1041. *Organotin Chemistry. Part II.*[1, 2] *Compounds of the Composition* $R_4Sn_2X_2O$.

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The compounds of the composition $R_4Sn_2X_2O$, which can be prepared by partial hydrolysis of R_2SnX_2 or by synthesis from R_2SnX_2 and R_2SnO, have been investigated by ^1H and ^{119}Sn magnetic resonance spectroscopy, and by vapour-pressure osmometry. It is concluded that in non-polar solvents, these compounds are dimeric and contain 4- and 5-co-ordinate tin, probably in the cyclic structure (IV) or (V).

THE exhaustive hydrolysis of dialkyltin(IV) compounds R_2SnX_2 (X = *e.g.*, halogen or carboxylate) under basic conditions gives the dialkyltin oxides R_2SnO which are insoluble, amorphous, infusible solids, and are usually regarded as being high polymers. If, however, the reaction is carried out with a deficiency of base, or with a weak base, at least two intermediate hydrolysis products, $R_4Sn_2X_2O$ and $R_4Sn_2X(OH)O$, can be isolated. These compounds are usually highly crystalline, soluble, and low-melting, and hence appear not to be highly polymeric. The same two families of compounds can also be made by dissolving the appropriate amount (1 or 3 mol., respectively) of the dialkyltin oxide in a solution of the compound R_2SnX_2 in an inert solvent, and they have frequently been reported as troublesome by-products in the preparation of organotin compounds. This paper describes an investigation of the compounds $R_4Sn_2X_2O$.

$$R_2SnX_2 \xrightarrow{HO^-} R_4Sn_2X_2O \xrightarrow{HO^-} R_4Sn_2X(OH)O \xrightarrow{HO^-} R_2SnO \qquad (1)$$

Composition.—The analytical values for the compositions $R_4Sn_2X_2O$ and $R_4Sn_2X_2$ are very similar (for example the compound $Bu_4Sn_2Cl_2O$ contains only 2·9% of oxygen) and, as the oxygen cannot be determined directly, its presence may easily be overlooked. The first publication on organotin compounds, by Löwig in 1852,[3] described the reaction between ethyl iodide and a tin–sodium alloy, which gave a compound thought to be a radical, Et_2SnI. Shortly after, Strecker showed[4] that the product had, in fact, the composition $Et_4Sn_2I_2O$, and that it could also be obtained by heating diethyltin di-iodide with diethyltin oxide.

A similar error was made much more recently by Johnson and his co-workers.[5] Dialkyltin dihalides in absolute alcohol were treated with 1 mol. of sodium ethoxide or an organic base such as triethylamine, and the products were regarded as distannanes:

$$R_2SnX_2 \xrightarrow[EtOH]{Base-} XR_2Sn{\cdot}SnR_2X \qquad (2)$$

These compounds, however, are identical in melting point, solubility behaviour, infrared and ^{119}Sn magnetic resonance spectra, and chemical properties with the products obtained by half-hydrolysis of the dihalides or by synthesis from the dihalides and oxides, and again have the composition $R_4Sn_2X_2O$;[6] the reactions were in fact basic hydrolyses by adventitious water.*

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* The true nature of these compounds has also been appreciated independently by Johnson,[7] and by Gibbons, Sawyer, and Ross.[8] We were not aware of Professor Johnson's correction when our preliminary note was published; we apologise for the oversight.

[1] The paper by Alleston and Davies, *J.*, 1962, 2050, is regarded as Part I of this series.

[2] The present work was presented at the International Symposium on Inorganic Polymers at Nottingham in July 1961, and was briefly reported by Alleston, Davies, and Figgis in *Proc. Chem. Soc.*, 1961, 457.

[3] Löwig, *Annalen*, 1852, **84**, 308.

[4] Strecker, *Annalen*, 1858, **105**, 306; 1862, **123**, 365.

[5] (*a*) Johnson and Fritz, *J. Org. Chem.*, 1954, **19**, 74; (*b*) Johnson, Fritz, Halvorson, and Evans, *J. Amer. Chem. Soc.*, 1955, **77**, 5857.

