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INVESTIGATION OF THE DIRECT SYNTHESIS OF TETRABUTYLTIN FROM BUTYL CHLORIDE

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Summary

The direct synthesis of tetrabutyltin from butyl chloride, has been investigated, and the various contributing reactions have been identified. A mechanism is proposed for the overall synthesis, which comprises radical-ionic processes for the liberation of metal atoms from the surfaces of the metal powders, followed by formation of bridging intermediates leading to the transfer of butyl groups from zinc to tin, until the synthesis of tetrabutyltin is complete. Although dibutyltin dihalides were shown to be probable intermediates in the process, the known organohalostannate complex $Bu_4N^+ [Bu_2SnCl_2I]^-$ was not found to be formed under the conditions used.

Introduction

We recently described a new reaction for preparing straight-chain tetraalkyltins from alkyl halides [1,2]. The reaction was carried out by adding the alkyl halide dropwise to a slurry of tin and zinc powders in tetrabutylammonium iodide at 160—170°C. After addition of the alkyl halide, the mixture was heated for 3 h, then the tetraalkyltin was extracted using light petroleum (40—60°C bpt). Other tetraalkylammonium iodides were found to be suitable as solvents [3,4], as were tetraalkylphosphonium iodides [4].

In the present paper, results are reported for a study designed to establish the

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nature of the reactions occurring in the direct synthesis of tetrabutyltin from butyl chloride (equation 1), a reaction which typically yields tetrabutyltin in 31—34%, yield based on tin taken (corresponding to 95—100% on tin consumed).

$$4\ \mathrm{BuCl} + \mathrm{Sn} + 2\ \mathrm{Zn} \xrightarrow[160\text{—}170^\circ\mathrm{C}]{\mathrm{Bu_4NI}} \mathrm{Bu_4Sn} + 2\ \mathrm{ZnCl_2} \qquad (1)$$

This particular reaction is of interest because the product, tetrabutyltin, is an intermediate in the synthesis of a wide range of industrially important organotin compounds having a variety of applications [5—8].

From the results we have been able to propose a mechanism for the overall synthesis.

Results and discussion

(i) The effect of temperature on the reaction

It has previously been demonstrated that this reaction requires a minimum of about 160°C [4], and the fact that this corresponds closely to the transition temperature of the phase change β-tin to γ-tin at 161°C [9] suggests that it is the γ-modification which undergoes reaction. Results in the present study showed that if the initial temperature significantly exceeded 170°C, there was a marked reduction in the yield of tetrabutyltin obtained. Thus, the optimum temperature range for this process is 160—170°C.

(ii) The reaction of tin with butyl chloride

In the absence of zinc, tin was found to react slowly with butyl chloride to yield a liquid organotin mixture having a hydrolysable chloride content of 12.00%. This corresponds to a mixture of tributyltin chloride and dibutyltin dichloride of 91.25% $\mathrm{Bu_3SnCl}$ and 8.75% $\mathrm{Bu_2SnCl_2}$, the yield of organotins being 26% based on tin taken.

(iii) The reaction of zinc with butyl chloride

When there was no tin in the reaction mixture, zinc, too, was found to react with butyl chloride at 160—170°C, to give a mixture which yielded no dibutylzinc under reduced pressure, even at 180°C (b.p. $\mathrm{Bu_2Zn}$ 80—85°C/9 mmHg [10]; no $\mathrm{Bu_2Zn}$ distilled at 180°C/11 mmHg). Destroying the organozinc species with ethanol and filtering off the unreacted zinc dust showed that there had been a 98.8% conversion of zinc to organozinc compounds.

