Applied Organometallic Chemistry (1987) 1 449–458

0268–2605/87/01508449/$03.50

The direct synthesis of triorganotin compounds: Process and reaction mechanism

Frank S Holland
Manchem Ltd, Ashton New Road, Clayton, Manchester M11 4AT, UK

Received 13 June 1987 Accepted 29 July 1987

The reaction of tin metal with alkyl halides in the presence of a stoichiometric amount of halide ion rapidly produces very high yields of triorganotin halides. An overview of these reaction conditions and those required for the catalytic preparation of diorganotin dihalides shows that these preparations follow the normal reactivity of the alkyl halides towards nucleophiles. Both processes are satisfactorily explained by a mechanism involving tin halogenoanions as nucleophiles. A similar mechanism also explains the formation of organomagnesium and organozinc halides.

Keywords: Triorganotin halides, diorganotin dihalides, synthesis, reaction mechanism, nucleophilic, Grignard, organozinc

INTRODUCTION

Triorganotin compounds are important industrial chemicals,[1,2] and are commonly made by indirect methods.[1–3] An earlier communication[4] gives an overview of the first commercially feasible synthesis of triorganotin compounds directly from tin. This involves the addition of an alkyl halide to tin metal dispersed in a melt containing a quaternary halide which rapidly and selectively produces the trialkyltin halide and a by-product containing the quaternary group as a tin halide complex. The quaternary halide, the tin and the halide ion are all recovered from the by-product by electrolysis and re-used.

This paper describes the processes in more detail and offers some ideas on the reaction mechanism; a later paper[5] will deal with the electrochemical aspects.[6]

EXPERIMENTAL

Reagents were commercial or prepared by conventional means. General laboratory techniques were used with no special precautions to exclude air (except the large-scale preparations). Gas liquid chromatography (GC) was generally as described[7] using a Pye 204 instrument. Tin analyses were performed using a Pye SP9 instrument (AA) using dimethylformamide as the solvent. The hydrocarbon used for extractions was Exsol D, boiling range 145–160°C, from Esso Chemicals.

Preparation of tri-*n*-butyltin bromide using pre-made quaternary halide

Tetra-*n*-butylammonium bromide (644 g, 2 mol) was melted and dendritic tin (600 g, 5 mol, from the electrolysis of dilute tin(II) bromide solution[5]) added. The temperature of the melt was increased to 120–140°C and *n*-butyl bromide (1096 g, 8 mol) added at a constant rate with stirring over 3 h. During this time more dendritic tin (190 g, 1.6 mol) was added. The reaction mass was stirred for a further hour at 120–140°C, cooled and extracted with hydrocarbon (three times with the reaction mass volume). The hydrocarbon extracts were combined and distilled leaving a residue of *n*-butyltin bromides (844 g) which analysed as 700 g tri-*n*-butyltin bromide (1.89 mol, 94.6% yield on the tetra-*n*-butylammonium bromide used) and 140 g di-*n*-butyltin dibromide.

Preparation of tri-*n*-butyltin bromide using quaternary halide made *in situ*

n-Butyl bromide (5560 g, 40.6 mol) was added to a stirred preheated mixture of tin powder (2370 g, 20 mol) in tri-*n*-butylamine (1850 g, 10 mol) at such a rate as to maintain the temperature at 130–140°C. After this heating was re-applied and the mixture kept at 130–140°C for a further 3 h. The excess *n*-butyl bromide was removed by distillation and the reaction mass extracted with hydrocarbon (three times with the reaction mass volume). The hydrocarbon extracts were combined and the hydrocarbon distilled, leaving a product (2870 g) analysing by GC as 89% tri-*n*-butyltin bromide (6.9 mol, 69% yield on the tri-*n*-butylamine used). The by-product halogenotin quaternary complex amounted to 6400 g.

Preparation of tri-*n*-butyltin bromide using electrolysed by-product

The catholyte from a two-phase electrolytic treatment of the halogeno tin quaternary by-product[6,8] (5070 g comprising 2180 g unelectrolysed by-product ($R^1_4QSnX_3$; Eqn [1]) 1400 g dendritic tin, 1780 g tetra-*n*-butylammonium bromide and 300 g water) was dried by heating under vacuum. *n*-Butyl bromide (2330 g, 17 mol) was added over 7 h with stirring such that the reaction temperature was maintained at about 150°C. The reaction mixture was cooled and extracted with Exsol hydrocarbon ($3 \times 3\,dm^3$) at 80°C leaving a yellow-to-khaki residue containing some tin. The hydrocarbon extracts were combined and distilled giving 1663 g of product, b.p. 150°C/10 mm, analysing at 80% tri-*n*-butyltin bromide (1330 g, 3.6 mol, 98% yield on recovered quaternary used) and 20% di-*n*-butyltin dibromide.

Preparation of tri-*n*-butyltin bromide from di-*n*-butyltin bromide

Tetra-*n*-butylammonium bromide (322 g, 1 mol) was stirred into a mixture of di-*n*-butyltin dibromide (409 g, 1.04 mol) and tri-*n*-butyltin bromide (83 g, 0.22 mol); there was a slight emission of heat as the organotin quaternary complex was formed. Granulated tin (237 g, 2 mol) and *n*-butyl bromide (137 g, 1 mol) were added and the mixture heated to 120–140°C for 2 h.

