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PRELIMINARY NOTES

New types of alkylchlorodistannoxanes

Dialkyltin oxides are known to react with dialkyltin dichlorides in boiling toluene to give 1,1,3,3-tetra-alkyl-1,3-dichlorodistannoxanes (I), which can be hydrolysed to 1,1,3,3-tetra-alkyl-1-chloro-3-hydroxydistannoxanes (II); both are dimeric in non-polar solvents[1].

$$R_2SnO + Cl_2SnR_2 \rightarrow \underset{(I)}{ClR_2Sn\cdot O\cdot SnR_2Cl} \xrightarrow{HO^-} \underset{(II)}{ClR_2Sn\cdot O\cdot SnR_2OH}$$

We now report that this type of reaction is not limited to the dialkyltin dichlorides, but that it occurs with other tin chlorides of the general formula $R_{4-n}SnCl_n$ ($n = 1$–4), giving rise to new families of alkylchlorodistannoxanes.

Dialkyltin oxides react exothermically at room temperature with alkyltin trichlorides ($n = 3$) to give 1,1,3-trialkyl-1,3,3-trihalogenodistannoxanes (III), which are usually crystalline solids with sharp melting points, and are monomeric in benzene.

$$R_2SnO + Cl_3SnR' \rightarrow \underset{(III)}{ClR_2Sn\cdot O\cdot SnR'Cl_2}$$

They are hydrolysed fairly rapidly in air, but form more stable complexes, presumably of the structure $ClR_2Sn\cdot O\cdot SnR'Cl_2L_2$ with ligands such as pyridine, 2,2'-bipyridyl, and phenanthroline. Dibutyltin oxide and butyltin triacetate react similarly in boiling benzene giving the trialkyltriacetatodistannoxane, and the reaction is probably general for many compounds besides chlorides and carboxylates. Some examples are given in Table 1.

TABLE 1

ALKYLCHLORODISTANNOXANES

Type	*Formula*	*M.p.* (°C)	ν_{max} *(SnOSn)* (cm^{-1})
IV	$ClBu_2Sn\cdot O\cdot SnEt_3$		680
IV	$ClBu_2Sn\cdot O\cdot SnBu_3$		675
III	$ClMe_2Sn\cdot O\cdot SnEtCl_2$	89–91	805
III	$ClBu_2Sn\cdot O\cdot SnBuCl_2$	34–35	690
III	$ClOct_2Sn\cdot O\cdot SnBuCl_2$	42–43	690
III	$AcOBu_2Sn\cdot O\cdot SnBu(OAc)_2$	305–310	680
V	$ClBu_2Sn\cdot O\cdot Sn(OH)Cl_2$	46–47	685[a]
V	$ClOct_2Sn\cdot O\cdot Sn(OH)Cl_2$	42–44	690[b]

[a] ν_{max} 3400 (OH); [b] ν_{max} 3440 (OH).

A similar reaction takes place between dialkyltin oxides and some trialkyltin chlorides ($n = 1$) in boiling benzene, to give 1,1,3,3,3-penta-alkyl-1-chlorodistannoxanes (IV) as very thick greases, which revert to the parent oxide and halide above 150°. These compounds are slightly associated in benzene, and now do not give isolable complexes with ligands such as bipyridyl.

$$R_2SnO + ClSnR'_3 \rightarrow \underset{\text{(IV)}}{ClR_2Sn\cdot O\cdot SnR'_3}$$

By analogy, it might be expected that dialkyltin oxides and tin tetrahalides ($n = 4$) should react to form 1,1-dialkyl-1,3,3,3-tetrahalogenodistannoxanes, but as yet we have obtained from these systems only the dialkyltin dihalides and tin oxyhalides by the reaction:

$$R_2SnO + X_4Sn \rightarrow R_2SnX_2 + OSnX_2 \qquad (X = Cl \text{ or } Br)$$

However, if the reaction is carried out with dialkyltin oxide which has not been completely dehydrated, condensation is accompanied by partial hydrolysis to give waxy solids which are apparently 1,1-dialkyl-1,3,3-trichloro-3-hydroxydistannoxanes (V), analogous to the compounds (II).

$$R_2SnO + Cl_4Sn \xrightarrow{H_2O} \underset{\text{(V)}}{ClR_2Sn\cdot O\cdot SnCl_2OH}$$

Some examples are included in the table; satisfactory analyses have been obtained for all these compounds.

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1 D. L. ALLESTON, A. G. DAVIES AND M. HANCOCK, *J. Chem. Soc.*, (1964) 5744, references given there.

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