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# ELECTROCHEMICAL PREPARATION OF SOME ORGANOTIN COMPOUNDS

J.J. Habeeb and D.G. Tuck

Department of Chemistry, University of Windsor
Windsor, Ontario N9B 3P4, Canada

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## Summary

Organotin dihalides $R_2SnX_2$ (X = Cl, Br, I) and their adducts with bidentate donor ligands have been prepared in high yield by the direct electrochemical reaction of metallic tin with alkyl or aryl halides in organic media at room temperature. Dimethyltin diiodide can be converted to tetramethyltin by reaction with methyl iodide at a cadmium anode. Electrochemical halide abstraction has been used to prepare $R_6Sn_2$ (R = Me, Ph) from the corresponding $R_3Sn$ halide. The mechanism of these reactions is discussed.

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## Introduction

Organotin compounds, and the related organotin halides, are amongst the best known areas of organometallic chemistry [1,2,3]. Two main procedures have been used in the synthesis of organotin halides. The first, and most obvious, is the direct (catalysed) reaction of metallic tin with alkyl or aryl halide, a reaction known since 1849 [4]. Typical conditions involve temperatures in the range 100 - 180°, for 1 - 50 h; a number of different catalysts have been used. Redistribution reactions

$$R_4Sn + SnX_4 \longrightarrow 2R_2SnX_2 \qquad (1)$$

have provided the other main synthetic route to these compounds, and here again high temperatures are necessary. Both of these methods, and others which have been proposed, give equilibrium mixtures of mono-, di- and trihalides, so that separation procedures are of considerable importance [5].

Workers in the USSR have described electrochemical procedures for the preparation of dibutyltin dibromide and similar compounds [6 - 9]. The experimental methods involved either a tin anode or a tin compound in solution, and bromine and zinc bromide were added to the mixed organic solvent reaction mixture containing the organic halide. The purity of the products was not always specified. The preparation of organotin compounds from a sacrificial electrode has also been reported by Ulery [10], Brown, Gonzalez and Wright [11] and Mengoli and Daolio [12]. There are significant differences between the procedures described by these authors and the present work, the most notable of which is that tin is anodic in our experiments but cathodic in theirs. We discuss these differences below.

As part of a programme of investigation of direct electrochemical synthesis of inorganic and organometallic compounds [13 - 15], we have examined the oxidation of anodic tin in the presence of alkyl and aryl halides, and find that this represents a simple synthetic route to these important $R_2SnX_2$ compounds. It has also been possible to form $R_4Sn$ and $R_6Sn_2$ compounds by electrochemical halide abstraction from $R_2SnX_2$ and $R_3SnX$ respectively by the use of anodic cadmium [16]. These syntheses can be carried out at room temperature, with simple equipment, and appear to offer several advantages over other synthetic routes. Reviews [17,18] of the use of electrochemical methods in inorganic and organometallic chemistry have emphasised that many interesting studies of electro-oxidation and reduction have not been pursued to the point of synthetic application. The present work suggests that direct electrochemical synthesis could usefully replace many of the methods in current use for the production of tin(IV) compounds.

## Experimental

### General

Tin (Alfa Inorganics) was in the form of a sheet (0.127mm thickness, M5N purity). Cadmium (m4N) was used as a rod (8.5 cm long, 0.25 cm diam.)

Methanol (analytical grade) was dried over Linde molecular sieve. Benzene was dried with sodium naphthaquinone and distilled. Methyl iodide and ethyl bromide were distilled before use; all other organic halides were reagent grade and were used as received, as were the neutral ligands, except that 1,10-phenanthroline was dehydrated at 110° before use.

Infrared and Raman spectra were recorded with Beckman IR-12 and Beckman 700 laser-Raman (argon ion, 488.0 nm excitation) instruments. Proton magnetic resonance spectra were obtained with a Varian EM-360 spectrometer operating at 60 MHz.

Halide analysis was by the Volhard method, and metal analysis by atomic absorption spectrophotometry.

