

## THE USE OF ORGANOSODIUM INTERMEDIATES IN THE SYNTHESIS OF ALKYL TIN CHLORIDES

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### Summary

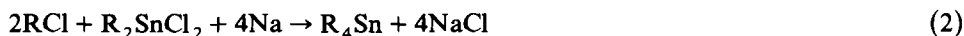
The synthesis of various  $R_xSnCl_{4-x}$  compounds (R = butyl, octyl, dodecyl) from reaction between tin(IV) chloride, or a dialkyltin dichloride, and alkylsodium compounds RNa was investigated. Optimum conditions were established and some competing side-reactions identified.

### Introduction

The primary intermediates required for the manufacture of organotin compounds used as thermal stabilizers for PVC or as biocides are the alkyltin chlorides  $R_xSnCl_{4-x}$  where R is commonly butyl and  $x = 2$  or 1 (stabilizers [1]) or 3 (biocides [2]). On the commercial scale tin(IV) chloride is alkylated with Grignard reagents or organoaluminium compounds, but neither method is entirely satisfactory [1]. Usually the tetraalkyltin compound is formed in a first stage and this is converted to the required alkyltin chloride by subsequent treatment with further tin(IV) chloride. An alternative approach, avoiding the use of an organometallic reagent, is to use the Wurtz reaction [3–12] (eq. 1).



The conversion of tin(IV) chloride is poor due to competing reduction by the sodium to tin(II) chloride and to tin metal. Better yields of the tetraalkyltin compound result if the tin(IV) chloride is replaced by dialkyltin dichloride which is not susceptible to reduction by sodium (eq. 2).



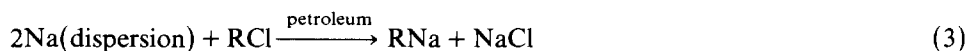
Some patents indicate that tin(IV) chloride can be converted to tetrabutyltin in high yields in Wurtz reactions by careful control of the size of the sodium particles [8–10] and the use of tetrabutyltin as solvent.

Another approach to minimize problems due to reduction by sodium has been the formation of an organosodium compound in a preliminary step followed by the

addition of tin(IV) chloride. This method has only been reported briefly in the patent literature [12,13] for the preparation of aryltin compounds and the present paper describes its evaluation as a route to alkyltin compounds.

## Results and discussion

For the preparation of alkylsodium compounds in high yield it is essential to be able to prepare uniform sodium dispersions [14–17] (see Experimental). The dispersions were stabilized by addition of a trace (~0.1% of the mass of sodium) of tin(IV) chloride dissolved in petroleum. The chloroalkane then reacts to give alkylsodium (eq. 3).



This was followed by reaction with tin(IV) chloride (eq. 4).

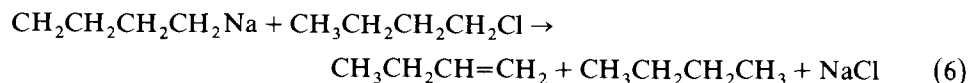


The composition of the organotin product was determined by methylation followed by gas chromatography of the methylated material [18]. To optimize the yield of tetraalkyltin, attention was given to the following factors: (i) the relative proportions of reactants, (ii) the temperatures at which reactions 3 and 4 were conducted, (iii) the relative amounts of petroleum and (iv) the rates of addition of the reactants at each stage. Typical results for tetrabutyltin are summarized in Table 1.

One problem is that of estimating the amount of alkylsodium present in the suspension from reaction 3. Although the double titration technique of Gilman [19] can be used, it is extremely difficult to withdraw an aliquot which is truly representative of the heterogeneous reaction mixture. We therefore assumed [16] that the alkylsodium was formed in 80% yield and then examined the effect of varying the proportion of tin(IV) chloride, bearing in mind that this is the most expensive reagent and excess organosodium would probably be required to obtain high conversions. From Table 1 it can be seen that when 67% of the stoichiometric quantity of tin(IV) chloride was used, a maximum yield of 91% of tetrabutyltin was obtained (Expt. I). Increasing this proportion to 90% of the stoichiometric amount lowered the yields to 85% (Expt. IV).

