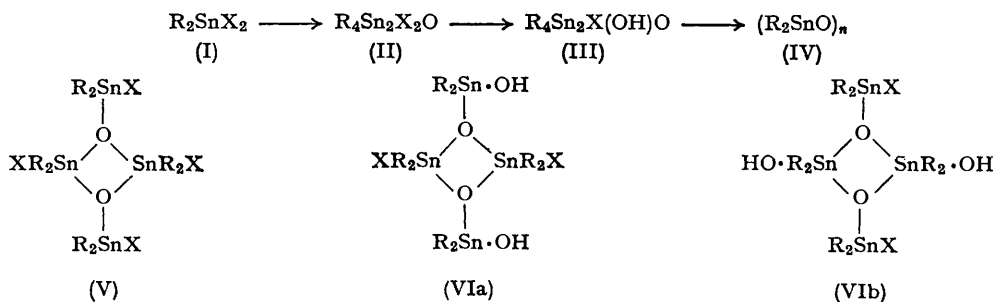


1098. Organotin Chemistry. Part III.^{1,2} Intermediates and Products in the Hydrolysis of Dialkyltin(IV) Compounds.

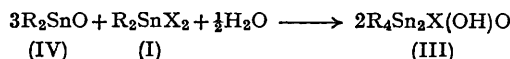
By D. L. ALLESTON, ALWYN G. DAVIES, and M. HANCOCK.

The hydrolysis of dialkyltin dihalides or dicarboxylates, R_2SnX_2 , gives, in order, compounds of the empirical formulae $R_4Sn_2X_2O$, $R_4Sn_2X(OH)O$, and R_2SnO . Arguments are presented for believing that the cyclodistannoxane ring is present in the structure of all these compounds.

THE first stable products in the hydrolysis of dialkyltin(IV) compounds (I) (X = halide or carboxylate, for example) have the empirical formula $R_4Sn_2X_2O$ (II). In Part II¹ we presented evidence that, in solution in benzene or carbon tetrachloride, these compounds have the molecular formula $(R_4Sn_2X_2O)_2$, and the structure (V).



Nature of the Compounds $R_4Sn_2X(OH)O$.—Further hydrolysis of these compounds (II), gives a second family of intermediates, (III), of the composition $R_4Sn_2X(OH)O$, which, like the former, can also be obtained by dissolving the oxide (IV) in a hot solution of the appropriate amount of the compound R_2SnX_2 (I) in a moist solvent.



In carbon disulphide solution the compounds (III) show absorption in the infrared by the OH group at *ca.* 3420 cm^{-1} , but this may be obscured in Nujol mulls. These compounds usually melt at about 200° over a range of 5–10°, but if they are “recrystallised” from alcohols, they are converted into the highly crystalline alkoxides, $R_4Sn_2X(OR')O$. The alkoxides are rapidly hydrolysed in the air back to the hydroxides, and in open tubes they melt over a wide range of temperature.

Harada³ determined the molecular weight of the compound $Et_4Sn_2Br(OH)O$ in naphthalene, and of $Et_4Sn_2I(OH)O$ in benzene and in naphthalene, and obtained consistent results indicating that these compounds had the molecular formula $[R_4Sn_2X(OH)O]_2$.^{*} He concluded that compounds (III) were of the nature $HO(R_2SnO)_3H, R_2SnX_2$, in which one or, more probably, two of the oxygen atoms in $HO(R_2SnO)_3H$ were co-ordinated to the R_2SnX_2 unit.

We have confirmed the dimeric nature of the compounds (III) (X = Cl, I, or OAc), using a thermistor vapour-pressure osmometer.† In the solvents benzene, chloroform, or acetone, consistent values were observed over the concentration range 0.01–0.1 M.

^{*} In contrast, Harada found that the compounds (II) gave results which varied with the concentration, and which were difficult to interpret (see Part II¹).

† The corresponding alkoxides were too sensitive to moisture to be investigated similarly.

¹ Part II, D. L. Alleston, A. G. Davies, M. Hancock, and R. F. M. White, *J.*, 1963, 5469.

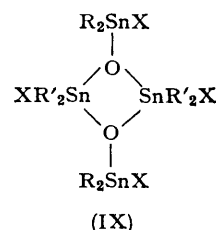
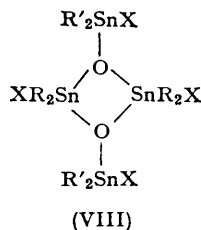
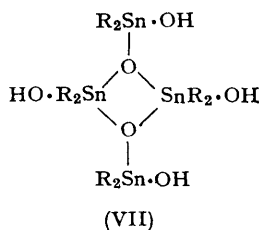
² This work was presented at the International Symposium on Inorganic Polymers, at Nottingham in 1961, and briefly described by D. L. Alleston, A. G. Davies, and B. N. Figgis, *Proc. Chem. Soc.*, 1961, 457.