### Electrochemical Preparation of $R_2SnX_2$ and Adducts

Tin metal (10 x 3 $cm^2$, approx. 3.5 g), supported by a platinum wire lead, formed the anode of the cell, in which a second platinum wire (∿ 1 mm diam.) was the cathode. The composition of the solution phase (total volume 30 - 70 $cm^3$) is shown in Table 1. In the early experiments, and following our previous work [13,14], small quantities of tetraethylammonium perchlorate were present, and hence methanol was added in order to dissolve this salt in the reaction solution, but in later work it was found possible to achieve significant current and reaction without the complications of adding such foreign material to the reaction vessel. In the preparation of adducts of 2,2'-bipyridyl, the low solubility of the ligand in benzene made the addition of methanol mandatory, but the use of 1,2-bis-(diphenylphosphino)ethane permitted the use of benzene alone as solvent in later work. Solid neutral ligands were used in approx. 1 g quantities; dimethylsulphoxide and acetonitrile were added in approx. 20 $cm^3$ amounts.

The applied voltage was 20 - 50 v, as dictated by the solution conditions, given that a current of 10 - 40 ma produced a reasonable rate of reaction without overheating the solution. We have used a Coutant 50/50 power supply, but other similar D.C. power equipment would no doubt suffice. The temperature was ambient (∿ 20°C), and all experiments were carried out under an atmosphere of dry nitrogen. Under such conditions, the initial precipitation of product was usually detected within 10 - 30 min. The solids were collected, washed with diethyl ether and dried under vacuum. In some cases, subsequent addition of ether to the reaction mixture caused further precipitation of product. Analytical results are given in Table 2.

Unless otherwise noted, yields (Table 1) were calculated relative to the quantity of tin dissolved from the anode; under the conditions described, this was typically 0.2 - 0.5 g, giving 1 - 1.5 g of product. In view of the good yields obtained, we have not investigated the effect of changes in voltage or other reaction conditions upon the yield, preferring at this stage to establish the usefulness and versatility of the electrochemical method.

Table 1. Reaction conditions for direct electrochemical synthesis of organotindihalides and adducts.

| Compound (a) | Vol. of alkyl halide (cm$^3$) (b) | Vol. of MeOH (cm$^3$) (b) | Voltage (v) | Initial Current Ma | Time (hrs) | Sn dissolved (g) | % Yield of Product |
|---|---|---|---|---|---|---|---|
| $(CH_3)_2SnI_2$ | 40 | 14 (c) | 30 | 40 | 2.25 | 0.20 | 81 |
| $(C_2H_5)_2SnI_2$ | 40 | 14 (c) | 30 | 25 | 2.25 | 0.18 | 76 |
| $(C_2H_5)_2SnI_2.2dmso$ | 35 | 7 (c) | 50 | 35 | 9 | (d) | (d) |
| $(C_2H_5)_2SnI_2.2CH_3CN$ | 35 | 7 (c) | 50 | 46 | 9 | 0.19 | 79 |
| $(CH_3)_2SnI_2$.diphos | 15 | - | 50 | 10 | 12 | 0.21 | 92 |
| $(C_2H_5)_2SnI_2$.diphos | 15 | - | 50 | 10 | 12 | 0.23 | 87 |
| $(C_2H_5)_2SnBr_2$.bipy | 15 | 10 (c) | 23 | 25 | 1.5 | 0.20 | 81 |
| $(C_2H_5)_2SnBr_2$.phen | 50 | 20 (c) | 30 | 40 | 2 | 0.27 | 76 |
| $(C_2H_5)_2SnBr_2$.diphos | 30 | - | 50 | 20 | 10 | 0.33 | 83 |
| $(\underline{n}-C_4H_9)_2SnCl_2$.diphos | 25 | - | 50 | 20 | 12 | 0.30 | 79 |
| $(n-C_4H_9)_2SnBr_2$.diphos | 25 | - | 50 | 20 | 12 | 0.41 | (f) |
| $c-C_4H_8SnBr_2$.diphos | 15 | - | >50 (e) | 10 | 8 | 0.47 | (f) |
| $(C_6H_5)_2SnBr_2$.diphos | 40 | 10 (c) | 50 | 30 | 10 | 0.51 | (f) |

(a) dmso = dimethylsulphoxide; diphos = 1,2-bis(diphenylphosphino)ethane; bipy = 2,2'-bipyridine; phen = 1,10-phenanthroline; $c-C_4H_8Sn$ = stannacyclopentyl group.