[6] Alleston and Davies, *Chem. and Ind.*, 1961, 949.

[7] Johnson, *J. Org. Chem.*, 1960, **25**, 2262.

[8] Gibbons, Sawyer, and Ross, *J. Org. Chem.*, 1961, **26**, 2304.

Preparation.—The Table shows the compounds $R_4Sn_2X_2O$ which we prepared by the hydrolytic or synthetic methods. At that time, few carboxylates, and no fluoride, thiocyanate, or camphorsulphonate had been described, but the formation of carboxylates

$$Bu_2Sn(OAc)_2 \xrightarrow{H_2O} Bu_4Sn_2(OAc)_2O \qquad (3)$$

$$Et_3Sn{\cdot}OR + Bz_2O_2 \xrightarrow{CH_2N_2} Ph{\cdot}CO_2R + Et_2Sn(OR)OBz \xrightarrow{H_2O} Et_4Sn_2(OBz)_2O \qquad (4)$$

$$2Ph_3Sn{\cdot}OH + 2R{\cdot}CO_2{\cdot}OH \longrightarrow Ph_4Sn_2(O{\cdot}CO{\cdot}R)_2O + 2PhOH\ (R = Me\ or\ Pr) \qquad (5)$$

by the reactions (3),[9] (4),[10] and (5) [11] has recently been reported, and Seyferth and his co-workers [12] have prepared the compounds $Bu_4Sn_2F_2O$ and $Et_4Sn_2F_2O$ by treating the corresponding dialkylperfluorovinyltin chloride with aqueous potassium fluoride.

Compounds $R_4Sn_2X_2O$.

No.	R	X	Hydrolysis: base	Synthesis: solvent	Recryst. from	M. p. Found	M. p. Lit.	Yield (%)
1	Me	Cl	Aq. MeOH †		C_6H_6	Chars 300°	>360° [13]	—
2	Et	Cl	Et_3N		Me_2CO	175	175d,[5b, 14]	—
3	Et	OCS *		PhMe	C_6H_6	270—280d	—	—
4	Bu	F		C_6H_6	MeCN	115—117	140 [12]	—
5	Bu	Cl	Et_3N ‡		Me_2CO	109—110	—	90
6			NaOH		Me_2CO	112·5°	115—116 [5a, 15] 109—110°	78
7				None; 111—112°	Me_2CO	109	—	—
8	Bu	Br	Et_3N §		EtOH	101·5—104	—	50
9				C_6H_6	EtOH	104	—	71
10	Bu	CNS		PhMe	Et_2O at −80°	84	—	55
11	Bu	OAc	Et_3N		Pentane at −80°	54—57	58—60 [9]	95
12				C_6H_6	Me_2CO ¶ at −15°	56—60	—	—
13	Bu	$O{\cdot}CO{\cdot}C_7H_{15}$		C_6H_6	Pentane at −80°	Oil	—	—

No.	Found C (%)	Found H (%)	Found X (%)	Found *M*	Formula	Required C (%)	Required H (%)	Required X (%)	Required *M*	Note
1			18·8		$(C_4H_{12}Cl_2OSn_2)_2$			18·4		
2			15·8	856	$(C_8H_{20}Cl_2OSn_2)_2$			16·1	882	
3	39·6	6·3			$(C_{28}H_{50}O_9S_2Sn_2)_2$	40·4	6·1			
4	36·8	7·1	7·5	998	$(C_{16}H_{36}F_2OSn_2)_2$	37·0	7·0	7·3	1040	
5	34·3	6·3	13·0			34·8	6·6	12·8		
6				1095	$(C_{16}H_{36}Cl_2OSn_2)_2$				1106	1
7			12·7							
9	30·5	6·1	24·8	1170	$(C_{16}H_{36}Br_2OSn_2)_2$	30·0	5·7	24·9	1283	
10	36·5	5·8	19·1	1168	$(C_{18}H_{36}N_2OS_2Sn_2)_2$	36·1	6·1	19·4	1196	2
12	40·0	6·8	19·5	1051	$(C_{20}H_{42}O_5Sn_2)_2$	40·0	7·1	19·6	1200	
13	50·1	8·1			$(C_{32}H_{66}O_5Sn_2)_2$	50·0	8·7			3

Compounds nos. **3**, **4**, **5** (**6**), **9**, **10**, **11** (**12**), and **13** are new.