The liquid phase was decanted from the residual tin which was washed with Exsol hydrocarbon leaving a residue of tin (110 g, 0.93 mol). The hydrocarbon washings were used to extract organotin product from the liquid reaction phase and two further extractions were made. The combined hydrocarbon extracts were distilled, affording tri-*n*-butyltin bromide (394 g, 1.06 mol) and di-*n*-butyltin bromide (71 g, 0.18 mol). This gives 84% yield of tri-*n*-butyltin bromide based on the quaternary complex used or 100% yield on the di-*n*-butyltin dibromide converted. The halogenotin quaternary complex by-product amounted to 678 g.

Preparation of mixed tri-*n*-butyltin bromide and chloride using preformed quaternary halide

n-Butyl chloride (138.7 g, 1.5 mol) was added over 60 h to a mixture of granulated tin (118.7 g, 1 mol) and tetra-*n*-butylammonium bromide (161 g, 0.5 mol) at 130–145°C. At the end of this reaction the reaction mass weighed 397 g. The unreacted tin was separated, washed and dried leaving 39 g of tin. The reaction liquor was extracted with hydrocarbon ($2 \times 400\,cm^3$) leaving a hydrocarbon-insoluble residue (281 g) which analysed at 23.3% tin, 12.1% bromine and 12.6% chlorine.

The hydrocarbon extracts were combined and distilled leaving an organotin residue (51 g) which analysed by GC as mainly a mixture of tri-*n*-butyltin bromide and chloride and analysed at 38% tin, 7.3% bromine and 7.4% chlorine.

Preparation of tri-*n*-octyltin bromide

n-Octyl bromide (289.6 g, 1.5 mol) was added over 9 h to a mixture of granulated tin (118.7 g, 1 mol) and tetra-*n*-butylammonium bromide (161 g, 0.5 mol) at 140–150°C; then the reaction mass was heated for a further 32 h. The unreacted tin was separated, washed and dried leaving 19.1 g of tin. The reaction liquor was in two layers; these were separated and the bottom layer extracted with hydrocarbon leaving a hydrocarbon-insoluble residue (340 g) analysing at 20.3% tin and 33% bromine. The hydrocarbon extracts were distilled leaving an organotin residue of 63 g; this and the top layer from the reaction liquor were combined to give 172 g, analysing at 20.3% tin and 15.3% bromine (tri-*n*-octyltin bromide requires 22.1% tin and 14.9% bromine) indicating a yield of approximately 64% based on the quaternary compound used.

Preparation of tri-*n*-butyltin bromide using quarternary halide made *in situ* in the absence of air

Tri-*n*-butylamine (18.5 kg, 100 mol), butyl bromide (54.8 kg, 400 mol), and granulated tin (23.75 kg, 200 mol) were heated in a glass-lined 250 dm^3 capacity steam heated vessel to 120–150°C for 24 h under nitrogen (without agitation). More tri-*n*-butylamine (37 kg, 200 mol) and granulated tin (73.5 kg, 620 mol) were added and the resulting mixture heated to 125–150°C; butyl bromide (110 kg, 800 mol) was added over 4 h and the mixture heated for a further 6 h. The reaction mass was cooled and a sample analysed by extracting with three volumes of hydrocarbon; the hydrocarbon-soluble portion was distilled to remove the hydrocarbon, leaving 13.2% by weight which analysed by GC as 97.5% tri-*n*-butyltin bromide and 2.5% di-*n*-butyltin dibromide. The hydrocarbon-insoluble portion was 69% by weight and contained 20.2% tin.

More granulated tin (25 kg, 219 mol) was added and the resulting mixture heated to 125–150°C for a further 4 h. The reaction mass was cooled and sampled and analysed as before. The organotin fraction was 34.9% by weight of the sample and analysed as 97% tri-*n*-butyltin bromide and 3% di-*n*-butyltin dibromide, and the hydrocarbon-insoluble portion was 61.6% by weight and contained 21.3% tin. The sample of reaction mixture when first taken was nearly white.

This indicates a yield of approximately 100% on the tri-*n*-butylamine used.

DISCUSSION

The direct synthesis of organotin halides

Aspects of the direct synthesis of organotin halides from tin metal appear to be more of an art than a science, and the literature (for reviews see Refs 9, 10) seems to treat this synthesis rather like the preparation of an organomagnesium halide (the Grignard reaction[11]) and the preparation of an organozinc halide (the Frankland reaction[12]). Thus Kizlink[10] documents the addition of iodine to help start the reaction and the use of alkyl iodides to help a reaction with an alkyl bromide or chloride. Catalysts which have some coordinating properties such as ethers, polyethers, dimethylformamide, hexamethylphosphoric triamide, etc., are used (particularly with added metal salts,[9,10] as are onium compounds or species such as amines and triamines, which are capable of forming onium compounds in the reaction medium.[9,10]

However other aspects are in accord with normal mechanistic predictions; thus the reactivity of the alkyl halides during the direct synthesis with tin obeys the normal nucleophilic reactivity of the alkyl halide (just as in the Grignard and Frankland reactions). The reactivity declines from iodide to chloride:

$$RI > RBr > RCl$$

and for any given halogen it declines with increasing size of the alkyl group:

$$MeX > EtX > PrX, \quad \text{etc.}$$

so that the direct reaction takes place well only with the iodides, less rapidly with the bromides and only slowly with the chlorides, and long-chain alkyl halides react more slowly than the corresponding short-chain species.[10] The atmospheric boiling point of any particular alkyl halide increases with the increasing size of the halogen (e.g. *n*-butyl chloride 78°C, *n*-butyl bromide 101°C, *n*-butyl iodide 130°C) so that the less reactive chlorides which require higher temperatures also require autoclaves equipped with efficient stirring.[10] But at high temperatures dehydrohalogenation of the alkyl halide becomes an important side reaction.[10] Further, the cost of the halogens and hence of the alkyl halides increases considerably with increasing size of the halogen.