(b) Plus 15 cm$^3$ of benzene in each case.

(c) 10 mg of $Et_4NClO_4$ also added.

(d) Not recorded: product is unstable (see text).

(e) Voltmeter not reliable over 50 V.

(f) Yield not calculated because of mechanical loss of tin from anode during electrolysis.

Table 2. Analytical results for organotin compounds.

| Compound | Found (%) | | Calculated (%) | |
|---|---|---|---|---|
| | Sn | Halogen | Sn | Halogen |
| $(CH_3)_2SnI_2$ (a) | 29.7 | 63.5 | 29.5 | 63.0 |
| $(C_2H_5)_2SnI_2$ | 27.6 | 58.9 | 27.6 | 59.0 |
| $(C_2H_5)_2SnI_2$.2dmso | - | 45.9 | - | 46.4 |
| $(C_2H_5)_2SnI_2.2CH_3CN$ | 23.1 | 48.7 | 23.2 | 49.5 |
| $(C_2H_5)_2SnI_2$.diphos | 14.7 | 31.7 | 14.9 | 31.7 |
| $(C_2H_5)_2SnI_2$.diphos | 14.3 | 30.6 | 14.4 | 30.6 |
| $(C_2H_5)_2SnBr_2$.bipy (b) | 24.2 | 32.4 | 24.1 | 32.5 |
| $(C_2H_5)_2SnBr_2$.phen (c) | 22.9 | 30.9 | 23.0 | 31.0 |
| $(C_2H_5)_2SnBr_2$.diphos | 16.2 | 21.9 | 16.2 | 21.8 |
| $(n\text{-}C_4H_9)_2SnCl_2$.diphos | 16.9 | 10.3 | 17.0 | 10.1 |
| $(\underline{n}\text{-}C_4H_9)_2SnBr_2$.diphos | 15.1 | 20.4 | 15.0 | 20.2 |
| $c\text{-}C_4H_8SnBr_2$.diphos | 16.2 | 21.8 | 16.2 | 21.8 |
| $(C_6H_5)_2SnBr_2$.diphos | - | 19.1 | - | 18.7 |
| $Sn(CH_3)_4$ | 66.7 | - | 66.5 | - |
| $(CH_3)_6Sn_2$ | 72.9 | - | 72.5 | - |
| $(C_6H_5)_6Sn_2$ | 33.7 | - | 33.9 | - |

(a) M. pt. 44°.
(b) M. pt. 210°
(c) M. pt. 236(dec).

Preparation of Tetramethyltin

Since it has been shown earlier [16] that anodic cadmium is an efficient electrochemical halide abstraction agent, it seemed reasonable to investigate the use of this method for the preparation of $(CH_3)_4Sn$ from $(CH_3)_2SnI_2$. Three different experiments were successful.

(a) A mixture of 20 $cm^3$ of methyl iodide, 20 $cm^3$ benzene, 10 $cm^3$ of methanol and 2.5 g of tetraethylammonium iodide was placed in a cell between a platinum cathode and electrodes of tin and cadmium. Each of these two metals served as the anode of the cell for alternating periods of 20 min , starting with tin. After 3 hr electrolysis at 18 v, 60 ma, 0.80 g of tin was found to have dissolved; 1.0 g of tetramethyltin (83% yield) was collected by distillation in vacuo. In a second experiment, (3 hr , 16 v, 68 ma), the weights of tin and cadmium dissolved were 0.75 and 1.49 g respectively (mole ratio Sn:Cd = 1:2.1) in agreement with the stoichiometry