* Camphorsulphonate. † Hydrol. of dimethyltin acetate chloride. ‡ And from the chloride bromide. § And by hydrolysis of the acetate bromide in air. ¶ The preferred solvent.

(1) Found: Sn, 43·0. Calc., 43·0%. (2) Found: N, 4·7; S, 9·7. Required: N, 4·7; S, 10·7%. (3) n_D^{20} 1·4921.

Johnson's hydrolytic method was to add an excess of (wet) ethanol to a solution of equimolar R_2SnX_2 and amine in ether. This often gives an orange impurity which is difficult to remove, and it is better to add a solution of the compound R_2SnX_2 to the amine

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[9] Kocheshkov, Panov, and Zemlyanskii, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1961, 2255.

[10] Vyazankin, Razuvaev, D'yachkovskaya, and Shchepetkova, *Doklady Akad. Nauk S.S.S.R.*, 1962, **143**, 1348 [*Proc. Acad. Sci.* (*U.S.S.R.*), *Chem. Sect.*, 1962, **143**, 343].

[11] Shushunov and Brilkina, *Doklady Akad. Nauk S.S.S.R.*, 1961, **141**, 1391 [*Proc. Acad. Sci.* (*U.S.S.R.*), *Chem. Sect.*, 1961, **141**, 1310].

[12] Seyferth, Raab, and Brändle, *J. Org. Chem.*, 1961, **26**, 2934.

[13] Okawara and Rochow, *J. Amer. Chem. Soc.*, 1960, **82**, 3285.

[14] Pfeiffer and Brack, *Z. anorg. Chem.*, 1914, **87**, 229.

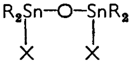
[15] B.P. 711,564 (*Chem. Abs.*, 1955, **49**, 14,797).

in ethanol. More conveniently, the hydrolysis can be carried out with aqueous sodium hydroxide.

In these reactions, the reactivity of the compounds R_2SnX_2 increases in the order $X = F < Cl < Br < I,OAc$. Dibutyltin chloride fluoride gave the fluoro-compound, the bromide chloride gave the chloro-compound, and the acetate bromide is hydrolysed in the air to acetic acid and the bromo-compound.[1] When an attempt was made to recrystallise the iodide, $Bu_4Sn_2I_2O$, it was hydrolysed further to a compound of the type $R_4Sn_2X(OH)O$.

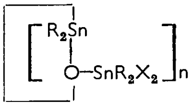
The synthetic reaction was usually carried out by heating the compounds R_2SnX_2 and R_2SnO together in benzene, toluene, or xylene. Progressively higher temperatures were needed along the series $X = F \longrightarrow I$ before clear solutions were obtained. The crude compound $Bu_4Sn_2I_2O$ could not be purified because it continually liberated iodine, even at low temperature.

Structure.—Pfeiffer and Brack[14] in 1914 assumed that the compounds $R_4Sn_2X_2O$ had the structure (I), and this has been accepted by most subsequent authors. In a long series of papers between 1939 and 1947, however,[16-20] Harada argued the case for a cylic oligomeric structure (II), where the tin has co-ordination numbers of four and of five; on rather insecure evidence, which is discussed below, he proposed that the value $n = 3$. A third possibility is shown in formula (III).*

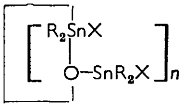


$$\underset{X}{R_2Sn}—O—\underset{X}{SnR_2}$$

(I)



(II)



(III)