For ethylzinc halides, the Schlenk equilibrium (eq. 2) has been found to

$$2\ \mathrm{EtZnX} \rightleftharpoons \mathrm{Et_2Zn} + \mathrm{ZnX_2} \qquad (2)$$

exist in ethereal solution [11]. In diethyl ether, the equilibrium lies well to the left, i.e. EtZnX is favoured. By contrast, in the standard preparation of dialkylzincs, including dibutylzinc, a zinc/copper couple is refluxed with a mixture of alkyl iodide and alkyl bromide, suggesting that the equilibrium for the butylzinc systems (3) must lie some way towards the right-hand side, since there is

$$2\ \mathrm{BuZnX} \rightleftharpoons \mathrm{Bu_2Zn} + \mathrm{ZnX_2} \qquad (\mathrm{X} = \mathrm{Br, I}) \qquad (3)$$

some dibutylzinc initially present to be distilled out. However, under the conditions prevailing in the direct synthesis reaction, no dibutylzinc could be removed by distillation. This may indicate that the equilibrium lies firmly to the left, and that the reaction proceeds as in equation 4.

$$\mathrm{BuCl + Zn \xrightarrow[160-170^\circ C]{Bu_4NI} BuZnCl} \qquad (4)$$

(iv) The reaction of tin with butylzinc chloride

Adding powdered tin over a period of 0.5 h to a previously prepared mixture of butylzinc chloride and tetrabutylammonium iodide at 160—170° C gave tetrabutyltin in 21% yield based on tin taken. The overall reaction was as shown in eq. 5. This reaction has previously been reported by Hargreaves [12], and is

$$\mathrm{4\ BuZnCl + Sn \xrightarrow[160-170^\circ C]{Bu_4NI} Bu_4Sn + 2\ ZnCl_2 + 2\ Zn} \qquad (5)$$

similar to that reported many years ago between ethylzinc iodide and tin, which gave tetraethyltin in good yield [13].

(v) The reaction between butyltin chlorides and butylzinc chloride

Adding butyl chloride dropwise to a mixture of dibutyltin dichloride, zinc and tetrabutylammonium iodide at 160—170° C gave a low conversion (16%) of dibutyltin dichloride to tetrabutyltin. On the other hand, the use of identical quantities of each reagent, but dropwise addition of a solution of the dibutyltin dichloride in the butyl chloride gave 76% conversion to tetrabutyltin. Similarly, adding tributyltin chloride in butyl chloride to zinc and tetrabutylammonium iodide at 160—170° C gave a 71% conversion to tetrabutyltin. These reactions are summarised in equations 6—8.

$$\mathrm{BuCl + Bu_2SnCl_2/Zn \xrightarrow[160-170^\circ C]{Bu_4NI} \underset{(16\%)}{Bu_4Sn}} \qquad (6)$$

$$\mathrm{BuCl/Bu_2SnCl_2 + Zn \xrightarrow[160-170^\circ C]{Bu_4NI} \underset{(76\%)}{Bu_4Sn}} \qquad (7)$$

$$\mathrm{BuCl/Bu_3SnCl + Zn \xrightarrow[160-170^\circ C]{Bu_4NI} \underset{(71\%)}{Bu_4Sn}} \qquad (8)$$

Thus, to achieve a good conversion of dibutyltin dichloride to tetrabutyltin, low steady-state concentrations of Bu_2SnCl_2 are required. Having dibutyltin dichloride present in bulk at the start of the reaction inhibited this conversion.

In reactions 7 and 8, zinc was present both as free metal and as butylzinc chloride, and in order to discover whether the latter compound alone was capable of converting dibutyltin dichloride to tetrabutyltin, a sample was prepared as described in section (iii). This mixture contained only a trace of free zinc, and to it was added dropwise a solution of dibutyltin dichloride in light petroleum. The light petroleum instantly distilled out of the reaction mixture at 160—170° C, and at the end of the reaction, tetrabutyltin was extracted in 71% yield (eq. 9). Significantly, reaction 9 was found to be inhibited by the

$$Bu_2SnCl_2 + 2\ BuZnCl \xrightarrow[160-170^\circ C]{Bu_4NI} \underset{71\%}{Bu_4Sn + ZnCl_2 + Zn} \quad (9)$$

presence of nitrobenzene, a known free-radical scavenger, strongly suggesting that this process has a free-radical mechanism.

(vi) The insertion of zinc into tin—chlorine bonds

The possibility of insertion of zinc into a tin—chlorine bond of dibutyltin dichloride to form a tin—zinc intermediate was suggested previously [14], and subsequently similar tin—zinc compounds were isolated [15]. It was thus of interest to discover whether such intermediates could be formed during the reaction under investigation.