³ T. Harada, *Sci. Papers Inst. Phys. Chem. Res., Tokyo*, 1939, 35, 290.

In view of the close relationship between the compounds (II) and (III) it seems probable that the latter have the same distannoxane ring as in the structure (V). A number of distributions of the groups X and OH are possible, the two most probable being shown in formulae (VIa) and (VIb). Okawara and Wada⁴ prefer the latter on the assumption that hydrolysis would occur most readily at the pentaco-ordinated tin atoms in structure (V).

Course of the Hydrolytic Reaction.—The initial product of the hydrolysis of the compound R_2SnX_2 might be expected to be $R_2SnX(OH)$. Gibbons, Sawyer, and Ross⁵ claim to have isolated the compound $Bu_2SnCl(OH)$, by adding water to a methanolic solution of the dichloride. The hydroxide chloride had m.p. 105–107°, its analysis and molecular weight were satisfactory, and it showed absorption due to an OH group at 3509 cm^{-1} . By the same procedure, we obtained only a compound with rather indefinite characteristics, and attempts to purify it gave only the compound $(Bu_4Sn_2Cl_2O)_2$, presumably by intermolecular dehydration of the hydroxide chloride.

The analytical data that have been reported for the compound usually described as diphenyltin hydroxide chloride⁶ do not preclude the composition $Ph_4Sn_2Cl_2O$. The authenticity of di-*t*-butyltin hydroxide chloride and di-*t*-pentyltin hydroxide bromide is more readily acceptable because there is evidence that the corresponding dihydroxides can be isolated.⁷ Here, the intermolecular dehydration is probably sterically hindered by the bulky alkyl groups. This is more apparent in the hydrolysis products of di-*o*-phenoxyphenyltin dichloride, from which, with aqueous sodium hydroxide at 0°, Poller⁸ obtained the dihydroxide $(o-PhO \cdot C_6H_4)_2Sn(OH)_2$; but the reaction with sodium hydrogen carbonate gave instead a compound of the empirical formula $(o-PhO \cdot C_6H_4)_4Sn_2(OH)_2O$, which has now been shown to be dimeric. This can therefore be regarded as a further hydrolysis product of compound (VI) and, in all probability, has the same skeletal structure, as shown in (VII); $R = o-PhO \cdot C_6H_4$). This might be taken to suggest that dialkyltin oxides in general are



formed by progressive dehydration of hydroxy-compounds (VII),[†] and hence that the distannoxane ring is present in the dialkyltin oxides. This same conclusion is indicated more forcibly when we consider the synthesis of the compounds $R_4Sn_2X_2O$ (V) from the components R_2SnO and R_2SnX_2 , and the properties of the dialkyltin oxides themselves.

Course of the Synthetic Reaction.—It might be assumed, as a working hypothesis, that the dialkyltin oxides, $(R_2SnO)_n$, are linear polymers; and that the reaction with a compound R'_2SnX_2 occurs by the co-ordination of oxygen to tin, followed by migration of halogen, and

[†] Zemlyanski, Panov, Slovokhorova, Shamagina, and Kocheshkov⁹ have prepared a series of oligomers which they represent as $AcO \cdot [R_2Sn \cdot O]_n \cdot R_2Sn \cdot OAc$, where $n = \text{up to } 14$. In view of the work discussed here, it seems unlikely that these oligomers are linear.

⁴ R. Okawara and M. Wada, *J. Organometallic Chem.*, 1963, **1**, 81.

⁵ A. J. Gibbons, A. K. Sawyer, and A. Ross, *J. Org. Chem.*, 1961, **26**, 2304.

⁶ B. Aronheim, *Annalen*, 1878, **194**, 145; R. F. Chambers and P. C. Scherer, *J. Amer. Chem. Soc.*, 1926, **48**, 1054; F. B. Kipping, *J.*, 1928, 2365. Cf. O. H. Johnson, H. E. Fritz, D. O. Halvorson, and R. L. Evans, *J. Amer. Chem. Soc.*, 1955, **77**, 5857.