The combination of these effects—reactivity, boiling point, dehydrohalogenation, and cost—has meant that the commercial use of the direct synthesis or organotin halides has been limited. Thus Bennett[13] reports that commercial production of organotin compounds using alkyl iodides was operated in Japan, but that this was only viable if a suitably inexpensive source of iodine was available and if the iodine could be efficiently recovered for re-use. An industrial process based on the use of alkyl bromides was operated in England in the mid-1960s,[13] although it does appear[14,15] that the bromides were assisted by the addition of the corresponding iodides. Again there was the need to recover the bromide.[16] Methyl chloride is the only alkyl chloride used in the direct synthesis[10,13,17] because it does not dehydrohalogenate so readily at the high temperatures (160–300°C) required for the reaction.[18]

Even within the above constraints, the direct synthesis of organotin halides from tin metal has been of limited industrial use since the dominant product was, until now, the diorganotin compound. However, when another metal is used as well (such as sodium, magnesium or zinc; see reviews in Refs 3, 9, 10) further alkylation can be achieved giving tri- and tetra- products. The other metal is commonly present as a tin alloy,[9] but more recently a process has been described[19] which is based on a mixture of zinc and tin powders in the presence of a molten onium compound, thus combining two organotin synthetic techniques. This process, which has been dealt with in three publications[20-22] as well as in patents,[19] gives the tetra- addition products.

When compounds having some coordinating properties or onium compounds, etc., are used as catalysts in the direct reaction of alkyl halides, the diorganotin dihalide is usually produced;[9,10] but the use of such species in stoichiometric amounts produces triorganotin halides in very high yields.[4,8] In the case of onium compounds the stoichiometry appears to be[4] (Eqn [1]):

$$3RX + R^1_4QX + 2Sn \rightarrow R_3SnX + R^1_4QSnX_3 \qquad (Q=N, P, As, Sb) \qquad [1]$$

As is shown in the Experimental section this new synthesis follows the general rules of direct organotin syntheses, thus:

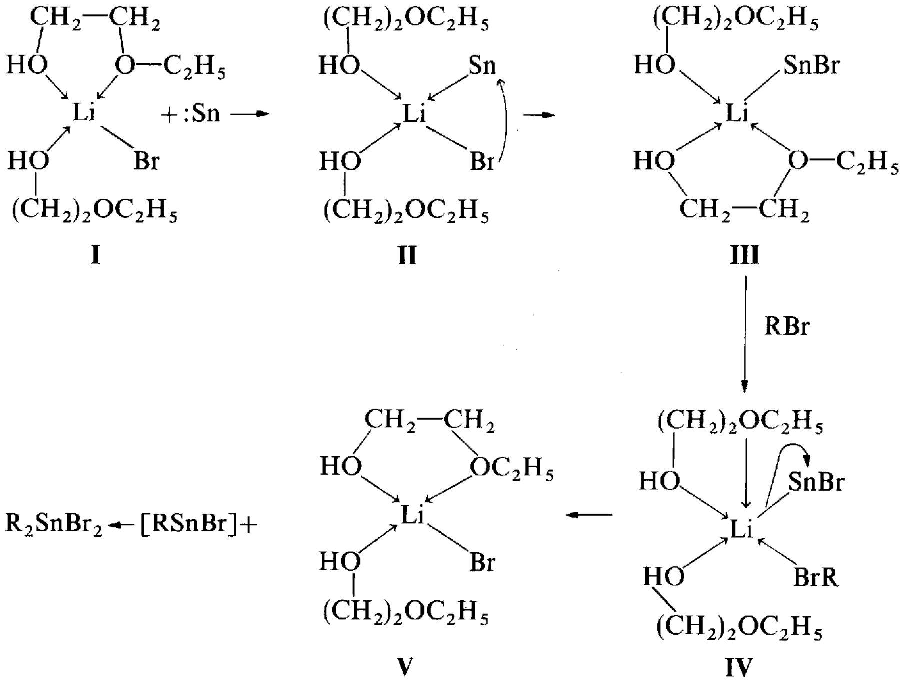
(a) the alkyl bromides are more reactive than the chlorides;
(b) the short-chain alkyl bromides react more rapidly than the longer-chain (butyl taking 3–4 h) whereas octyl takes 40 h);
(c) high-surface-area tin (powder and dendritic) is more reactive than lower-surface-area tin (granulated).

The reagent amount of the onium compound can be pre-made, made *in situ*, or recovered electrolytically from the by-product.