It was found that on adding dibutyltin chloride in light petroleum to a mixture of zinc and tetrabutylammonium iodide at 160—170° C, the petroleum again instantly distilled off to leave a butyltin mixture containing 1.12% hydrolysable chloride (i.e. Bu_4Sn: 89.8%, Bu_3SnCl: 10.2%). The total yield of butyltins was 40% (by tin content). Similarly, dropwise addition of tributyltin chloride to a similar mixture of zinc and tetrabutylammonium iodide gave tetrabutyltin in 50% yield. The stoichiometrically unbalanced equations appear below (eq. 10, 11). It was thus found that both dibutyltin dichloride

$$Bu_2SnCl_2 + Zn \xrightarrow[160-170^\circ C]{Bu_4NI} \underset{(36\%)}{Bu_4Sn} + \underset{(4\%)}{Bu_3SnCl} \quad (10)$$

$$Bu_3SnCl + Zn \xrightarrow[160-170^\circ C]{Bu_4NI} \underset{(50\%)}{Bu_4Sn} \quad (11)$$

and tributyltin chloride react with zinc to yield tetrabutyltin, and this reaction probably proceeds in the way previously suggested for similar organotins [14, 15], that is, via unstable tin—zinc compounds.

Finally, it was discovered that heating a large quantity of dibutyltin dichloride, zinc and tetrabutylammonium iodide together at 160—170° C for 3 h gave no tetrabutyltin. This was in contrast to reaction 10, and showed that this reaction, too, needed low steady-state concentrations of dibutyltin dichloride.

(viii) The reaction of organohalogenostannate(IV) complexes

Dibutyltin dichloride is able to react with tetrabutylammonium iodide to yield an organohalogenostannate(IV) complex [16] (eq. 12). By contrast, tri-

$$Bu_2SnCl_2 + Bu_4NI \rightarrow Bu_4N^+[Bu_2SnCl_2I]^- \quad (12)$$

butyltin chloride does not appear to react in this way, attempts to prepare $Bu_4N^+[Bu_3SnClI]^-$ having so far proved unsuccessful [16,17].

In view of the known reaction of dibutyltin dichloride (eq. 12), it was decided to attempt to react this complex with zinc to discover whether the complex may be formed in the usual direct synthesis process. Accordingly, the complex was added dropwise in butyl chloride to powdered zinc at 160—170°C, but this gave tetrabutyltin in only 14% yield (eq. 13). This contrasts with the

$$Bu_4N^+[Bu_2SnCl_2I]^-/BuCl + Zn \xrightarrow{160\text{—}170^\circ C} \underset{(14\%)}{Bu_4Sn} \qquad (13)$$

yield from reaction 7, and implies not only that such a complex is not involved in the direct synthesis, but also that it inhibits the formation of tetrabutyltin. The similarity in yield between reaction 6 and reaction 13 suggests that the former reaction also had the organohalogenostannate(IV) complex present, formed as a result of the high concentration of dibutyltin dichloride in tetrabutylammonium iodide.

(ix) Effect of coordination number of tin on reaction of butyltin chlorides

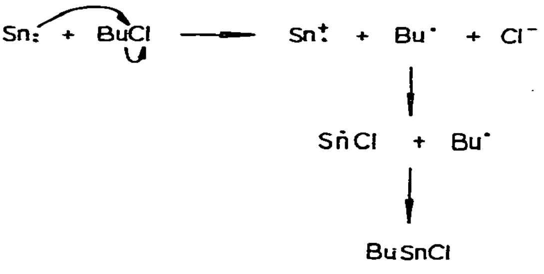
It seems from the preceding section that increasing the coordination number at tin interferes with subsequent reaction of the dibutyltin dichloride. To confirm this, a known neutral complex, $Bu_2SnCl_2 \cdot$ 2pyridine was prepared in butyl chloride [18], and added dropwise to a zinc/tetrabutylammonium iodide mixture. This reaction (eq. 14) gave no tetrabutyltin.

$$Bu_2SnCl_2 \cdot 2\text{pyridine} + Zn \xrightarrow[160\text{—}170^\circ C]{Bu_4NI} \text{no reaction} \qquad (14)$$