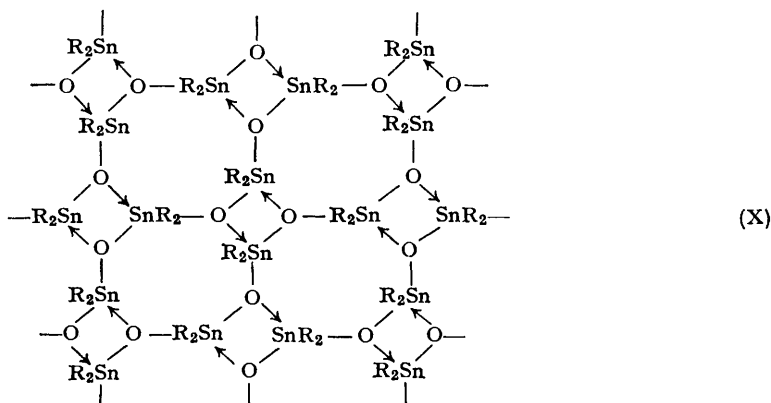
⁷ E. Krause and K. Weinberg, *Ber.*, 1930, **63**, 381; G. A. Baum and W. J. Considine, *J. Polymer Sci., Part B, Polymer Letters*, 1963, **1**, 517.

⁸ R. C. Poller, *J.*, 1963, 706.

⁹ (a) K. A. Kocheshkov, E. M. Panov, and N. N. Zemlyanskii, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1961, 2255 (*Bull. Acad. Sci. U.S.S.R.*, 1961, 2116); (b) N. N. Zemlyanskii, E. M. Panov, N. A. Slovokhorova, O. P. Shamagina, and K. A. Kocheshkov, *Doklady Akad. Nauk S.S.S.R.*, 1963, **149**, 312 [*Proc. Acad. Sci. (U.S.S.R.)*, 1963, **149**, 205].

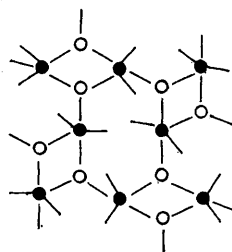
fission of the stannoxane chain to give the distannoxane, $\text{XR}_2\text{Sn}\cdot\text{O}\cdot\text{SnR}'_2\text{X}$, which then dimerises.

Harada's report,¹⁰ confirmed by Okawara,¹¹ is crucial here, namely that, under the same conditions, the reactions between R_2SnO and $\text{R}_2'\text{SnX}_2$ on the one hand, and $\text{R}_2'\text{SnO}$ and R_2SnX_2 on the other, give different products, both of composition $\text{R}_2\text{R}'_2\text{Sn}_2\text{X}_2\text{O}$, which we now presume to have the structures (VIII) and (IX). If this is accepted, the distannoxane, $\text{XR}_2\text{Sn}\cdot\text{O}\cdot\text{SnR}'_2\text{X}$, which would be a common intermediate from both pairs of reagents on the above picture, cannot be involved in the reaction, and the picture needs modifying.



The facts can be accommodated if it is assumed that the distannoxane ring is already present in the initial dialkyltin oxide, and is not altered during the above transformations.

Such an oxide, formed by intermolecular dehydration of structure (VII), could contain only 5-co-ordinated or both 4- and 5-co-ordinated tin. The former possibility is represented two-dimensionally in the formula (X). If we accept Okawara's description of the distannoxane ring, and assume a trigonal bipyramidal configuration about the tin atoms, the three-dimensional structure will be that shown in (XI). This is a layer-lattice structure;* it may



(XI)

● = Sn

○ = O

The alkyl groups are omitted for clarity.

* The tin(IV) oxides and sulphides thus obey the general rule that, as bonds become more covalent, there is a tendency for a transition through the structural types rutile \rightarrow CdF_2 layer-lattice \rightarrow molecular structure;¹² SnO_2 has the rutile structure and SnS_2 a layer-lattice, whereas R_2SnO has apparently a layer-lattice and R_2SnS a molecular structure.¹³

¹⁰ T. Harada, *Sci. Papers Inst. Phys. Chem. Res., Tokyo*, 1947, **42**, 64; *Report Sci. Res. Inst. (Japan)*, 1948, **24**, 177 (*Chem. Abstr.*, 1951, **45**, 2356).

¹¹ R. Okawara, personal communication; see also ref. 1.

¹² R. C. Evans, "Crystal Chemistry," Cambridge University Press, 1952, p. 193.

¹³ T. Harada, *Bull. Chem. Soc. Japan*, 1942, **17**, 281, 283.

describe only the short-range order, and need not necessarily occur regularly throughout the macromolecule.

