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THE REACTION OF COMPOUNDS OF THE COMPOSITION $R_8Sn_4X_4O_2$ WITH HYDROGEN SULPHIDE

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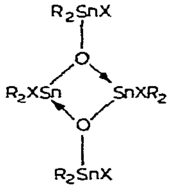
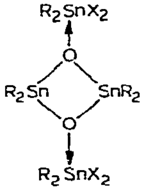
Although complete hydrolysis of organotin dihalides, R_2SnX_2, gives the polymeric oxides $(R_2SnO)_x$, use of controlled conditions gives partially hydrolysed products. It was recently shown[1] that, in the case of organotin diisocyanates, these intermediates are necessary stages in the hydrolysis. In most cases the first stable intermediate that can be isolated is $R_8Sn_4X_4O_2$ and two alternative structures have been proposed[2] *viz.* (I) or (II).


(I)


(II)

There are many examples in organotin chemistry of the replacement, under very mild conditions, of oxygen bound to tin by sulphur by the passage of hydrogen sulphide through a solution of the compound concerned. It was thought that it might be possible to choose between structures (I) and (II) by examining the products of reaction of these compounds with hydrogen sulphide. If structure (I) were correct the product would be $R_2XSn\text{–}S\text{–}SnXR_2$ whereas a compound of structure (II) would give a mixture of R_2SnX_2 and R_2SnS.

The following four $R_8Sn_4X_4O_2$ compounds were examined: R = Bu, X = Cl; R = Bu, X = OAc; R = Bu, X = NCS; R = Ph, X = Cl. In all cases the products of reaction with hydrogen sulphide were R_2SnX_2 and R_2SnS. For this to be acceptable as evidence in favour of structure (II) it is necessary to show that compounds of the type $R_2XSn\text{–}S\text{–}SnXR_2$ are stable and do not rearrange to give mixtures of R_2SnX_2 and R_2SnS. The only report[3] on this class of compound concerns the preparation of bis(chlorodibutyltin) sulphide by the reaction of tributyltin chloride with sulphur. We were unable to repeat this work, and, using the reaction conditions specified (180–190°, 14 h), we isolated only dibutyltin dichloride and stannous sulphide.

Attention was then turned to alternative methods of synthesis of bis(halogenodiorganotin) sulphides and reactions of the type

$$R_2SnX_2 + Na_2S \rightarrow R_2XSn\text{–}S\text{–}SnXR_2 + 2\ NaX$$

R = Bu, X = Cl; R = Ph, X = Cl; R = Bu, X = NCS were attempted but, in all cases, the diorganotin sulphide R_2SnS and unchanged R_2SnX_2 were isolated. Attempts to replace specifically the acetate group in dibutyltin chloride acetate using various inorganic sulphides under anhydrous conditions gave only unchanged starting material.

Other possible routes to, specifically, bis(chlorodibutyltin) sulphide examined were, firstly, treatment of the dibutyltin sulphide trimer with two equivalents of hydrogen chloride; this reaction gave dibutyltin dichloride and unchanged dibutyltin sulphide. Secondly interaction between bis(triphenyltin) sulphide and two equivalents of diphenyltin dichloride was investigated and here the products were triphenyltin chloride and dibutyltin sulphide.

If it is accepted that, despite our attempts to prepare such compounds, the bis(halogenodiorganotin) sulphides $R_2XSn\text{–}S\text{–}SnXR_2$ are capable of stable existence then our experiments with hydrogen sulphide indicate that structure (II) is the more likely for the compounds $R_8Sn_4X_4O_2$. Alternatively if it is assumed that compounds of the type $R_2XSn\text{–}S\text{–}SnXR_2$ are not stable then our experiments do not allow a choice to be made between structures (I) and (II). We prefer the latter view and recent NMR measurements[4] on $Me_8Sn_4(OSiMe_3)_4O_2$ suggest that structure (I) is more likely.

EXPERIMENTAL

The reaction of hydrogen sulphide with $R_8Sn_4X_4O_2$ compounds

(a) With $Bu_8Sn_4Cl_4O_2$. The organotin compound (1.34 g) was dissolved in acetone (40 ml) and hydrogen sulphide passed through the solution for one hour. 2,2′-Bipyridine (0.38 g) in acetone (20 ml) was added and the resulting solution evaporated to dryness. The residue was dissolved in hot light petroleum (b.p. 40–60°), on cooling the solution deposited crystals of 2,2′-bipyridinedibutyltin dichloride (1.05 g), m.p. and mixed m.p. 180–181° (lit.[5] m.p. 180°).

Evaporation of the mother liquor under reduced pressure gave an oil which on keeping in a desiccator slowly solidified to give dibutyltin sulphide (0.39 g), m.p. 65–69° (lit.[6] m.p. 63–69°).

(b) With $Bu_8Sn_4(NCS)_4O_2$. Hydrogen sulphide was passed into a solution of $Bu_8Sn_4(NCS)_4O_2$ (1.23 g) in acetone (10 ml) for 30 minutes. Evaporation of the solvent left a residue consisting of solid and oily components which were separated mechanically.