(x) The influence of zinc chloride

As the synthesis of tetrabutyltin proceeds, zinc chloride is formed as a by-product (3 mol/mol Bu_4NI), and at the same time there is a notable increase in the viscosity of the reaction mixture. Having zinc chloride present at the start of the reaction (3 mol $ZnCl_2$/mol Bu_4NI) also caused the mixture to have a very high viscosity. Moreover, the mixture gave no tetrabutyltin on treatment with butyl chloride, the reaction of the butyl chloride being extremely slow. By contrast, replacing the zinc chloride by an equivalent amount of sodium chloride gave a mixture of much lower viscosity. Treatment with butyl chloride gave tetrabutyltin in 30% yield, only fractionally lower than the yield usually obtained in the absence of sodium chloride. Thus, the effect of zinc chloride was probably not due specifically to its ionic nature, but rather, to its rôle in increasing the viscosity of the reaction mixture. This increase in viscosity reduces the mobility of the reacting species in the solution, and thus interferes with the production of tetrabutyltin.

SCHEME 1



(xi) The proposed mechanism of the reaction

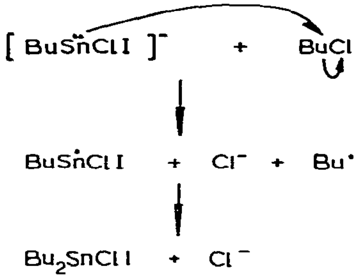
The initial reaction of tin may be assumed to proceed via the radical-ionic mechanism suggested by Murphy and Poller [19]. The initial stage of this process is illustrated in Scheme 1.

The stannylene thus formed appears to require coordination by iodide ions for stabilization [19]:

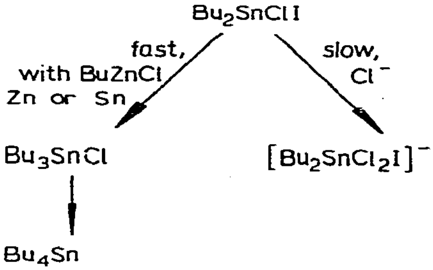
$BuSnCl + I^- \rightarrow \{BuSnClI\}^-$

Subsequent reaction of this species is shown in Scheme 2. This step is similar to the one proposed by Murphy and Poller [19], but takes account of the stabilizing effect of the iodide ion. Since we have shown that the organohalostannate complex reacts less readily than uncomplexed dibutyltin dichloride, we assume that the species Bu_2SnClI does not undergo complexation with the available chloride, but reacts more readily in other ways (Scheme 3).

SCHEME 2



SCHEME 3

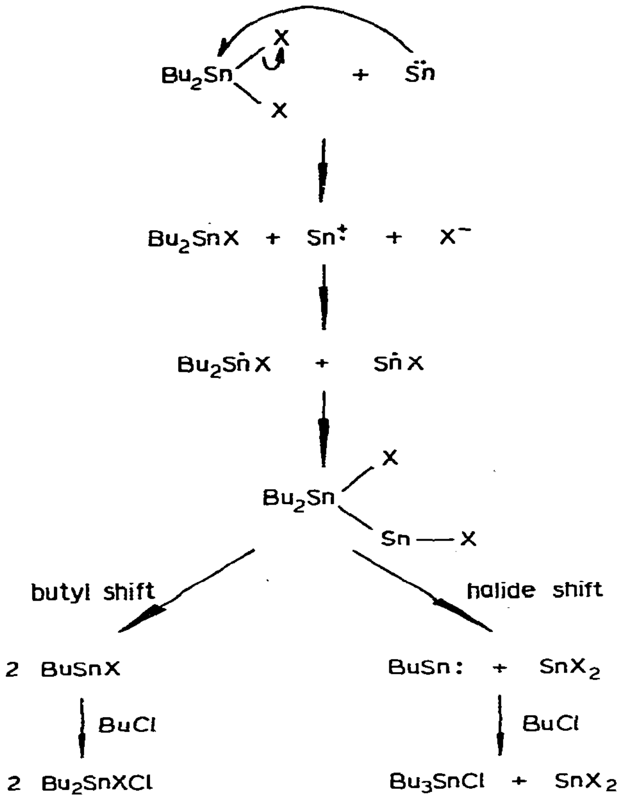


The reaction with no zinc present (section (ii)) generated mainly Bu_3SnCl, implying that Bu_2SnClI is able to react with free tin. The next stage of the reaction (Scheme 4) is probably also a radical-ionic one.

