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Chemical Reactions Promoted by Tin Atoms*

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Tin derivates of 2-ethylhexyl thioglycolate (I) are readily prepared from the thiol and tin tetrachloride in the presence of sodium carbonate:

$$SnCl_4 + \underset{\mathbf{I}}{2HSCH_2COOCH_2CHEtBu} + Na_2CO_3 \longrightarrow$$

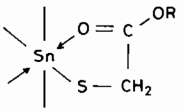
$$\underset{\mathbf{II}}{Cl_2Sn(SCH_2COOCH_2CHEtBu)_2} + 2NaCl + H_2O + CO_2$$

$$SnCl_4 + 4HSCH_2COOCH_2CHEtBu + 2Na_2CO_3 \longrightarrow$$

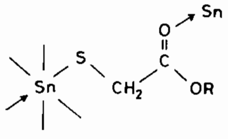
$$\underset{\mathbf{III}}{Sn(SCH_2COOCHEtBu)_4} + 4NaCl + 2H_2O + 2CO_2$$

This thioglycolate (I), which is important because its organotin derivatives are widely used as heat stabilizers for PVC [1], gives atypical thiolates. Thus, tin derivatives of simple thiolates form crystalline adducts with suitable donors, for example $Sn(SPh)_4 \cdot$ 2,2′-bipyridyl [2], whereas the tetrathioglycolate (III) does not appear to react. The dichlorotin compound (II), expected to be a stronger Lewis acid, does interact with 2,2′-bipyridyl but only low-melting ill-defined products were obtained.

The IR spectra show that the ester carbonyl group is free in **III**, ν(CO) 1735 cm^{-1} but coordinated in **II**, ν(CO) 1640 cm^{-1}. Coordination is confirmed by the ^{119}Sn Mössbauer spectrum of **II**, δ = 0.96 mm sec^{-1} (w.r.t. SnO_2), Δ = 1.86 mm sec^{-1}. This coordination may be intramolecular (**IIa**) or intermolecular (**IIb**). (Compound **II** appears to be identical with material prepared independently by direct reaction between equimolecular proportions of tin tetrachloride and **III** [3].)



IIa

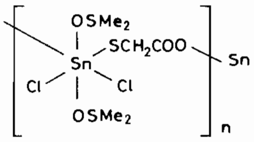


IIb

The corresponding dichlorotin bis(methyl thioglycolate), $Cl_2Sn(SCH_2COOMe)_2$ (IV), was also prepared using the sodium carbonate method.

Addition of dimethyl sulphoxide (DMSO) at room temperature to a solution of **II** in toluene gave an immediate precipitate of the polymeric product **V**. Other products formed in this reaction are 2-ethylhex-1-ene (IV) and the disulphide (VII):

$$Cl_2Sn(SCH_2COOCH_2CHEtBu)_2 \xrightarrow{DMSO}$$

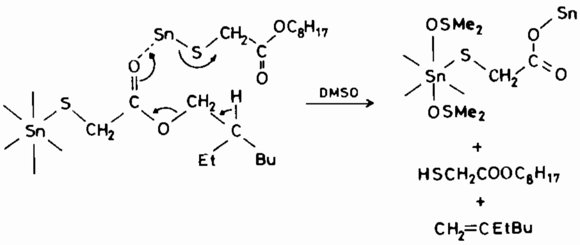


V

M.p. 144–146 ℃
IR ν(CO) 1662 cm^{-1}
ν(SO) 910 cm^{-1}
nmr CH_3 δ 2.51(6);
CH_2 δ 3.33(2)
Mössbauer δ 0.55 (w.r.t. SnO_2)
Δ 1.10 mm sec^{-1}

$$+ \underset{\mathbf{VI}}{CH_2{=}CEtBu} + \underset{\mathbf{VII}}{(SCH_2COOCH_2CHEtBu)_2}$$

The ready conversion of an ester to an alkene is remarkable as this process normally requires high temperature pyrolysis in the gas phase [4]. A plausible mechanism for this reaction is as follows, with the thiol being subsequently oxidised to the disulphide:



When the corresponding methyl ester (IV) was treated with DMSO, the same polymeric product (V) was obtained but, now the thioglycolate group was eliminated as the methyl sulphide (VIII) and no disulphide could be detected. It appears that when the alkyl group cannot be eliminated as an alkene, it alkylates the sulphur atom as indicated:

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*Satisfactory analyses were obtained for all new compounds.

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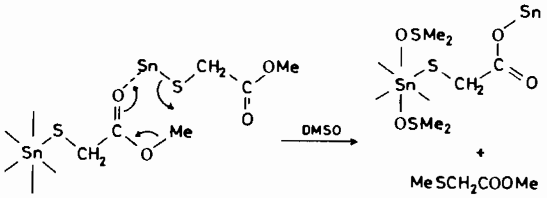
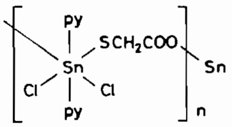


VIII

Compound **II** reacted with pyridine to give the polymeric product **(IX)** analogous to that obtained with DMSO.



M.p. 170–175 °C decomp.
ν(CO) 1610 cm^{-1}
Mössbauer δ 0.51 (w.r.t. SnO_2)
Δ 0.0 mm sec^{-1}

IX

When benzylamine was added to either **II** or **IV** there was an immediate precipitate of the corresponding amide as its benzylamine complex **(X)**:

$$Cl_2Sn(SCH_2COOR)_2 + 4PhCH_2NH_2 \longrightarrow$$

$$Cl_2Sn(SCH_2CONHCH_2Ph)\cdot 2PhCH_2NH_2 + 2ROH$$

X

In this more familiar reaction, ester decomposition again occurs, this time by alcohol elimination since the base can act as a proton source.

Acknowledgement

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References

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