Such a structure would be in accord with the physical properties of the dialkyltin oxides which, in contrast to the corresponding poly(dialkylsiloxanes), are usually insoluble, amorphous, infusible materials. They show sharp lines in the X-ray powder photographs, indicating a fairly ordered intermolecular arrangement,¹⁴ and the infrared band which is ascribed to the Sn—O group is at much lower frequency than in the bis(trialkyltin) oxides, but in the same region as that in the compounds $(R_4Sn_2X_2O)_2$.¹⁵

The problems discussed here concerning the chemical environment and the co-ordination number of the tin atoms would be amenable to investigation by Mössbauer spectrometry, and the few results which have been reported largely support our conclusions. Gol'danskii *et al.* have concluded that the spectra of a number of dialkyl- and diaryl-tin oxides imply a cross-linked polymeric structure in which the tin has a co-ordination number of five, in accord with the structure which we propose here.¹⁶ Alexandrov and Delyagin and their co-workers report¹⁷ the spectrum of a compound which is given the formula $Bu_2Sn(OH) \cdot O \cdot SnBu_2(OH)$; they do not describe its preparation or characterisation, but the chemical shift and quadrupole splitting do not imply the presence of non-equivalent tin atoms.

EXPERIMENTAL

Molecular weights were determined over the concentration range *ca.* 0.01—0.1M at 25° with a Mechrolab Vapour Pressure Osmometer, model 301A.

Attempts to Isolate Dibutyltin Chloride Hydroxide.—Water (60 c.c.) was added to a solution of dibutyltin dichloride (3.0 g.) in methanol (6 c.c.), giving immediately a white precipitate. The solid was separated and dried overnight over silica gel at 20 mm. pressure, when it melted over the range 50—80°. It was washed with water and dried over phosphoric oxide for 4 hr.; it then had m. p. 95—98° [Found: *M*, in chloroform, 562, independent of concentration; next day, 665. Calc. for $Bu_2Sn(OH)Cl$: *M*, 285]. If the preparation was carried out in ethanol, the crude material had m. p. 102—105° (*M*, *ca.* 900); after recrystallisation from acetone, m. p. 102—105° (*M*, 982). The compound $(Bu_4Sn_2Cl_2O)_2$ has m. p. 110°; *M*, 1106.

Preparation of Compounds $R_4Sn_2X(OR')O$ and $R_4Sn_2X(OH)O$.—(a) *By hydrolysis of R_2SnX_2 .* A solution of dibutyltin dichloride (5.06 g.) in ethanol (25 c.c.) was added to a stirred solution of triethylamine (6.75 g., 4 mol.) in ethanol (25 c.c.). After a few minutes, a granular white precipitate appeared. The mixture was stirred for 25 min. after the addition was complete, then the solid was separated and recrystallised from ethanol, giving the compound $Bu_4Sn_2Cl(OEt)O$ (2.25 g., 45%), m. p. 85—140°, as white, rather waxy crystals, soluble in the cold in all common organic solvents except alcohols (Found: C, 37.9; H, 7.1; Cl, 6.3, 6.4. $C_{18}H_{41}ClO_2Sn_2$ requires C, 37.3; H, 7.5; Cl, 6.4%). The corresponding hydroxy-compound requires C, 36.0; H, 7.0; Cl, 6.6%). Yields of 71—84% were obtained when the product was recrystallised from the original heated solution.

The ethoxy-compound gave an iodoform test, and reacted with 8-hydroxyquinoline in the presence of triethylamine to give dibutylbis-(8-quinolyloxy)tin in good yield as yellow needles, m. p. 155° (lit.,¹⁸ 154.5—155.5°). The ethoxide was unaffected by triethylamine in boiling ethanol, and did not react with bipyridyl; under the same conditions, the compound $(Bu_4Sn_2Cl_2O)_2$ gave the complex $Bu_2SnCl_2 \cdot bipy$ in 15% yield. In the air, the ethoxide was hydrolysed, the OH band appearing in the infrared spectrum at 3420 cm^{-1} (Found: in the

† Kocheshkov *et al.*^{9a} have recently isolated the compound $Bu_4Sn_2(OAc)_2O$, m. p. 58—60°, by treating dibutyltin diacetate with diazomethane and water. Whereas we found it to be dimeric by vapour-pressure osmometry in benzene at 20°,¹ they find it to be monomeric by cryoscopy in benzene.

¹⁴ W. T. Reichle, *J. Polymer Sci.*, 1961, **49**, 521.

¹⁵ R. C. Poller, *J. Inorg. Nuclear Chem.*, 1962, **24**, 593.

¹⁶ V. I. Gol'danskii, E. F. Makarov, R. A. Stukan, V. A. Trukhtanov, and V. V. Khrapov, *Doklady Akad. Nauk S.S.S.R.*, 1963, **151**, 351. See also A. V. Alexandrov, K. P. Mitrofanov, O. U. Okhlokystin, L. S. Polak, and V. S. Shpinel, *ibid.*, 1963, **153**, 370.