Since the conversion of tin(IV) chloride was below 100% in the presence of excess butylsodium it appeared that a side reaction was occurring. To test the possibility that tin(IV) chloride was being lost by reduction with excess sodium, it was replaced in some experiments by dibutyltin dichloride (e.g. Expt. VII). In this case the yield fell to 86% indicating that reduction by metallic sodium was not causing losses of tin(IV) chloride.

A more certain side reaction which can lead to lowered yields is decomposition of butylsodium by  $\beta$ -hydrogen elimination to give but-1-ene and either sodium hydride (eq. 5) or butane and sodium chloride (eq. 6).



The sodium hydride is unlikely to have effected reduction of tin(IV) chloride but higher temperatures and prolonged reaction times may cause major losses of butylsodium by reactions 5 or 6. Butene formation was minimized by operating at 0–5°C (compare experiments IV at 0–5°C, 85% yield and V 35–45°C, 73% yield). Evidence for the presence of butene was obtained by carrying out one of the experiments (Conditions III) in a stream of argon which was led into a solution of bromine in chloroform. At the end of the experiment this solution was found to contain 1,2-dibromobutane.

Another unwanted side reaction is coupling of butylsodium and chlorobutane to give octane (eq. 7). This reaction might be expected to be minimized by low concentrations and slow rates of addition. Concentration effects were as expected but small. Thus the relative overall concentrations in experiments I, II and VI are in the approximate ratio 1/2/3 whereas the yields are respectively 91, 86 and 83%.



With regard to rates of addition, in reaction 3 a slow rate of addition of chlorobutane to the sodium dispersion is desirable to avoid local temperature surges as well as to minimize coupling (reaction 7). The reaction between tin(IV) chloride and butylsodium is also exothermic so that effective temperature control in reaction 4 is also aided by a slow rate of addition. In Experiment III the time for both additions is halved compared with the optimum conditions (Expt. I) and the yield only fell by 6%.

Some experiments in which sodium was replaced by potassium were carried out (e.g. No. VIII). Although butylpotassium was formed it reacted preferentially by coupling and metallation reactions to give exclusively hydrocarbon products and no butyltin compounds were obtained.

The use of alkylsodium compounds for the preparation of octyl- and dodecyltin derivatives was examined. In these cases, however, the results obtained were inferior to those given by the normal Wurtz reaction. A major problem is the tendency of octylsodium to form gels even at much lower concentrations than those employed for butylsodium. The marked increase in viscosity prevents efficient mixing and large amounts of hexadecane were obtained with no more than 50% yield of octyltin compounds being obtained. Since the intermediates most in demand in industry are the dialkyltin dichlorides, attempts were made to prepare dioctyltin dichloride directly by inverse addition i.e. addition of the suspension of octylsodium to the tin(IV) chloride. Although substantial amounts of the dichloride were formed, the major product was trioctyltin chloride with an overall yield of 55% octyltin compounds.

The method failed completely in the attempted preparation of dodecyltin compounds. Intractable gels were formed even at very low concentrations and only the coupling product, tetraeicosane appeared to be formed.

To summarize, the alkylsodium procedure is an effective process for the preparation of tetrabutyltin in high yield. The method could probably be extended to alkyl groups with less than 4 C atoms. Due to gel formation octyltin compounds were obtained in only moderate yields and dodecyltin compounds not at all.

## Experimental

Petroleum b.p. 100–120°C, used as solvent and dispersion medium in the preparations was dried by distillation from calcium hydride and stored over molecular sieves. All preparations were conducted in an atmosphere of argon and carried out at least twice to ensure reproducibility.