The reactions proceed very readily using the quaternary ammonium bromide as the reagent and at temperatures between 120–150°C. This contrasts sharply with the reports on the tetra-addition using zinc by Nicholson, Douek and Collins,[31,22] who show that the quaternary ammonium iodide is essential (no reaction taking place with the bromide alone) and the minimum temperature is 160°C. However the same authors[23] were able to obtain some tri- addition using tin powder in the absence of zinc.

The mechanism of the direct synthesis of organotin halides

Various authors have suggested a variety of mechanisms for the direct reaction of tin with alkyl halides. Oakes and Hutton[15] proposed a mainly ionic mechanism which involved the reaction of a coordinated lithium bromide (the catalyst) with tin metal (see Scheme 1). Kijima *et*



Scheme 1

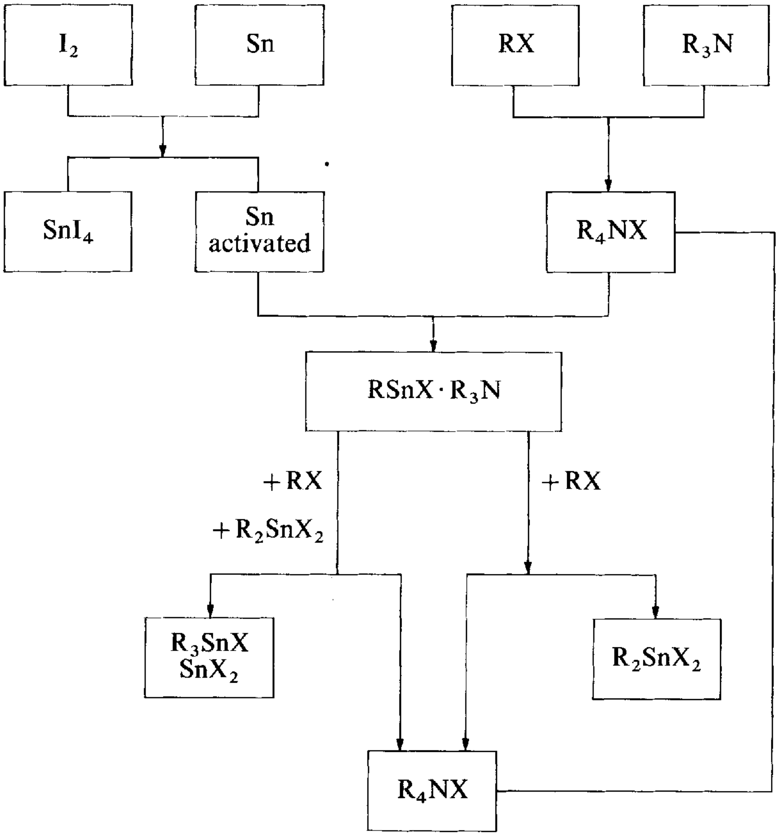
al.[24] also suggested an ionic mechanism with the onium cation (the catalyst) enhancing the polarization of the carbon-to-iodine bond in the butyl iodide so that nucleophilic attack by metallic tin is increased (see Scheme 2). Matschiner *et al.*[25] proposed a mechanism in which the onium compound (the catalyst) lost an alkyl group (and halogen) to the tin forming a trialkylamine, which was subsequently requaternized with more alkyl halide (see Scheme 3). This might seem unlikely since it would result in scrambling of the alkyl groups if these were different in the alkyl halide and the onium compounds. This either does not occur,[9,10] or does so only to a very small extent.[20,21] In their review Murphy and Poller[9] propose a mixed ionic and radical process (see Scheme 4) without any clear involvement of the catalyst, although they do suggest some involvement of iodide in stabilizing the intermediates. Douek *et al.*[20] and Nicholson *et al.*[22] adopt a substantially similar approach.

$$\begin{gathered}
\mathrm{Sn{:}} + \mathrm{Bu}^{\delta+}\text{—}\mathrm{I}^{\delta}\rightarrow[\mathrm{NR_4}]^+\mathrm{X}^-\\
\downarrow\\
[\mathrm{BuSn{:}}]^+ + \mathrm{I}^- + \mathrm{R_4N^+X^-}\\
\downarrow\\
[\mathrm{BuSnI}] + \mathrm{R_4N^+X^-}\\
\downarrow\\
[\mathrm{BuSnI}] + \mathrm{Bu}^{\delta+}\text{—}\mathrm{I}^{\delta-}\rightarrow[\mathrm{NR_4}]^+\mathrm{X}\\
\downarrow\\
[\mathrm{Bu_2SnI}]^+ + \mathrm{I}^- + \mathrm{R_4N^+X^-}\\
\downarrow\\
\mathrm{Bu_2SnI_2} + \mathrm{R_4N^+X^-}
\end{gathered}$$

Scheme 2

$$\begin{aligned}
&\mathrm{Sn{:}} + \mathrm{R}\text{—}\mathrm{X} &&\rightarrow \mathrm{Sn}^{\circ+} + \mathrm{R}^{\circ} + \mathrm{X}^-\\
&\mathrm{Sn}^{\circ+} + \mathrm{X}^- &&\rightarrow \mathrm{SnX}^{\circ}\\
&\mathrm{SnX}^{\circ} + \mathrm{R}^{\circ} &&\rightarrow \mathrm{RSnX}\\
&\mathrm{RXSn} + \mathrm{X}\text{—}\mathrm{R}\rightarrow \mathrm{RSnX}_2^{\circ} + \mathrm{R}^{\circ}\rightarrow \mathrm{R_2SnX_2}
\end{aligned}$$