Non-equivalence of the tin atoms. In structure (I) the two tin atoms are equivalent, whereas structures (II) and (III) contain non-equivalent tin atoms. The ^{119}Sn magnetic resonance spectra of the compounds $Bu_4Sn_2Cl_2O$ and $Bu_4Sn_2Br_2O$ in benzene or carbon tetrachloride at room temperature consist of two broad overlapping bands of approximately equal intensity, indicating the presence of two non-equivalent types of tin atom. The Pfeiffer structure (I) is thus excluded [as is Johnson's distannane structure $(SnR_2X)_2$], and oligomeric structures such as (II) and (III) are permitted. An unsymmetrical monomer $R_3Sn{\cdot}O{\cdot}SnRX_2$ would not be incompatible with this result, but it is excluded on other chemical and physical evidence presented below.

Non-equivalence of the Alkyl Groups. The alkyl groups also are equivalent in structure (I), and non-equivalent in structures (II) and (III). Harada's strongest evidence[19d,20] against structure (I) was that the reaction between diethyltin dibromide and dipropyltin oxide gave a solid of m. p. 85—87°, whereas the product from dipropyltin dibromide and diethyltin oxide had m. p. 104—105°; both compounds were analysed for halogen only. If it is accepted that both have the composition $Et_2Pr_2Sn_2Br_2O$, the simple structure (I) is again inadequate. Combinations of other alkyl groups were tried, but the products were hydrolysed during recrystallisation.

We attempted to confirm Harada's work by isolating two isomers of the composition $Et_2Bu_2Sn_2Cl_2O$. But whereas diethyltin dichloride and dibutyltin oxide in boiling toluene

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* Association through a halogen bridge seems unlikely since dibutyltin dichloride is monomeric in benzene at 25° over the range 0·01—0·1M (Found: *M*, 301. Calc.: 304. I. F. Graham, personal communication).

[16] Harada, *Bull. Chem. Soc. Japan*, (*a*) 1927, **2**, 105; (*b*) 1929, **4**, 266; (*c*) 1931, **6**, 240.

[17] Harada, *Sci. Papers Inst. Phys. Chem. Res., Tokyo*, (*a*) 1939, **35**, 290; (*b*) 1939, **36**, 497; (*c*) *ibid.*, p. 501; (*d*) *ibid.*, p. 504; (*e*) 1940, **38**, 115; (*f*) *ibid.*, p. 146.

[18] Harada, *Bull. Chem. Soc. Japan*, 1940, **15**, 455.

[19] Harada, *Sci. Papers Inst. Phys. Chem. Res., Tokyo*, (*a*) 1942, **39**, 419; (*b*) 1947, **42**, 57; (*c*) *ibid.*, p. 62; (*d*) *ibid.*, p. 64.

[20] Harada, *Report Sci. Res. Inst.* (*Japan*), 1948, **24**, 177.

gave one of the required compounds, dibutyltin dichloride and diethyltin oxide gave a mixture from which the symmetrical disproportionation product, $Bu_4Sn_2Cl_2O$, was obtained.

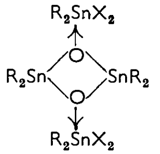
We therefore turned our attention to the proton magnetic resonance spectra of the compounds $R_4Sn_2X_2O$. The compound $Me_4Sn_2Cl_2O$ in chloroform showed the presence of two types of methyl group in approximately equal amount. Again, this is compatible with structures (II) and (III), but not with the monomeric structure (I).

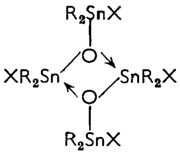
Molecular weights. In the past, molecular-weight determinations, which should be decisive for or against an oligomer of structure (I), have been singularly confusing. For the compounds $Et_4Sn_2Cl_2O$, $Et_4Sn_2Br_2O$, $Pr_4Sn_2Cl_2O$, and $Pr_4Sn_2Br_2O$ in freezing benzene, Pfeiffer and Brack[14] obtained values of n varying from 1·4 to 1·8, but independent of concentration. Any structural implications of this were ignored, and the monomeric formula (I) was adopted. Harada[19b] found that the acetate $Me_4Sn_2(OAc)_2O$, when examined cryoscopically in benzene or naphthalene, showed an apparent molecular weight which increased rapidly with concentration; for a reason which is not clear, he chose a value $n = 3$ for the structure (II). The compounds $Et_4Sn_2Br_2O$,[17a] and the two isomers $Et_2Pr_2Sn_2Br_2O$,[19d] on the other hand, showed a rapid *decrease* of apparent molecular weight with increasing concentration, and no meaningful extrapolation of his results to infinite dilution is possible.

