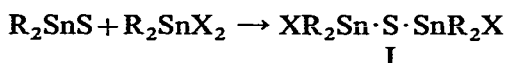


### Functionally substituted distanthianes.

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 distannoxanes,  $XR_2Sn \cdot O \cdot SnR_2X$ , under the same conditions are relatively inert.



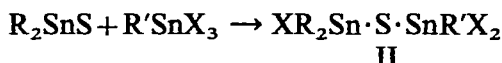
The distanthianes (I) (unlike the corresponding distannoxanes<sup>3</sup>) are monomeric in benzene, and are stable to air, but react immediately with bipyridyl to give  $R_2SnX_2 \cdot bipy$  and  $R_2SnS$  in good yield. This ready reversion to progenitors may explain why other attempts to isolate the distanthianes (I) have failed<sup>4</sup>; 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<sup>5</sup>.

TABLE I

FUNCTIONALLY SUBSTITUTED DISTANTHIANES

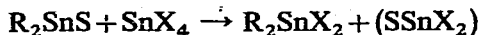
Type	Formula	M.p. (°C)
I	$ClMe_2Sn \cdot S \cdot SnMe_2Cl$	59–61
I	$BrMe_2Sn \cdot S \cdot SnMe_2Br$	39–42
I	$FBu_2Sn \cdot S \cdot SnBu_2F$	90–93
I	$ClBu_2Sn \cdot S \cdot SnBu_2Cl$	35.5–37
I	$SCNBu_2Sn \cdot S \cdot SnBu_2NCS$	115–117
I	$MeO \cdot Bu_2Sn \cdot S \cdot SnBu_2 \cdot OMe$	86–88
I	$C_7H_{15}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



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.



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<sup>1</sup> 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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