Scheme 4



Scheme 3

The development of the direct route to triorganotins was helped by a speculative approach to a reaction mechanism. The normal nucleophilic reactivity of the alkyl halides is followed during the direct synthesis of organotin halides, so the question arose as to what is the nucleophile during the reaction. The suggested answer is that the nucleophile is a halogenotin anion[8] such as:

SnX_3^- SnX_4^{2-}
$RSnX_4^-$ $RSnX_5^{2-}$
$R_2SnX_3^-$ $R_2SnX_4^{2-}$

which in the presence of the ionium compound cation could be:

$R_4^1NSnX_3$ $(R_4^1N)_2SnX_4$
$R_4^1NRSnX_4$ $(R_4^1N)_2RSnX_5$
$R_4^1NR_2SnX_3$ $(R_4^1N)_2R_2SnX_4$

with the unalkylated tin compounds being tin(II) compounds and the others tin(IV) compounds. Such complexes are well known; thus Clark *et al.*[26] and Goldstein and Tok[27] have described the tin(II) compounds and Nicholson[28] has reviewed the tin(IV) compounds.

The proposed mechanism[8] for the synthesis of diorganotin dihalides and triorganotin halides from tin is shown in Scheme 5 (showing the bromide ion version). This mechanism was supported firstly by Devaud and Madec's[29] proposal of a nucleophilic substitution during the first stage of the so-called Pfeiffer reaction (see Ref. 17), and secondly by the nucleophilic mechanism suggested by Freidrich and Vartanian[30] for the quaternary ammonium bromide catalysed chloride-for-bromide redistribution between the carbon of alkyl halides and the tin of tri-*n*-butyltin halides. The third and perhaps strongest support comes from the very rapid and quantitative conversion of di-*n*-butyltin bromide using tin, tetra-*n*-butylammonium bromide and *n*-butyl bromide as shown in the Experimental section.

Scheme 5 can be used to explain the formation of diorganotins or triorganotins depending on the amount of halide ion introduced by the onium compound (or other similar species) used, as follows:

Initiation

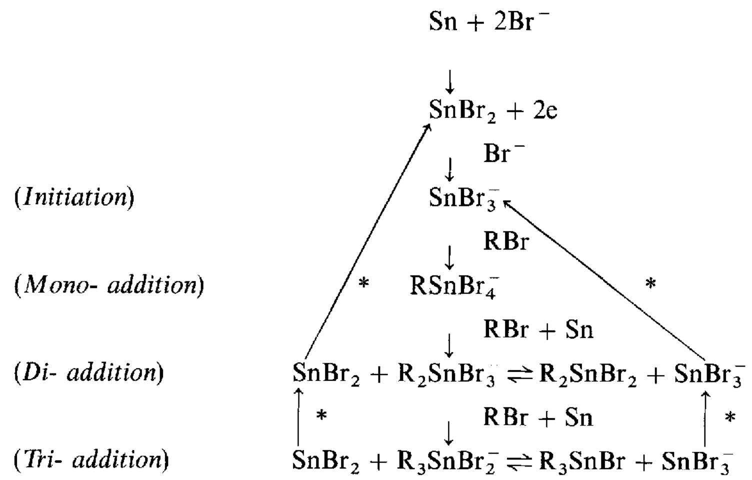
The addition of iodine in many direct syntheses[10] would cause the corrosion of tin (Eqn [2]):

$$Sn + I_2 \rightarrow SnI_2 \tag{2}$$

and any additional halide present (from the catalyst) would give the required nucleophile (Eqn [3]):

$$SnI_2 + X^- \rightarrow SnI_2X^- \tag{3}$$

Many of the patented processes for making diorganotins[10] deliberately add the nucleophilic reagent from the previous preparation (for example, see Ref. 31).



Scheme 5

* = Continuation. N.B. counter-ions are $R_4^1N^+$

In the direct synthesis of triorganotin halides using recycled electrolytically recovered onium compound (see Experimental section and Refs 6, 8) a large amount of nucleophile is present before the addition of the alkyl halide. Once the nucleophile is made it is regenerated so that it is only necessary to invoke a mechanism like that of Matschiner *et al.*[25] (Scheme 3) for a very small amount of the process and this would result in only a very small amount of scrambling as has been observed.[20,21]

Mono- addition

The initial nucleophile is trihalogenotin(II) anion (with the onium cation as the counter-ion). This attacks the alkyl halide to give the monoalkyl stannate(IV) complex anion, i.e. there is effectively oxidative addition of the alkyl halide to the nucleophile. A similar reaction is shown by Devaud and Madec[29] and it is reasonable to expect the trihalogenotin(II) anion to be a powerful nucleophile since it has both the negative charge and the lone pair of electrons. Alkyl iodides are commonly added to bromide or chloride systems as primers.[9,10] Since the iodides are more susceptible to nucleophilic attack they can react first to give the monoalkyl iodostannate(IV) anion which can then be involved during di- addition (see below) with the alkyl bromide or chloride.