This cycle may be seen either to generate further dibutyltin dihalide or to yield tributyltin chloride.

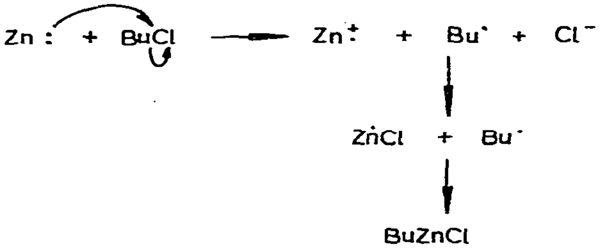
The zinc insertion reactions (equations 10 and 11) probably proceed in an exactly analogous way. The products of the butyl shift, though, would be the butylhalostannylene and butylzinc halide. Butylzinc chloride was shown to react with dibutyltin dichloride to yield tetrabutyltin (eq. 9), and this explains why the zinc insertion reaction, though leading initially to the formation of butylzinc halide, ultimately yields mainly tetrabutyltin.

SCHEME 4



Under the conditions prevailing in the direct synthesis of tetrabutyltin, butyl chloride has been shown to undergo reaction with zinc to give butylzinc chloride. This is assumed to proceed by a radical-ionic process on the basis of analogy with the reaction of tin [19], and the formation of Grignard reagents [20] (Scheme 5).