The solid was crystallised from chloroform giving dibutyltin diisothiocyanate (0.70 g), m.p. 138–140° (lit.[7] m.p. 145°). The oily product had an infrared spectrum identical with that of authentic dibutyltin sulphide except for the presence of a ν_{as}(NCS) band at 2080 cm^{-1} due to contamination with dibutyltin diisothiocyanate. It was therefore dissolved in light petroleum (b.p. 30–40°) and a solution of 2,2′-bipyridine in the same solvent added dropwise until no further precipitation occurred. Filtration gave 2,2′-bipyridinedibutyltin diisothiocyanate, m.p. 153° (lit.[5] m.p. 153°). Evaporation of the mother liquor gave an oil which slowly solidified giving dibutyltin sulphide (0.32 g), m.p. 65–69°, infrared spectrum identical with that of an authentic specimen.

The compounds $Ph_8Sn_4Cl_4O_2$ and $Bu_8Sn_4(AcO)_4O_2$ behaved similarly when treated with hydrogen sulphide.

The reaction of tributyltin chloride and sulphur (Cf. Schumann and Schmidt[3])

Tributyltin chloride (9.81 g) was heated with sulphur (1.93 g) at 180–190° for 14 h. The product was distilled and the fraction collected at b.p. 111–113°/5 mm crystallised on cooling. This product was washed with a small volume of light petroleum and shown to be dibutyltin dichloride, m.p. 40–41°, mixed m.p. with an authentic specimen 39–41° (lit.[8] m.p. 40.5°). This material gave negative tests for sulphur and when dissolved in light petroleum and treated with a solution of 2,2′-bipyridine in the same solvent there was immediate precipitation of 2,2′-bipyridinedibutyltin dichloride m.p. 183–185°.

The involatile residue (1.50 g) remaining in the distillation flask was black and inorganic. It was transparent to infrared radiation and also gave positive tests for sulphur and for Sn(II) and therefore identified as stannous sulphide.

The reaction of diorganotin dihalides (and dipseudohalides and halide acetates) with inorganic sulphides

The following two experiments are typical.

(a) Diphenyltin dichloride and hydrated sodium sulphide. A mixture of sodium sulphide nonahydrate (0.60 g, 0.0025 mole), diphenyltin dichloride (1.71 g, 0.005 mole) and benzene (20 ml) was boiled under reflux for 2 h.

The suspension was filtered from sodium chloride and the filtrate evaporated to dryness. The residue was dissolved in hot ethanol and, on cooling, crystals of diphenyltin sulphide (0.70 g, 0.0027 mole) were obtained, m.p. 183–184° (lit.[9] m.p. 183–184°). On evaporation of the ethanol an oil was left which slowly crystallised and was found to be unreacted diphenyltin dichloride (0.60 g, 0.0018 mole), m.p. 40–42° (lit.[10] m.p. 42°).

(b) Dibutyltin chloride acetate and silver sulphide. Silver sulphide (0.70 g, 0.0028 mole) was suspended in a solution of dibutyltin chloride acetate (1.83 g, 0.0056 mole) in dry benzene (30 ml) and the mixture boiled under reflux for one hour. Filtration and evaporation to dryness gave unchanged dibutyltin chloride acetate (1.8 g), m.p. 60–61° (lit.[11] m.p. 61°). Similarly unchanged starting material was isolated when the same reactants were heated for two hours in boiling nitromethane.

The reaction of diphenyltin sulphide with hydrogen chloride

Hydrogen chloride (0.038 g, 0.001 mole) in ethanol (10 ml) was added dropwise to diphenyltin sulphide (0.42 g, 0.00047 mole) in benzene (30 ml) and the solution allowed to stand at room temperature for 24 h. Concentration gave crystals of unchanged diphenyltin sulphide (0.19 g, 0.0002 mole), m.p. 181–183°.

Complete evaporation of the filtrate gave an oil which could not be induced to crystallise but on the addition of 2,2′-bipyridine (0.08 g, 0.0005 mole) in light petroleum (b.p. 40–60°) there was an immediate white precipitate of 2,2′-bipyridinediphenyltin dichloride (0.24 g, 0.0005 mole), m.p. 242–245° (lit.[5] m.p. 243–245°).

The reaction of bis(triphenyltin) sulphide with diphenyltin dichloride

Bis(triphenyltin) sulphide (2.18 g, 0.003 mole) in dry benzene (25 ml) was added dropwise to a warm, stirred, solution of diphenyltin dichloride (2.04 g, 0.006 mole) in the same solvent (10 ml) and the resulting solution boiled under reflux for 90 min. After concentration and the addition of light petroleum (b.p. 60–80°) a solid was obtained which, after crystallisation from light petroleum (b.p. 60–80°) gave triphenyltin chloride (1.66 g), m.p. and mixed m.p. 106–107°.

The filtrate from this crystallisation on standing deposited crystals of diphenyltin sulphide (0.60 g), m.p. 179–182°. The filtrate was then evaporated to dryness and the residue examined by chromatography on a silica gel column. By this means a further 0.46 g of triphenyltin chloride (m.p. 104–105°) was obtained and an oil (0.70 g) which, although it could not be induced to crystallise, was considered to be unchanged diphenyltin dichloride from its ready conversion to 2,2'-bipyridinediphenyltin dichloride, m.p. 242–244°.

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SUMMARY

It is shown that compounds of the type $R_8Sn_4X_4O_2$ react with hydrogen sulphide to give mixtures of the corresponding dihalide, R_2SnX_2, and sulphide, R_2SnS. The structural implications of this are discussed and are shown to be dependent upon the stability of compounds of the type $XR_2Sn{-}S{-}SnR_2X$. Various attempts to prepare this class of compound are reported.

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