Di- addition

The nucleophile now appears to be the monoalkyl stannate(IV) complex anion ($RSnX_4^-$) and this requires the involvement of tin metal to assist in the next nucleophilic reaction with alkyl halide. The tin could act in two ways; firstly it could weaken the carbon-to-halogen bond of an adsorbed alkyl halide so that nucleophilic reaction was enhanced. Or, more likely, the tin could reduce the $RSnX_4^-$ species back to a tin(II) species so that the active nucleophile is probably a monoalkyl stannate(II) anion ($RSnX_2^-$) adsorbed on the metal surface, which would again have the advantage of both the negative charge and the lone pair of electrons.

The product of the nucleophilic reaction depends on the availability of halide ion. If there is only a small amount available, as in the catalytic case, then the first equilibrium shown in Scheme 5 is pushed to the right, resulting in the formation of the diorganotin dihalide and regenerating the initial nucleophile (SnX_3^-) so that the process can continue. If, on the other hand, there is a high concentration of added halide as in the stoichiometric case, then the first equilibrium remains to the left, probably because any SnX_2 produced is removed by combination with excess halide to form SnX_3^-.

Tri- addition

The nucleophile now appears to be the dialkyl stannate(IV) complex anion ($R_2SnX_3^-$) stabilized by the high concentration of halide ion in the melt. This also requires the involvement of tin metal to assist in the next nucleophilic reaction with alkyl halide. Again it seems likely that the tin reduces this species down to the tin(II) state so that the active nucleophile is probably a dialkyl stannate(II) complex anion (R_2SnX^-) adsorbed on the metal surface. The product of this reaction is shown in Scheme 5 as $R_3SnX_2^-$, but such species are the least stable of the stannate(IV) complexes[32] so that the second equilibrium is pushed over to the right. Thus, when there is a stoichiometric amount of halide available the products are the triorganotin halide and the trihalogenotin(II) compound of the onium or other species used.

Tin corrosion

The di- addition and tri- addition steps in Scheme 5 require the corrosion of tin and the stoichiometry requires the dissolution of two tin atoms per molecule of R_3SnX produced. The corrosion of a metal is commonly viewed as an electrochemical process[33] requiring an anodic reaction and a cathodic reaction occurring at the metal–electrolyte interface.

The anodic reaction is very likely to be the dissolution of tin helped by the halide ion (Eqn [4]):

$$Sn + 2X^- \rightarrow SnX_2 + 2e \qquad [4]$$

leaving the two electrons behind on the corroding tin particle. The cathode reaction is probably the reduction of the monoalkyl stannate(IV) and dialkyl stannate(IV) complex anions (Eqns [5] and [6]):

$$RSnX_4^- + 2e \rightarrow RSnX_2^- + 2X^- \qquad [5]$$

$$R_2SnX_3^- + 2e \rightarrow R_2SnX^- + 2X^- \qquad [6]$$

So that the overall surface corrosion processes are given by Eqns [7] and [8].

$$RSnX_4^- + Sn \rightarrow RSnX_2^- + SnX_2 \qquad [7]$$

$$R_2SnX_3^- + Sn \rightarrow R_2SnX^- + SnX_2 \qquad [8]$$

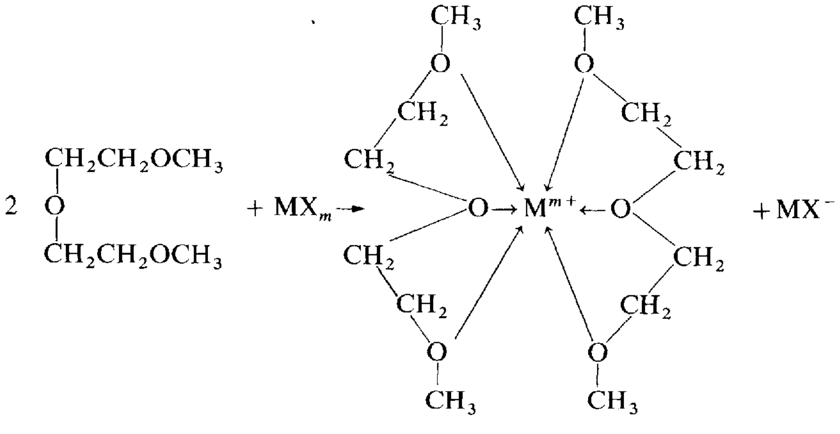
The counter-ions

The ionic mechanism shown in Scheme 5 requires counter-ions to balance the system electrolytically. In Scheme 5 and in much of the present and other work[9,10] such counter-ions have been onium cations. Onium halide compunds are good conductors in non-aqueous systems because they are nearly completely ionized. Thus they generate a high activity of halide ions so that the nucleophiles shown in Scheme 5 can be readily generated and stabilized. Onium compounds or species capable of generating such in the reaction medium have been found to be the best catalysts[9,10] for the di- additions and reagents for the tri-additions.