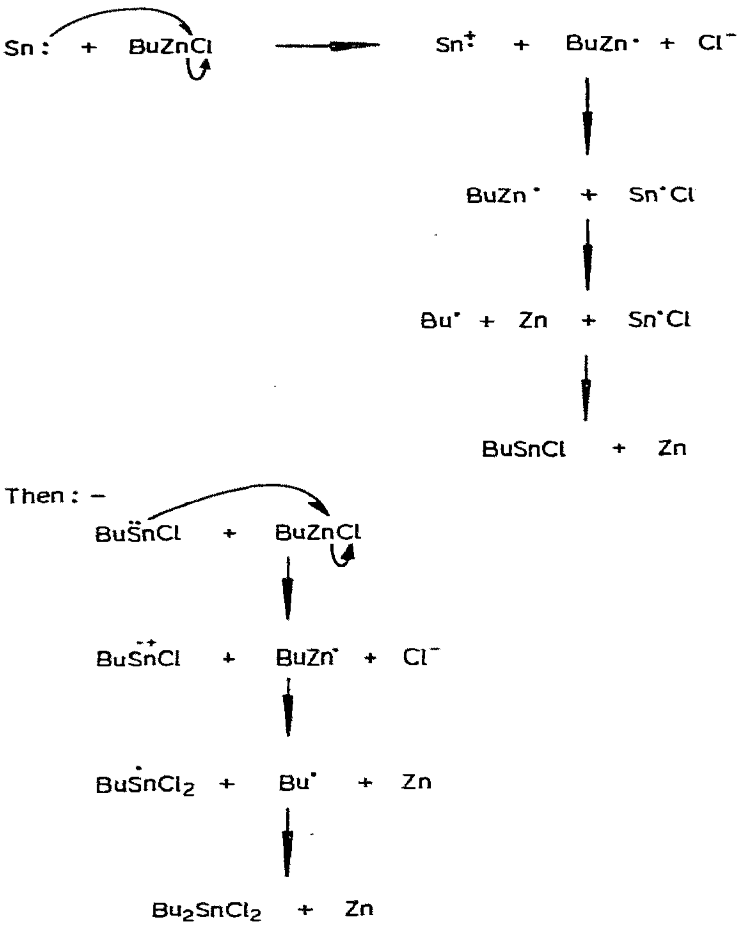
SCHEME 5



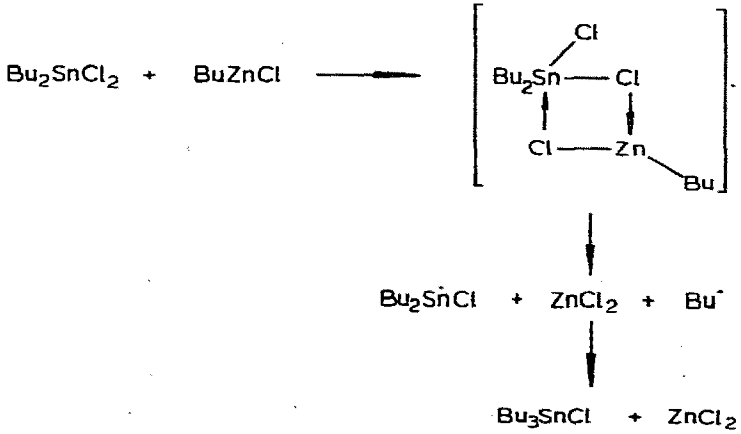
Tin was shown to react with butylzinc chloride (eq. 4), and a possible mechanism for this is shown in Scheme 6.

The reaction between butylzinc chloride and dibutyltin dichloride (eq. 7) was shown to be inhibited by coordination numbers at tin greater than 4. Thus, it seems that the transition state involves coordination at the tin atom, and a

SCHEME 6



SCHEME 7

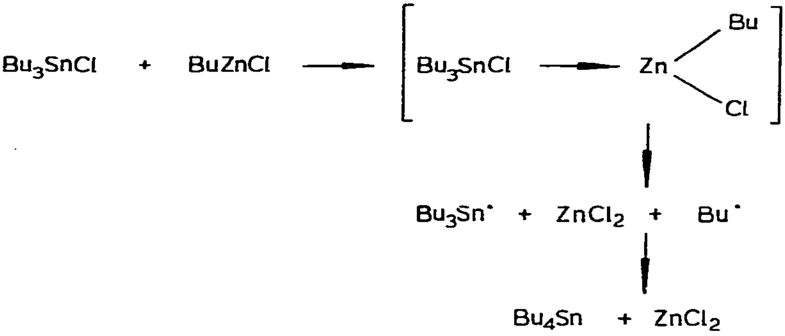


possible explanation for this is given by the transition state in Scheme 7. The bridging chlorine from tin to zinc seems a highly probable feature of this structure, in view of the fact that a chlorine atom is transferred from tin to zinc as the reaction proceeds. It is also likely in view of the known donor properties of the chlorine atom and the acceptor properties of organozinc compounds [11].

The subsequent step, the simultaneous fracture of the tin—chlorine bonds, and the zinc—butyl bond to generate free radicals, is proposed because the reaction between dibutyltin dichloride and butylzinc chloride is inhibited by nitrobenzene, a free-radical scavenger.

Finally, tributyltin chloride is able to react with butylzinc chloride (Scheme 8). In this case, in view of the reduced acceptor strength of the tin atom in tributyltin chloride compared with dibutyltin dichloride [7], it is probable that the transition state is not a four-centre one, but a simple bridged structure as illustrated in Scheme 8.

SCHEME 8



Experimental

(i) Synthesis of Bu_4Sn

To a 500 cm^3 round bottomed reaction flask fitted with a reflux condensor and a glass stirrer paddle was added tetrabutylammonium iodide (24.7 g, 0.067 mol), zinc dust (26.1 g, 0.400 mol) and tin powder (23.7 g, 0.200 mol). The air inside the flask was removed by passing in dry nitrogen, and the flask was heated with continual stirring. The temperature inside the flask was monitored frequently until it lay in the region 160—170°C when addition of butyl chloride (37.0 g, 0.400 mol) was begun. This was carried out dropwise until all the butyl chloride had been added, a process which generally took 2 h. The mixture was then heated for a further 3 h, after which it was cooled slightly and the isolation procedure begun.

Isolation of tetrabutyltin was carried out using light petroleum (b.p. 40—60°C). 100 ml was added slowly to the reaction mixture, gradually bringing its temperature down to the reflux temperature of light petroleum, where it was maintained for 45 min. The mixture was then allowed to cool, and the light petroleum solution removed from the grey residue by decantation. The residue was washed with further small portions of petroleum, and the washings combined with the main extract. The petroleum was removed by distillation, and left tetrabutyltin, typically 23 g, of purity better than 99% as estimated either by titration or by gas-liquid chromatography (i.e. 33% yield of Bu_4Sn based on tin taken, ca. 99% based on tin consumed).