*Preparation of tetrabutyltin (optimum conditions).* A mixture of sodium (30.0 g, 1.30 mol) and petroleum (550 cm<sup>3</sup>) was maintained at 115°C for 30 min. Dispersion was effected by stirring at approx. 20000 r.p.m. using a Jancke and Kunkel 18 N Ultra-Turrax high speed stirrer, while the temperature was allowed to fall slowly to room temperature. The dispersion was stabilized by addition of one drop of tin(IV) chloride in 10 drops of petroleum when the temperature reached ~ 105°C. The high speed stirrer was replaced by a conventional stirrer and the temperature lowered to 0–5°C. A solution of 1-chlorobutane (60.3 g, 0.65 mol) in petroleum (130 cm<sup>3</sup>) was added dropwise over 3 h while the temperature was maintained at 0–5°C. Stirring was continued at the same temperature for a further 75 min after the addition was complete. Tin(IV) chloride (28.3 g, 0.109 mol) in petroleum (90 cm<sup>3</sup>) was then added dropwise over 2 h with the temperature maintained at 0–5°C. When addition was complete the mixture was stirred for a further 2 h and the temperature allowed to rise to 20–25°C. The mixture was filtered under argon and the filter cake treated with excess t-butanol to remove sodium and butylsodium. Removal of the solvent from the petroleum filtrate by distillation at 60°C/20 mmHg gave tetrabutyltin (34.2 g, 91% based on tin(IV) chloride). This material was shown to be pure by methylation followed by gas chromatography (see below).

Many experiments of a similar nature were carried out with systematic variations in experimental conditions, as noted in Table 1.

TABLE 1  
EFFECT OF EXPERIMENTAL CONDITIONS ON YIELDS IN THE PREPARATION OF TETRABUTYL TIN FROM BUTYLSODIUM AND TIN(IV) CHLORIDE

Experiment number	Sodium dispersion		Preparation of BuNa			
	Weight of Na (g)	Volume petrol (cm <sup>3</sup> )	Weight of BuCl (g)	Volume of petrol (cm <sup>3</sup> )	Temperature of BuCl addition (°C)	Time of BuCl addition (min)
I	30.0	550	60.3	130	0–5	180
II	60.0	550	120.6	60	0–5	180
III	30.0	550	60.3	130	0–5	90
IV	30.0	550	60.3	130	0–5	180
V	22.0	550	40.2	100	35–45	180
VI	60.0	250 <sup>c</sup>	120.6	177	0–5	180
VII	30.0	550	60.3	130	0–5	165
VIII	30.0 <sup>e</sup>	550	35.6	60	0–5	180

<sup>a</sup> Percentage yields based on theoretical yields of tetrabutyltin. <sup>b</sup> Hydrocarbon impurities also present.

<sup>c</sup> Dispersion made using 550 cm<sup>3</sup> petroleum; 300 cm<sup>3</sup> removed by distillation before adding BuCl.

*Detection of butene.* In one of the preparations of tetrabutyltin (conditions as in III, see Table 1) a stream of argon was passed over the reaction mixture and the effluent gases led into a solution of bromine in chloroform. Examination of chloroform solution (after removal of bromine) by gas chromatography showed that 1,2-dibromobutane was present in amounts which indicated that  $\leq 3\%$  of the chlorobutane had been converted to but-1-ene.

*Preparation of tetraoctyltin.* Sodium (12.0 g, 0.52 mol) was dispersed in petroleum (550 cm<sup>3</sup>) in the same manner described in the preparation of tetrabutyltin. 1-Chlorooctane (32.3 g, 0.22 mol) in petroleum (110 cm<sup>3</sup>) was then added over 3 h with the reaction mixture maintained at 30–40°C. The resulting mixture tended to gel so further petroleum (150 cm<sup>3</sup>) was added and the suspension stirred for a further 1 h. Tin(IV) chloride (14.2 g, 0.055 mol) in petroleum (95 cm<sup>3</sup>) was added over 75 min at 30–40°C. The same temperature was maintained while the mixture was stirred for another hour. Filtration and evaporation of the filtrate as before gave 21.0 g of crude tetraoctyltin. Methylation and gas chromatography showed that this material had the following composition (C<sub>8</sub>H<sub>17</sub>)<sub>4</sub>Sn 54.3; (C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>SnCl 15.2; (C<sub>8</sub>H<sub>17</sub>)<sub>2</sub>SnCl<sub>2</sub> 3.7%. This is equivalent to a yield of 50% octyltin compounds (calculated at (C<sub>8</sub>H<sub>17</sub>)<sub>4</sub>Sn).