For the compound which we now know to be $Bu_4Sn_2Cl_2O$, in freezing benzene or dioxan, Johnson[5] found that the value of n varied from about 2/3 to 2 as the concentration was increased. On the other hand, Okawara reported that $Pr_4Sn_2Cl_2O$ and $Et_4Sn_2Cl_2O$ were dimeric at ~0·07M-concentrations in freezing benzene, but that the apparent molecular weight *increased* in more dilute solutions.[21]

Our preliminary ebulliometric experiments with benzene and carbon tetrachloride as solvents indicated that the butyl chloride and butyl bromide compounds were dimeric. Subsequent more accurate measurements with a thermistor vapour-pressure osmometer gave the molecular weights shown in the Table. In benzene at 25°, all the compounds studied, with two exceptions, gave values within 4% of those required for the dimers $(R_4Sn_2X_2O)_2$, and these were independent of concentration over the range 0·01—0·1M.* The butyl bromide and butyl acetate compounds, although apparently chemically pure, gave values about 10% lower than those required for the dimers, but which again did not vary with concentration.

(IV)





(V)

The compounds $R_4Sn_2X_2O$ therefore appear to have the molecular structure (IV) or (V).

Location of the groups X. We attempted to decide between the two possibilities (IV) and (V) by determining the ^{19}F magnetic resonance spectrum of the compound $(Bu_4Sn_2F_2O)_2$ in benzene. At room temperature, however, only one very broad band was obtained, perhaps implying that the fluorine is exchanging or intramolecularly bridging between tin atoms, or that the $O \longrightarrow Sn$ links, which are formally represented as co-ordinate bonds in formulæ (IV) and (V), break to give 4- and 5-co-ordinate tin in equilibrium. A

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* This is contrast to the corresponding disiloxanes, $ClR_2Si{\cdot}O{\cdot}SiR_2Cl$, which are monomeric in freezing benzene,[22] and to the aryl-lead carboxylates, $Ph_4Pb_2(OAc)_2O$ and $Ph_4Pb_2(O{\cdot}CO{\cdot}Pr^i)_2O$, which are monomeric at the m. p. of stilbene (124°);[23] we are investigating this further.

[21] Okawara, Internat. Symp. on Inorganic Polymers, Nottingham, July 1961; *Proc. Chem. Soc.*, 1961, 383; and personal communication.

[22] McCusker and Ostdick, *J. Amer. Chem. Soc.*, 1958, **80**, 1103.

[23] Panov, Zemlyanskii, and Kocheshkov, *Doklady Akad. Nauk S.S.S.R.*, 1962, **143**, 60 [*Proc. Acad. Sci.* (*U.S.S.R.*), *Chem. Sect.*, 1962, **143**, 222].

similar weak broad ^{19}F resonance is observed with a saturated solution of stannous fluoride,[24] and with amine or ether complexes of stannic fluoride dissolved in an excess of the ligand.[25]

To check the possibility of intramolecular bridging by the anionic group between two tin atoms, dibutyltin dithiocyanate and its derivative $[Bu_4Sn_2(CNS)_2O]_2$ were prepared, and their infrared spectra were determined. In solution both gave a strong single absorption at 2050 cm.$^{-1}$ for the carbon–nitrogen stretching frequency, suggesting that, in this case at least, no bridging occurs.