The other effective catalyst systems are those in which there is a compound capable of co-ordinating with an added metal ion,[9,10] such as the system described by Oakes and Hutton.[14,15] In such cases, as shown in Scheme 6, a complex can be formed which generates the halide ions required to form the nucleophilic reagents of Scheme 5 (the polyether is diglyme and MX_m is any metal halide). Clearly the amount of halide ion available and therefore the efficacy of the catalyst system depends on the stability of the complex ion formed, i.e. the position of the equilibrium, which is what Oakes and Hutton[15] found. If the coordinating compound is used as a solvent then the equilibrium in Scheme 6 can be expected to be pushed to the right so that there will be sufficient nucleophile-generating halide ions available. In such a case the system could be a good catalyst for di- addition. This has been demonstrated by Fostein and Pommier,[34] who showed that tin reacts with alkyl halides to give di- addition under mild conditions (20–80°C) when the reaction is run in hexamethylphosphoric triamide as solvent containing a small amount of copper(I) iodide.

The mechanism of the formation of other organometallic halides

Many of the techniques used to initiate and sustain the reaction of tin with alkyl halides[9,10] are also used in the formation of organo-magnesium[11] and organozinc[12] compounds. This raises the question of whether there is a common reaction mechanism. There are many similarities; thus it is considered good practice in the preparation of a Grignard reagent to retain an excess of activated magnesium from the previous batch and to add some pre-made Grignard reagent to the ether used. Iodine is commonly used to initiate the process and more active alkyl halides such as ethyl iodide are commonly added as primers. The strongly coordinating polyethers such as diglyme are known to improve the process; thus Cohen and Wright[35] have demonstrated improvement using dimethoxyethane rather than diethyl ether. Very significantly, Ashby and Reed[36] produced butylmagnesium chloride in 93% yield



Scheme 6

under mild conditions by using triethylamine in benzene. Further, Galli *et al.*[37] have shown that the presence of complexing agents or halide ions can greatly enhance the formation of and the reactivity of Grignard reagents. All of this suggests that enhancing the activity of the halide ions accelerates the process in a similar fashion to the organotin processes described above.

The preparation of organozinc halides from zinc and alkyl halides is older[12,38,39] than the Grignard reaction and very similar empirical improvements to the process have been made. These involve the use of iodine as a starter, addition of alkyl iodides as primers, and the use of coordinating solvents such as dimethoxyethane, diglyme, DMSO and DMF.[40–42] Finally, Nicholson *et al.*[22] has claimed 99% conversion of zinc to organozinc compounds by passing butyl chloride through molten tetra-*n*-butylammonium containing zinc powder. Again all of this suggests the involvement of halide ions in a similar fashion to the organotin processes described above.

A similar reaction mechanism to that proposed in Scheme 5 for tin is proposed in Scheme 7 for magnesium and zinc. The anodic reaction in the corrosion of the metal is very likely to be the dissolution of magnesium or zinc helped by the halide ion (Eqn [9])

$$M + 2X^- \rightarrow MX_2 + 2e \qquad [9]$$

and subsequent formation of MX_3^- and RMX_2^- ions.

The cathodic reaction could be the reduction of the MX_2^- ion and the RMX_2^- ion (Eqns [10] and [11]).

$$MX_3 + e \rightarrow MX_3^{2-} \qquad [10]$$

$$RMX_2^- + e \rightarrow RMX_2^{2-} \qquad [11]$$

so that the overall corrosion processes are given by Eqns [12] and [13]:

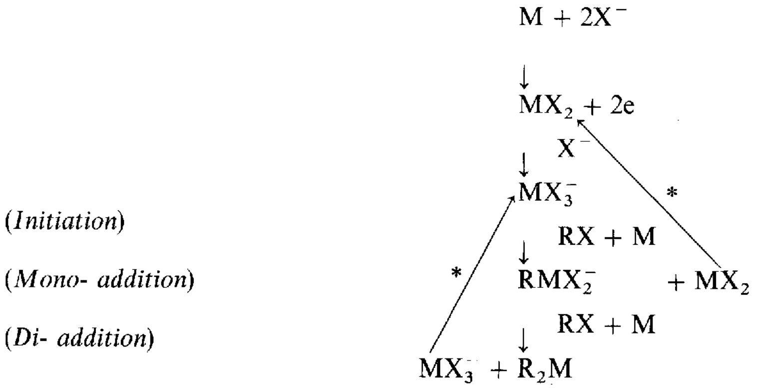
$$2MX_3^- + M + 2X^- \rightarrow 2MX_3^{2-} + MX_2 \qquad [12]$$

$$2RMX_2^- + M + 2X \rightarrow 2RMX_2^{2-} + MX_2 \qquad [13]$$

Again this implies that the actual nucleophiles are adsorbed magnesium(I) and zinc(I) halogenodianion species. These reactions occur on the metal surface or in the adjacent diffusion layer. The nucleophiles are proposed to be formed as short-lived species adsorbed at the metal–liquid interface and do not have independent existence in the solution phase.

CONCLUSION

It has been shown that the direct reaction of tin with an alkyl halide in the presence of a stoichiometric amount of compounds known to produce



Scheme 7

* = Continuation; M = Mg or Zn; X = Cl, Br, I; the counter-ions are onium cations or coordination compounds of M^{2+}.

high activities of halide ions (onium halides) rapidly produces very high yields of triorganotin halides. In attempting to understand how this tri-addition reaction works a speculative reaction mechanism has been evolved which also quite satisfactorily explains the functions of the catalysts in the preparation of diorganotins. This mechanism is based on the formation of metal halogenoanions (stabilized by the addition of halide ions) and the nucleophilic attack on the alkyl halides by these anions. Because of the strong experimental similarities between the formation of organotin, organomagnesium and organozinc halides the suggested reaction mechanism has been extended to the last two organometallics.