(ii) Synthesis of BuZnCl

This was carried out by adding butyl chloride dropwise to a mixture comprising tetrabutylammonium (24.7 g, 0.067 mol) and zinc dust (26.1 g, 0.0400 mol) at 160—170° C. The addition typically took 3.5 h.

(iii) Synthesis of tetrabutyltin from butyltin chlorides

Three methods were used to convert butyltin chlorides to tetrabutyltin. In the first of these, a mixture of the particular butyltin chloride (0.067 mol for Bu_2SnCl_2; 0.042 mol for Bu_3SnCl) in butyl chloride (37.0 g, 0.400 mol) was added dropwise to a slurry of zinc dust (26.1 g, 0.400 mol) in tetrabutylammonium iodide (24.7 g, 0.067 mol) at 160—170° C. After addition was complete, the mixture was heated for 3 h, then extracted with light petroleum as described above for the standard synthesis of tetrabutyltin. With dibutyltin dichloride, this procedure gave tetrabutyltin in 76% yield and with tributyltin chloride it gave tetrabutyltin in 71% yield. In each case, the product was of very high purity (99% or better) as estimated by titration.

In the second method, butylzinc chloride was prepared as described in the preceding section and then dibutyltin dichloride (20.3 g, 0.067 mol) dissolved in light petroleum (25 cm^3) was added dropwise, the flask being fitted for distillation, and the petroleum thus being able to distil out from the reaction mixture. When the addition was complete, the mixture was heated for 3 h, then extracted with light petroleum. This method gave tetrabutyltin (16.5 g, 71% yield) of high purity.

Finally, the third method used was the zinc insertion reaction. In this the appropriate butyltin chloride (0.067 mol) was added slowly to a mixture of zinc (26.1 g, 0.400 mol) and tetrabutylammonium iodide (24.7 g, 0.067 mol) at 160—170° C. In the case of dibutyltin dichloride it was necessary to have the organotin compound dissolved in light petroleum (25 cm^3), and to evaporate the solvent from the hot reaction mixture as before. Once the addition was complete, the mixture was heated for 3 h, then extracted with light petroleum. In each case the product comprised tetrabutyltin substantially contaminated with tributyltin chloride, and, in the case of the reaction of Bu_3SnCl, an amount of unidentified material which was thought to be hexabutylditin.

(iv) Analysis of products

The products were analysed mainly by the titration method described below, and also by gas-liquid chromatography. The titration method relies on the fact that under alkaline conditions organotin chlorides, such as tributyltin dichloride, undergo hydrolysis:

$$Bu_3SnCl + OH^- \rightarrow Bu_3SnOH + Cl^-$$

then

$$2\ Bu_3SnOH \rightarrow (Bu_3Sn)_2O + H_2O$$

Approximately 2.0 g samples of petroleum-free organotin liquid were accurately weighed into 250 cm^3 conical flasks, diluted with acetone (50 cm^3), and treated with sodium hydroxide (10.0 cm^3 of 0.1 molar NaOH). As the sodium hydroxide was added the mixture became cloudy and eventually formed two-phases. Using phenolphthalein as indicator, the amount of sodium hydroxide remaining was determined by back-titration with hydrochloric acid (0.1 molar). This method assumes that all the hydrolysable chloride was present as tributyltin chloride, with no dibutyltin dichloride present, an assumption which was shown to be justified using GLC.

GLC was carried out using a Pye 104 Chromatograph fitted with a thermal conductivity detector. The column was a 2 ft × $\frac{1}{8}$ in. I.D. glass one packed with 20% neopentylglycol succinate on Diatomite CQ (90/100). Carrier gas was helium at 40 p.s.i. and 100 cm^3/min. Samples of size 1 μl were chromatographed using a temperature gradient of 170 to 200°C/at 12°C/min. Under these conditions, the following retention times were found: Bu_4Sn 1.2 min, Bu_3SnCl 3.2 min, Bu_2SnCl_2, 3.9 min, $BuSnCl_3$ 2.8 min. A test mixture of all four species gave well resolved peaks.

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