¹⁷ A. U. Alexandrov, N. N. Delyagin, K. P. Mitrofanov, L. S. Polak, and V. S. Shpinel, *Doklady Akad. Nauk, S.S.S.R.*, 1963, **148**, 126. In the English translation, *Proc. Acad. Sci. (U.S.S.R.)*, *Phys. Chem. Sect.*, 1963, **148**, 1, the formula is misprinted as $Bu_2Sn(OH)O_5SnBu_2(OH)$.

¹⁸ D. Blake, G. E. Coates, and J. M. Tate, *J.*, 1961, 756.

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ultimate hydroxide, M , in benzene, 1094; in acetone, 1089, both independent of concentration. Calc. for $[\text{Bu}_4\text{Sn}_2(\text{OH})\text{ClO}]_2$, M , 1068).

By the similar hydrolysis of dimethyltin dichloride, the compound $\text{Me}_4\text{Sn}_2\text{Cl}(\text{OH})\text{O}$ was obtained, insoluble in the common organic solvents except alcohols; it had m. p. $> 300^\circ$ (lit.,⁴ $> 200^\circ$) (Found: Cl, 9.32. Calc.: 9.63%).

Diethyltin dichloride likewise gave the compound $[\text{Et}_4\text{Sn}_2\text{Cl}(\text{OH})\text{O}]_2$, m. p. 236° (lit.,⁴ 215 — 217° ; 218°) (Found: Cl, 8.4%; M , in chloroform, 833. Calc.: Cl, 8.7%; M , 812).

(b) *By hydrolysis of $\text{R}_4\text{Sn}_2\text{X}_2\text{O}$.* Crude $\text{Bu}_4\text{Sn}_2\text{I}_2\text{O}$ was synthesised from dibutyltin di-iodide and dibutyltin oxide as described in Part II. Attempted crystallisation from ethanol gave large crystals of $\text{Bu}_4\text{Sn}_2\text{I}(\text{OEt})\text{O}$, melting range 71.5 —*ca.* 85° [Found: C, 32.1; H, 6.4; I, 20.3. $(\text{C}_{18}\text{H}_{41}\text{O}_2\text{Sn}_2)_2$ requires C, 32.0; H, 6.4; I, 19.7%]. In air, it was hydrolysed to the corresponding hydroxide (Found: M , in benzene, 1140; in chloroform, 1176. Calc.: 1233).

The compound† $\text{Bu}_4\text{Sn}_2(\text{OAc})_2\text{O}$ (m. p. 54 — 57°)¹ separated from warm aqueous ethanol as a lower oily layer which, during several weeks, deposited large crystals of $\text{Bu}_4\text{Sn}_2(\text{OAc})(\text{OH})\text{O}$, m. p. *ca.* 129° [Found: C, 38.9; H, 6.8; Sn, 43.5; OAc (by hydrolysis), 11.25%; M , in chloroform, 1039. $(\text{C}_{18}\text{H}_{40}\text{O}_4\text{Sn}_2)_2$ requires C, 39.5; H, 7.35; Sn, 43.3; OAc, 10.8%; M , 1065]. The infrared spectrum showed strong broad bands at 3230 cm.^{-1} (OH) and 1590 cm.^{-1} (C=O).

(c) *By synthesis from R_2SnO and R_2SnX_2 .* Dibutyltin oxide (3.75 g.) was stirred in a boiling solution of dibutyltin dichloride (1.52 g., 0.33 mol.) in toluene (25 c.c.). After 1 hr. a clear solution was obtained. The solvent was removed under reduced pressure, and the residue was recrystallised from ethanol, yielding the compound $\text{Bu}_4\text{Sn}_2\text{Cl}(\text{OEt})\text{O}$ (4.50 g., 81%), melting range 85 — 140° , identical with the material obtained from the hydrolysis of dibutyltin dichloride.

Molecular Weight of the Compound $(o\text{-PhO}\cdot\text{C}_6\text{H}_4)_4\text{Sn}_2(\text{OH})_2\text{O}$ (VII).—Poller⁸ has reported that, during a few days, the benzene solution of this compound deposits crystals with the same analysis and infrared spectrum; he kindly supplied specimens of both compounds. We found, for compound (VII) in benzene [time (min.), M]: 0, 1890 (Calc. for the dimer: 1928); 30, 1680; 60, 1560; 120, 1500; for the less soluble compound, in chloroform, M , 1796.

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