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Functionally substituted distanthianes.

Dialkyltin oxides, R_2SnO, have recently been shown to react with tin halides, $R'_{4-n}SnX_n$, to give functionally substituted distannoxanes of the general formula $XR_2Sn \cdot O \cdot SnR'_3$, $XR_2Sn \cdot O \cdot SnR'_2X$, $XR_2Sn \cdot O \cdot SnR'X_2$, and $XR_2Sn \cdot O \cdot SnX_2 \cdot OH$[1]. Similar reactions have now been established for dialkyltin sulphides, giving functionally substituted distanthianes.

If dialkyltin sulphides in benzene or carbon tetrachloride are warmed briefly with compounds R_2SnX_2 ($X = F$, Cl, Br, I, CNS, OMe, $O \cdot CO \cdot R$), the appropriate distanthianes (I), are formed in good yield. The same products are obtained when the compounds $R_2Sn(OMe)X$[2] are treated with hydrogen sulphide, but the distannooxanes, $XR_2Sn \cdot O \cdot SnR_2X$, under the same conditions are relatively inert.

$$R_2SnS + R_2SnX_2 \rightarrow \underset{\text{I}}{XR_2Sn \cdot S \cdot SnR_2X}$$

The distanthianes (I) (unlike the corresponding distannoxanes[3]) are monomeric in benzene, and are stable to air, but react immediately with bipyridyl to give $R_2SnX_2 \cdot$bipy and R_2SnS in good yield. This ready reversion to progenitors may explain why other attempts to isolate the distanthianes (I) have failed[4]; the only previous example of a compound of this type appears to be 1,1,3,3-tetrabutyl-1,3-dichlorodistanthiane (m.p. 35°), which was obtained by Schmidt and Schumann by heating tributyltin chloride with sulphur at 180–190° for 14 h[5].

TABLE 1

FUNCTIONALLY SUBSTITUTED DISTANTHIANES

Type	*Formula*	*M.p. (°C)*
I	$ClMe_2Sn \cdot S \cdot SnMe_2Cl$	59–61
I	$BrMe_2Sn \cdot S \cdot SnMe_2Br$	39–42
I	$FBu_2Sn \cdot S \cdot SnBu_2F$	90–93
I	$ClBu_2Sn \cdot S \cdot SnBu_2Cl$	35.5–37
I	$SCNBu_2Sn \cdot S \cdot SnBu_2NCS$	115–117
I	$MeO \cdot Bu_2Sn \cdot S \cdot SnBu_2 \cdot OMe$	86–88
I	$C_7H_{15} \cdot CO \cdot O \cdot Bu_2Sn \cdot S \cdot SnBu_2 \cdot O \cdot CO \cdot C_7H_{15}$	oil
II	$ClBu_2Sn \cdot S \cdot SnPhCl_2$	38–38.5
II	$ClBu_2Sn \cdot S \cdot SnBuCl_2$	28–30
II	$BrBu_2Sn \cdot S \cdot SnBuBr_2$	oil

Dialkyltin sulphides and alkyltin trichlorides or tribromides react exothermically on mixing to give 1,1,3-trialkyl-1,3,3-trihalogenodistanthianes (II).

$$R_2SnS + R'SnX_3 \rightarrow \underset{\text{II}}{XR_2Sn \cdot S \cdot SnR'X_2}$$

These are again stable to air and are monomeric in benzene.

The reaction of tin tetrachloride or tetrabromide with dibutyltin sulphide was similar to that of dry dibutyltin oxide: only the dialkyltin dihalide, and no distanthiane, was obtained.

$$R_2SnS + SnX_4 \rightarrow R_2SnX_2 + (SSnX_2)$$

No reaction could be established between dialkyltin sulphides and trialkyltin halides, but it appears possible that 1,1,3,3,3-pentaalkyl-1-halogenodistanthianes may be prepared by treating the corresponding distannoxanes[1] with hydrogen sulphide.

Examples of these functionally substituted distanthianes are given in Table 1; satisfactory analyses have been obtained for all these compounds.

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