*Attempted preparation of dioctyltin dichloride.* Sodium (12.0 g, 0.52 mol) was dispersed in petroleum (550 cm<sup>3</sup>) in the usual manner. 1-Chlorooctane (32.3 g, 0.22 mol) in petroleum (70 cm<sup>3</sup>) was then added over 3 h at ~40°C. The resulting suspension of octylsodium was kept agitated at 20–25°C while being transferred in 10 cm<sup>3</sup> portions to a stirred solution of tin(IV) chloride (28.4 g 0.11 mol) in petroleum (150 cm<sup>3</sup>) under argon over 2 h at 20–40°C. Filtration and evaporation gave 30.4 g of crude product, shown by methylation/gas chromatography to consist of (C<sub>8</sub>H<sub>17</sub>)<sub>4</sub>Sn 14, (C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>SnCl 46 and (C<sub>8</sub>H<sub>17</sub>)<sub>2</sub>SnCl<sub>2</sub> 22%. This is equivalent to a yield of 55% octyltin compounds (calculated as (C<sub>8</sub>H<sub>17</sub>)<sub>2</sub>SnCl<sub>2</sub>).

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Reaction of BuNa with SnCl<sub>4</sub>

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Weight of SnCl <sub>4</sub> (g)	Volume of petrol. ether (cm <sup>3</sup> )	Temperature of SnCl <sub>4</sub> addition (°C)	Time of SnCl <sub>4</sub> addition (min)	Composition of product (%)				Yield of Bu <sub>4</sub> Sn g crude/% pure <sup>a</sup>
				Bu <sub>4</sub> Sn	Bu <sub>3</sub> SnCl	Bu <sub>2</sub> SnCl <sub>2</sub>	BuSnCl <sub>3</sub>	
28.3	90	0–5	120	100	–	–	–	34.2/91
56.6	75	0–5	120	100	–	–	–	65.0/86
28.3	90	0–5	60	100	–	–	–	32.0/85
38.2	83	0–5	105	78.3 <sup>b</sup>	1.2	0.3	0.1	54.5/85
28.3	90	35–45	90	65.7 <sup>b</sup>	10.8	3.5	–	34.2/73
68.0	38	0–5	120	97.5 <sup>b</sup>	–	–	–	77.0/83
99.1 <sup>d</sup>	100	0–5	165	78.2 <sup>b</sup>	0.1	6.4	–	114.9/86
25.0	90	0–5	120	–	–	–	–	trace <sup>f</sup>

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<sup>d</sup> Bu<sub>2</sub>SnCl<sub>2</sub> used instead of SnCl<sub>4</sub>. <sup>e</sup> Potassium used instead of sodium. <sup>f</sup> Main product was a mixture of hydrocarbons.

*Analysis of organotin products.* The crude organotin product (2–3 g) in diethyl ether (20 cm<sup>3</sup>) was added dropwise to the Grignard reagent made from magnesium (1.0 g) and methyl iodide (6.2 g) in diethyl ether (35 cm<sup>3</sup>). The mixture was heated at reflux temperature for 35 min, cooled to 0°C and treated cautiously with saturated aqueous ammonium chloride solution (20 cm<sup>3</sup>). Separation of the organic layer, washing and drying over molecular sieves followed by evaporation gave the methylated product.

Solutions of the methylated material in chloroform (5%) were added to a gas chromatography column (1.5 m, 4 mm i.d. glass column packed with a polar silicone [3% OV-17] on fine mesh diatomite). The carrier gas was dry nitrogen at 60 cm<sup>3</sup> min<sup>-1</sup>; injector and detector temperature = 250°C. Oven temperature programmes: butyl compounds 100°C (15 min) raised at 24° min<sup>-1</sup> to 148°C (40 min); octyl compounds 170°C (15 min) raised at 24° min<sup>-1</sup> to 218°C (80 min). The long periods at elevated temperatures were necessary to eliminate traces of ditins. Hydrocarbon contaminants were determined on the same column at 50°C with a nitrogen flow rate of 30 cm<sup>3</sup> min<sup>-1</sup>.

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