 (46.23)	18.67 (18.71)	4.08 (4.12)
	n-Pr	178–92 (188–205)	41.77 (41.67)	25.46 (25.30)	5.08 (5.13)
	n-Bu	134–40	37.99 (37.94)		

* Reported value as $H(R_2SnO)_3OH \cdot R_2SnX_2$ in Ref. 1.

TABLE 3

PROPERTIES OF $XR_2SnOSnR_2OR'$

X	*R*	*R'*	*M.p. (°C)*		*% Sn*	
			Found	*(Reported)**	*Found*	*(Calculated)*
Cl	Me	Me	ca. 200		62.55	(62.47)
Cl	Et	Me	144		54.86	(54.43)
Br	Me	Me	ca. 200	(– – –)	55.66	(55.93)
I	Me	Me	220	(– – –)	50.35	(50.35)
I	Me	Et	210	(215–18)	48.92	(48.90)
I	Et	Me	148		45.22	(45.00)
I	Et	Et	142	(137–98)	44.12	(43.84)

* Reported value as $R'(R_2SnO)_3OR' \cdot R_2SnX_2$ in Ref. 1.

by analysis for tin, the change of melting point, and especially of the infrared absorption spectrum: appearance of a new band due to SnO–H near 3500 cm^{-1} and disappearance of a strong band associated with SnO–C near 1060 cm^{-1}.

Preparation of $R_3SnOSnR_3$ (R = *n*-Pr, *n*-Bu)

These compounds were prepared by the hydrolysis of trialkyltin acetates and identified by the analysis of tin or by the refractive indices. $Pr_3SnOSnPr_3$: n_D^{20} = 1.4927. (Found: Sn, 46.43. $C_{18}H_{42}OSn$ Calcd.: Sn, 46.37%.) $Bu_3SnOSnBu_3$: n_D^{20} = 1.4880 (Reported[1] 1.4872).

Determination of molecular weight

The molecular weight of $XR_2SnOSnR_2X$ (X = Cl, R = Et, *n*-Pr, *n*-Bu; X = Br, R = *n*-Bu), $XBu_2SnOSnBu_2OH$ (X = Cl, I) and $R_3SnOSnR_3$ (R = *n*-Pr, *n*-Bu) were determined cryoscopically in benzene. Some representative results are shown in Fig. 1 together with that for $Me_3SiOMe_2SnOSnMe_2OSiMe_3$[12] in cyclohexane.

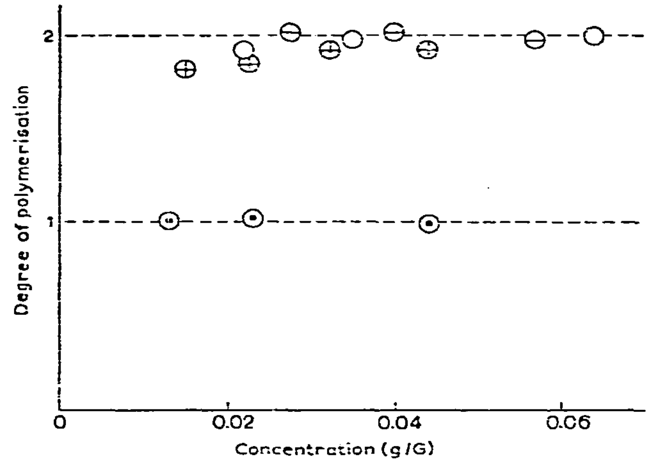


Fig. 1. Degree of polymerization of distannoxanes.
○ $ClBu_2SnOSnBu_2Cl$ (in benzene);
⊖ $IBu_2SnOSnBu_2OH$ (in benzene);
⊕ $Me_3SiOMe_2SnOSnMe_2OSiMe_3$ (in cyclohexane);
⊙ $Bu_3SnOSnBu_3$ (in benzene).

Analysis of products

The gravimetric analyses for tin were conducted as described elsewhere[4]. Those of the bromides, however, gave too low values by this method. The successful results shown in Tables 1–3 were obtained by adding concentrated H_2SO_4 and an additional few drops of concentrated HNO_3 to the sample, letting the mixture stand for one day, and then following the same procedure as was used for the other compounds. Carbon and hydrogen analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

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SUMMARY

Distannoxane derivatives of types $XR_2SnOSnR_2OH$ and $XR_2SnOSnR_2OR'$ were mainly prepared from $XR_2SnOSnR_2X$. The preparation and properties of nineteen compounds, of which nine are new compounds, are described. These compounds were found to be dimeric in solution. Dimerization of these distannoxanes results by the pairing of two Sn–O–Sn bonds to form a four-membered ring, in which two kinds of tin atoms, tetra- and penta-coordinated, are involved. In the two types of derivatives discussed, it is suggested that an additional intramolecular coordination within the dimer or intermolecular coordination in the solid from each oxygen atom of the OH or OR′ group to each tetra-coordinated tin atom is possible. In this way we have all tin atoms penta-coordinated, and we can interpret the peculiar stability of the Sn–OH toward condensation and the absence of isomers in these derivatives.

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