Chemical Reactions.—No cyclic oligomeric dialkyltin oxides are known, in contrast to the corresponding organosilicon and organogermanium series, and it was hoped to remove two R_2SnX_2 units from the molecule to leave cyclobis(dibutyltin oxide). With $[Bu_4Sn_2Cl_2O]_2$ in ether, however, 2,2'-bipyridyl gave only a 15% yield of (2,2'-bipyridyl)-dibutyltin dichloride. More drastic reagents were therefore investigated. Diazomethane (equivalent to the chloride) was much less reactive than towards dibutyltin dichloride, and a compound of the composition $Bu_4Sn_2Cl(OH)O$ was obtained [compare reaction (3)]; butylmagnesium bromide gave tetrabutyltin, and sodium sulphide gave dibutyltin sulphide, but again no oligomeric dibutyltin oxide could be isolated.

Conclusion.—We conclude that, in benzene or carbon tetrachloride, and probably in other non-polar solvents, the compounds $R_4Sn_2X_2O$ (X = halogen, carboxylate, sulphonate or thiocyanate) are dimeric and have the structure (IV) or (V). Of these two structures we prefer the latter, but no definite decision can be made on our present evidence. By an *X*-ray study, however, Okawara has recently shown that in the crystalline state the compound $Me_4Sn_2(O{\cdot}SiMe_3)_2O$ has the structure (V), in which the peripheral tin atoms are arranged *trans* about the essentially square (2·2 × 2·3 Å) tin–oxygen ring.[21]

Such a structure where, *e.g.*, R = Me and X = Cl would be given the systematic name di-μ-(chlorodimethylstannyloxo)bis(chlorodimethyltin).

The fact that we obtained simple products of the type $(R_4Sn_2Cl_2O)_2$ from the mixed reactants R_2SnCl_2 and R'_2SnO suggests reversible fission of the four-membered ring under mild conditions. We have recently obtained some compounds of the type $(R_4Sn_2X_2O)_2$ where X = ArO, RO, and RO·O. In benzene at 25°, the phenoxides are extensively dissociated into monomeric units to an extent depending on the substituent in the aromatic ring.[26] This confirms and extends some unpublished work by Dr. W. J. Considine and his co-workers.

EXPERIMENTAL

Methods of analysis, and of preparing some of the starting materials, are described in Part I.[1]

Dibutyltin Dithiocyanate.—Dibutyltin dichloride was treated with potassium thiocyanate in boiling ethanol;[27] potassium chloride (99%) was precipitated, and the filtrate yielded *dibutyltin dithiocyanate* as fine white needles, m. p. 142·5—144° (Found: SCN, 32·8. $C_{10}H_{18}N_2S_2Sn$ requires SCN, 33·3%).

Diethyltin Di(camphorsulphonate).—Diethyltin oxide (1·92 g.) was dissolved in a warm solution of (+)-camphorsulphonic acid (4·64 g.) in ethanol, giving the *di(camphorsulphonate)* (4·8 g., 73%; from ethanol–ether), m. p. 282—286° (decomp.), $[\alpha]_D$ +24·8° (l 1; *c* 5·378 in EtOH) (Found: S, 9·5. $C_{24}H_{40}O_8S_2Sn$ requires S, 10·0%). With bipyridyl in ethanol it gave *(2,2'-bipyridyl)diethyltin di(camphorsulphonate)*, m. p. 186—188° (Found: S, 8·3; N, 3·9. $C_{34}H_{48}N_2O_8S_2Sn$ requires S, 8·1; N, 3·5%).

Preparation of Compounds $(R_4Sn_2X_2O)_2$.—Examples are given of the preferred methods. The results are summarised in the Table.

By hydrolysis. (*a*) With triethylamine. A solution of dibutyltin dibromide (7·86 g.) in ether (50 c.c.) was added slowly to a stirred solution of triethylamine (2·02 g., 1 mol.) in ethanol (20 c.c.). Triethylammonium bromide (3·51 g., 98%) was precipitated almost immediately,

[24] Burke and Lauterbur, *J. Amer. Chem. Soc.*, 1961, **83**, 326.