Acknowledgements The author, a freelance consultant, wishes to thank the Directors of Manchem Ltd for supporting this project and for permission to publish this paper, and is particularly grateful to the chemists, P Womersley, J Curran, JM Jaskolka and JM Hilton for their contribution to the project.

REFERENCES

1. Blunden, S, Cusack, PA and Hill, R *The Industrial Uses of Organotin Compounds*, Royal Society of Chemistry, London, 1985
2. Evans, CJ and Karpel, S *J. Organomet. Chem. Library*, 1985, 16
3. *Gmelin Handbook of Inorganic Chemistry, Sn, Organotin Compounds*, Parts 5 and 7, Springer-Verlag, Berlin, 1978 and 1980
4. Holland, FS *Appl. Organomet. Chem.*, 1987, 1: 185
5. *Appl. Organomet. Chem.* (to be submitted for publication).
6. US Patent 4 437 949, 1984
7. Tonge, BL *J. Chromatog.*, 1965, 182
8. US Patent 4 510 095, 1985
9. Murphy, J and Poller, RC *J. Organomet. Chem. Library*, 1979, 9: 189
10. Kizlink, J *Chem. Listy*, 1984, 78: 134
11. Kharasch, MS and Reinmuth, O *Grignard Reactions of Non-Metallic Substances*, Prentice-Hall Inc, Englewood Cliffs, NJ, 1954
12. Coates, GE, Green, MLH and Wade, K *Organometallic Compounds*, Vol. 1, Methuen, London, 1967
13. Bennett, RF *Ind. Chem. Bull.*, 1983, 171
14. Oakes, V and Hutton, RE *J. Organomet. Chem.*, 1965, 3: 472
15. Oakes, V and Hutton, RE *J. Organomet. Chem.*, 1966, 6: 133
16. Anon *Chemical Age*, 8 February 1964, 229
17. Davies, AG and Smith, PJ *Comprehensive Organometallic Chemistry*, Vol. 1, Wilkinson, G (ed), Pergamon Press, Oxford, 1982, p 545
18. Smith, AC and Rochow, EG *J. Am. Chem. Soc.*, 1953, 75: 4103
19. British Patent 1 548 365, 1979
20. Douek, JA, Nicholson, JW and Collins, JD *3rd Intern. Conf. Organomet. and Coordin. Chem. Ge, Sn and Pb*, Dortmund, July 1980
21. Nicholson, JW, Douek, JA and Collins, JD *J. Organomet. Chem.*, 1982, 233: 169
22. Nicholson, JW, Douek, JA and Collins, JD *J. Organomet. Chem.*, 1982, 233: 173
23. British Patent 1 580 792, 1980
24. Kijima, I, Asakawa, A, Kanisawa, H and Katayama, M *Kogyo Kagaku Zasshi*, 1969, 72: 1353
25. Matschiner, H, Voigtlander, R and Tzschach, A *J. Organomet. Chem.*, 1974, 70: 387
26. Clark, JH, Maresca, L and Smith, PJ *J. Chem. Soc. (A)*, 1970, 2687
27. Goldstein, M and Tok, GC *J. Chem. Soc. (A)*, 1971, 2303
28. Nicholson, JW *Coordin. Chem. Rev.*, 1982, 47: 263
29. Devaud, M and Madec, MC *J. Organomet. Chem.*, 1975, 93: 85
30. Friedrich, EC and Vartanian, PF *J. Organomet. Chem.*, 1976, 110: 159
31. British Patent 1 115 646, 1968
32. Poller, RC *The Chemistry of Organotin Compounds*, Logos Press, London, 1970, Chapter 11
33. Bockris, JO'M and Reddy, AKN *Modern Electrochemistry*, Vol. 2, Plenum Press, New York, 1977, Chapter 11
34. Fostein, P and Pommier, JC *J. Organomet. Chem.*, 1976, 114: C7
35. Cohen, HL and Wright, CF *J. Org. Chem.*, 1953, 18: 432
36. Ashby, EC and Reed, R *J. Org. Chem.*, 1966, 31: 971
37. Galli, R, Giannaccari, BM and Cassar, L *J. Organomet. Chem.*, 1970, 25: 429
38. Noller, CR *Org. Synth., Collective Vol. III*, 1953, p 184
39. Nesmeyanov, NI and Kocheshkov, KA *Methods of Elemento Organic Chemistry*, Vol. 3, Zn and Cd (translated from Russian), North-Holland Publishing, Amsterdam, 1967
40. *Methoden Der Organischen Chemie*, Muller, E (ed), Band XIII, 2a, Nutzel, K Organo-zink-verbindungen, Georg Thieme, Stuttgart, 1973, p 553
41. Zakharkin, LI and Okhlobystin, OY *Izv. Akad. Nauk SSR, Ser. Khim.*, 1963, 193; *Chem. Abstr.*, 1963, 58: 12589a
42. Bucourt, R and Joly, R *C.R. Seances Acad. Sci., Ser. 2*, 1962, 254: 1665 (and see British Patent 880 945, 1961)