A New Route to Tris(dimethyltin sulphide) with Tetramethyltin as Co-product; the Wider Implications of This and Some Other Reactions leading to Tetramethyl-tin and -lead from Iodomethane

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We describe a new light-promoted rearrangement of $(Me_3Sn)_2S$ leading to cyclic $(Me_2SnS)_3$ and Me_4Sn which has an important implication for the methylation of heavy metals in the environment and we also note some reactions of the natural product iodomethane leading to tetramethyl-tin and -lead.

For some years we have had an interest in organometallic reactions in aqueous media which may act as models for environmental processes. In particular, partially methylated heavy metal species (*e.g.* $MeHg^+$) may react with H_2S or S^{2-} (which are often present in the environment) to produce organometallic sulphide intermediates [*e.g.* $(MeHg)_2S$] which easily decompose to give fully methylated metallic products (*e.g.* Me_2Hg).[1-3] Since then we have been interested in the generality of such a process for other metals (*e.g.* tin and lead) and in the importance of the generation of volatile hydrophobic methylated species as transfer agents for metals in a general biogeochemical cycling process.[4] The present work with tin has demonstrated the reaction for this element and has also led to an alternative synthetic method for cyclic $(Me_2SnS)_3$, *viz.* equation (1).

$$Me_3Sn^+ \xrightarrow{S^{2-}} (Me_3Sn)_2S \xrightarrow{h\nu} (Me_2SnS)_3 + Me_4Sn \qquad (1)$$

The intermediate $(Me_3Sn)_2S$ was prepared by a literature method[5] and was characterised by elemental analysis, i.r. and n.m.r. spectroscopy, and by g.c.-mass spectroscopy.

Fragments appropriate to Me_nSn_2S were observed clustered about *m/e* 360, 345, 330, 315, 300, 285, and 270 ($n = 6 \rightarrow 0$) with correct isotopic ratios for tin. The molecular ion was observed at *m/e* 360.[6,7] Electron-capture gas chromatography demonstrated the purity of the material; no Me_4Sn was present.

Samples of $(Me_3Sn)_2S$ were placed in sealed flasks and exposed to daylight simulation radiation. After a short time a colourless crystalline deposit was observed within the oily starting material; after 48 h most of the oil had disappeared. The solid generated was dissolved in hot cyclohexane, recrystallised, and washed. Prior to this the head space vapours were analysed.

Me_4Sn was shown to be present here by g.c. retention time compared with an authentic sample and by g.c.-m.s. data. The Me_3Sn^+ fragments were observed clustered at *m/e* 165, together with Me_2Sn^+ (150), $MeSn^+$ (135), and Sn^+ (120). In addition we were able to detect the parent ion at *m/e* 180. The spectrum was identical to that of an authentic sample. Isotopic ratios were correct.

The solid product of the reaction was identified as the known[8] cyclic $(Me_2SnS)_3$ and was characterized by m.p., elemental analysis, i.r. spectroscopy, and by g.c.-mass spectroscopy. The latter shows a family from $Me_5Sn_3S_3^+$ clustered about *m/e* 527 and includes clusters from $Me_nSn_2S_2^+$ about *m/e* 362, 347, 332, 317, and 302 ($n = 4 \rightarrow 0$). Isotopic ratios were as predicted. Conversion was 70% under those conditions (48 h).

An important consequence of this reaction is that it suggests that partially methylated tin species, present in the environment, may react with naturally occurring sulphides to produce Me_4Sn. This latter compound is less toxic than its precursor Me_3Sn^+ species[9] but being more volatile would be subject to greater transport possibilities in the environment. We believe these experiments demonstrate a potential general importance for methyl metal–sulphide interactions under environmental conditions. In addition the relatively mild conditions used in the reaction make this a useful synthetic method for $(Me_2SnS)_3$ involving a novel methyl migration between tin atoms, equation (2).

$$3(Me_3Sn)_2S \xrightarrow{h\nu} (Me_2SnS)_3 + 3Me_4Sn \qquad (2)$$

We also report that iodomethane present in the environment as a natural[10,11] as well as an anthropogenic product, will react with lead and tin metal and with tin(II) salts to produce tetramethyl-lead and -tin respectively in aqueous media. Typically the metal species was placed in a sealed tube with iodomethane in water and kept in darkness at room temperature for up to two weeks. Samples of the head space vapours were analysed by g.c. and by g.c.-m.s. and were characterised as containing the tetramethyl products. The production of Me_4Sn from tin powder is interesting as this reaction has been reported to produce Me_2SnI_2 only,[12] whereas the reaction of lead metal with iodomethane has recently been reported to produce Me_4Pb from aqueous media under different conditions.[13] We also find Me_4Sn generated from tin(II) chloride and tin(II) sulphate and iodomethane in this aqueous abiotic system. In this case the presence of magnesium metal appeared to be a requirement; no volatile metal-containing product was formed from magnesium and iodomethane alone, suggesting a reductive mechanism. We have not detected Me_4Pb in the head space from reactions with lead(II) salts with or without the presence of magnesium though others have reported this under other conditions.[14]

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