[25] Muetterties, *J. Amer. Chem. Soc.*, 1960, **82**, 1082.

[26] Aspden, Davies, and Graham, unpublished work.

[27] Seyferth and Rochow, *J. Amer. Chem. Soc.*, 1955, **77**, 1302.

and was filtered off. The filtrate was concentrated under reduced pressure, giving di-μ-(bromodibutylstannyloxo)bis(bromodibutyltin), as white, slightly waxy crystals (from ethanol; 3·22 g., 50%), m. p. 101·5—104°. This compound was extremely soluble in aromatic or chlorinated hydrocarbons, but was insoluble in light petroleum.

When the same procedure was applied to dibutyltin diacetate, no salt was precipitated. The solvent was removed under reduced pressure, the resulting paste was shaken with a mixture of water and ether, and the product was isolated from the ethereal layer.

(*b*) With aqueous sodium hydroxide. Aqueous 0·5N-sodium hydroxide (120 c.c.) was added slowly to a stirred solution of dibutyltin dichloride (18·2 g.) in ethanol (40 c.c.). The white precipitate was recrystallised from acetone (200 c.c.), giving di-μ-(chlorodibutylstannyloxo)bis-(chlorodibutyltin) (12·9 g., 78%), m. p. 112·5°.

By synthesis. A mixture of dibutyltin dithiocyanate (3·49 g.) and dibutyltin oxide (2·49 g.) in toluene (20 c.c.) was stirred and heated. The solution became clear well before the b. p. The solvent was distilled off, leaving white crystals which recrystallised from ether at −80°. *Di-μ-(thiocyanatodibutylstannyloxo)bis(thiocyanatodibutyltin)*, m. p. 84°, was soluble in all common solvents except light petroleum. The infrared spectrum of the solution in acetophenone showed a strong maximum at 2050 cm.$^{-1}$.

Nuclear Magnetic Resonance.—(*a*) ^{119}Sn. Solutions of the following compounds, nearly saturated at 25°, were prepared: Bu_2SnCl_2 (in benzene, *ca.* 85% w/w solution); $(Bu_4Sn_2Cl_2O)_2$ (in benzene, *ca.* 69%; in carbon tetrachloride, *ca.* 48%); $(Bu_4Sn_2Br_2O)_2$ (in benzene, *ca.* 73%). A Varian V-4300 B spectrometer was operated at 12 mc. sec.$^{-1}$, and two conditions for the detection of ^{119}Sn resonances were used, both with phase-sensitive detection. (1) " Fast-passage conditions " (R.F. power, 200 milligauss; sweep rate, 5000 milligauss sec.$^{-1}$). (2) " Slow-passage conditions " (R.F. power, 7 milligauss; sweep rate, 3·3 milligauss sec.$^{-1}$).

Dibutyltin dichloride gave a single broad resonance. The three solutions of the complex halides each showed two broad resonances (separation 20 p.p.m.) of approximately equal intensity and within 20 p.p.m. of the resonances of the parent halides. These two peaks overlapped considerably, but the resolution was sufficient to show conclusively the presence of two non-equivalent tin nuclei. The spectrum of the liquid $[Bu_4Sn_2(O{\cdot}CO{\cdot}C_7H_{15})_2O]_2$ showed only a single broad resonance.

(*b*) ^{1}H *and* ^{19}F. Both ^{1}H and ^{19}F magnetic resonance spectra were determined at 60 mc./sec. with an AEI RS2 spectrometer. The compound $[Me_4Sn_2Cl_2O]_2$ in chloroform gave two ^{1}H peaks of approximately equal area with τ values of 8·81 and 8·85 (tetramethylsilane as reference standard).

Molecular Weights.—(1) *By an ebulliometer.* Samples were added as weighed pellets to the pure dry solvents, giving solutions covering the concentration range 1—7% (*i.e.*, *ca.* 0·015—0·105M on the basis of the formula $R_4Sn_2X_2O$). Temperatures were estimated to 0·001° by a micro-Beckmann thermometer. The results were as follows.