$$4CH_3I + Sn + 2Cd \longrightarrow Sn(CH_3)_4 + 2CdI_2 \qquad (1)$$

or, in terms of stepwise reactions

$$2CH_3I + Sn \longrightarrow (CH_3)_2SnI_2 \qquad (2)$$

$$(CH_3)_2SnI_2 + 2CH_3I + 2Cd \longrightarrow Sn(CH_3)_4 + 2CdI_2 \qquad (3)$$

(b) 0.43 g of $(CH_3)_2SnI_2$ in 20 $cm^3$ of 1:1 (v/v) methanol:benzene was electrolysed for 3 hr between a cadmium anode and a platinum cathode, under nitrogen, at 45 v, 20 ma, but with no added methyl iodide. Cadmium iodide deposited in the bottom of the vessel (Found Cd 29.9; I 69.2%; calcd. for $CdI_2$ Cd 30.7; I 69.3%), and tetramethyltin (0.076 g, 79% theoretical based on weight of Cd dissolved) was collected by distillation in vacuo. The simplest stoichiometry that one can write for this process is

$$2(CH_3)_2SnI_2 + 2Cd \longrightarrow Sn(CH_3)_4 + 2CdI_2 + Sn \qquad (4)$$

and in a subsequent reaction we were able to collect the metallic tin which had deposited in the bottom of the cell. The weight of cadmium dissolved in this case was 0.128 g (1.14 mmol), and the weight of tin collected 0.034 g (0.029 mmol), which is appreciably less than required by eq(4) (calcd. for 0.128 g Cd, 0.067 g Sn); the tin was however very finely divided, so that appreciable losses must have occurred in collecting the metal. We therefore tentatively conclude that the overall reaction is indeed that described by eq(4).

(c) A procedure much like (b) above, except for the presence of excess tetraethylammonium iodide (2.5 g) resulted in the final cadmium product being $(C_2H_5)_4N[CdI_3]$ (0.36 g) (cf. refs. 15,19).

Preparation of Hexaphenyl- and Hexamethylditin

The cadmium halide abstraction method [16] was used successively to obtain these compounds from $Ph_3SnBr$ and $Me_3SnCl$ respectively.

(a) 0.48 g of $(C_6H_5)_3SnBr$ and 15 mg of tetraethylammonium perchlorate in 80 $cm^3$ of 3:1 (v/v) benzene:acetone was electrolysed under nitrogen between a cadmium anode and a platinum cathode (40 v, 30 ma, 7 hr). The white product formed in the bottom of the cell, shown to be $CdBr_2$, was removed by filtration and the volume of the filtrate reduced to 15 $cm^3$; the white solid which deposited was collected, washed with ether and dried in vacuo (Yield 53%, based on original weight of $(C_6H_5)_3SnBr$). Tin analysis (Table 2) and the Raman spectrum (138, 178, 212 and 262 $cm^{-1}$) identified the product as hexaphenylditin [20].

(b) An analogous experiment involved 1.1 g of $(CH_3)_3SnCl$ and 100 mg. of $(C_2H_5)_4NClO_4$ dissolved in 60 $cm^3$ of 5:1 benzene: methanol. At 50 v, the initial current was 100 ma, which fell to 20 ma after about 30 min; the total length of electrolysis was 12 hr. Isolation of the product followed the method used for hexaphenylditin (Yield 59%, based on original weight of trimethyltin chloride taken).

Tin analysis confirmed the formation of $(CH_3)_6Sn_2$, as did two other analytical procedures. Firstly, exposure to air for 10 hr., followed by drying in vacuo, resulted in a decrease in the tin content to 68.7%, indicating the formation of $[(CH_3)_3Sn]_2O$ (calcd. Sn 69.2%). Secondly, titration of

$(CH_3)_6Sn_2$ in methanol:benzene (1:1) with $I_2$ was in agreement with the stoichiometry

$$(CH_3)_6Sn_2 + I_2 \longrightarrow 2(CH_3)_3SnI \qquad (5)$$

and $(CH_3)_3SnI$ was subsequently isolated from this reaction mixture (Found Sn 40.6, I 43.9%; calcd. Sn 40.9, I 43.6%). The Raman spectrum (137, 152, 199 and 512 $cm^{-1}$) also confirmed the identity of the product [21].