$[Bu_4Sn_2Cl_2O]_2$. Found, in carbon tetrachloride: *M*, 1110, 1010, 1010, 1050; in benzene, 1410, 1220, 1220. Calc.: 1106.

$[Bu_4Sn_2Br_2O]_2$. Found: in benzene, *M*, 1450, 1180, 1190, 1160. Calc.: *M*, 1283.

(2) *By a thermistor vapour-pressure osmometer.* A commercial instrument manufactured by the Mechrolab Instrument Co., California, was used. The principle is described by Brady, Huff, and McBain.[28] Measurements were made at 25° on benzene solutions covering the concentration range 0·5—10% (*i.e.*, *ca.* 0·0075—0·15M on the basis of the formula $R_4Sn_2X_2O$). Variations in the apparent molecular weight were not systematic and were within the experimental error; the mean values are quoted in the Table.

(3) *By* X-*ray crystallography.* An attempt was made to determine the molecular weight of the compound $[Bu_4Sn_2Cl_2O]_2$ from the *X*-ray diffraction of single crystals. The results showed, however, that the crystals were aggregates of smaller crystals, and their waxy nature made it impossible to obtain single crystals. We are grateful to Dr. H. J. Milledge for her assistance with these experiments.

Chemical Reactions of $(Bu_4Sn_2Cl_2O)_2$.—(1) *With bipyridyl.* The compound $(Bu_4Sn_2Cl_2O)_2$ (5·53 g.) and 2,2′-bipyridyl (1·59 g.) were dissolved in dry ether (70 c.c.). White crystals of (2,2′-bipyridyl)dibutyltin dichloride (m. p. and mixed m. p. 180°) appeared slowly after 2 min.; after 90 min. they (0·68 g., 15%) were filtered off. A further small amount was obtained when

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[28] Brady, Huff, and McBain, *J. Phys. Colloid Chem.*, 1951, **55**, 304.

the solvent was removed from the filtrate, but the bulk of the residue melted over the range 60—120°. Similar results were obtained when the reagents were heated in benzene for 1 hr. and then kept at room temperature for 2 days.

(2) *With butylmagnesium bromide.* The compound $[Bu_4Sn_2Cl_2O]_2$ (27·6 g.) in ether (120 c.c.) was added slowly to a stirred solution of butylmagnesium bromide [from butyl bromide (13·7 g.) and magnesium (2·55 g.)] in ether (60 c.c.) at 0°. The mixture was heated under reflux for 3 hr., then the ether was distilled off, and the residue kept at 100° for 1 hr. The product was hydrolysed with aqueous ammonium chloride, yielding tetrabutyltin (12·7 g., 73%), b. p. 96°/0·2 mm., n_D^{25} 1·4722. The residue, a cream wax, was extracted with acetone, yielding a waxy solid which melted over the range 92—102°, and probably had the composition $Bu_4Sn_2Cl(OH)O$ (Found: Cl, 6·2. Calc.: 6·6%).

(3) *With diazomethane.* A 1·03M-solution (42·8 c.c.) of diazomethane in ether was added slowly to a stirred solution of the compound $(Bu_4Sn_2Cl_2O)_2$ (11·1 g.) in dry ether (200 c.c.) at $-11°$. Even the first portion of the diazomethane gave a persistant colour to the solution, in contrast to the immediate reaction of diazomethane with dibutyltin dichloride. The mixture was allowed to warm to room temperature, but the colour was still present after a further 30 min. Copper powder was then added, and the colour disappeared during 45 min., with no apparent increase in the small amount or polymethylene which was already present. The solvent was removed, and the residue was recrystallised from methanol, giving the compound $Bu_4Sn_2Cl(OMe)O$ as white crystals melting over the range 80—120° (Found: C, 37·0; H, 7·2; Cl, 7·4. $C_{17}H_{39}ClO_2Sn_2$ requires C, 37·2; H, 7·2; Cl, 6·5%).

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