## Results and Discussion

We note here certain aspects of the preparative work, and the nature of the evidence which supports the identification of the products. The physical and spectroscopic properties of the dialkyltin dihalides, and of their adducts, are well established, so that the thrust of this discussion is to establish the purity of the compounds prepared, and in particular to show that single compounds were obtained rather than mixtures of $R_4Sn$, $R_3SnX$, $R_2SnX_2$, $RSnX_3$ and $SnX_4$.

### $(CH_3)_2SnI_2$, $(C_2H_5)_2SnI_2$

A freshly prepared sample of $(CH_3)_2SnI_2$ dissolved in $CCl_4$ showed only a single peak in the nmr spectrum at $\tau = 8.33$, with $^{117}Sn$ and $^{119}Sn$ satellites. No resonances attributable to $Me_4Sn$, or to other methyltin halides, were detected, establishing that the freshly prepared material is indeed $Me_2SnI_2$ [22]. Resonances from the redistribution products $(CH_3)_3SnI$, etc., were detected in solutions of $(CH_3)_2SnI_2$ in $CDCl_3$ or $CH_3OD$, especially if the solution were allowed to stand for some hours at room temperature. Similar results were obtained with $(C_2H_5)_2SnI_2$, in that no resonances from $Sn(C_2H_5)_4$ or $C_2H_5SnI_3$ were detected; the $^1H$ spectrum corresponded with that reported in the literature for $(C_2H_5)_2SnI_2$ [23].

The method described then provides a simple and direct route to $(CH_3)_2SnI_2$ and $(C_2H_5)_2SnI_2$, and the extension to other alkyl and aryl compounds should present no problems, given the ease with which adducts of such species can be obtained (see below). The relative insolubility of $(CH_3)_2SnI_2$ in the reaction mixture leads to precipitation of the product, and this is an important, if unexpected, feature of the system. The material which is obtained in short experiments (3 hr or less) is pure $R_2SnI_2$, but longer electrolyses lead to a mixture of $R_4Sn$, $R_3SnI$, etc., readily identified by nmr spectroscopy. There are two possible explanations for this, both related to the small but finite solubility of $R_2SnI_2$ in the reaction mixture; (a) $R_2SnI_2$ in solution undergoes a series of slow redistribution reactions to $R_4Sn$, etc. (cf. [1]), or (b) $R_2SnI_2$ in solution reacts with the tin anode by a process similar to eq(4), namely

$$2R_2SnI_2 + Sn \longrightarrow R_4Sn + SnI_4 + Sn \qquad (6)$$

followed by exchange reactions between $R_4Sn$ and $SnI_4$.

## Adducts of $R_2SnX_2$

There is an extensive literature on the physical properties of the adducts of the dialkyltin dihalides (cf. [1,2,3]. The infrared spectra of the adducts of $(C_2H_5)_2SnBr_2$ with 2,2'-bipyridyl and 1,10-phenanthroline confirm the presence of these two ligands, bonded via nitrogen. The $\nu$(Sn-C) infrared vibrations are observed at 542 w and 535 w $cm^{-1}$ respectively (KBr disc), somewhat higher than the previously reported values of 523m and 520w $cm^{-1}$ (Nujol) [24]. In general, the infrared data, together with the elemental analysis, confirm the production of these well known adducts. We note here that the results given in Table 1 for $(C_2H_5)_2SnI_2$.2dmso (dmso = dimethylsulphoxide) are for the freshly prepared compound, which loses dmso on standing (Sn content after 48 hr. 53.7%).

Adducts of organotin compounds with 1,2-bis(diphenylphosphino)ethane do not appear to have been reported previously, and it therefore seemed worthwhile to single out this bidentate ligand in the preparative studies. The resultant compounds unfortunately yield little by way of useful spectroscopic information. The infrared spectrum of the parent ligand has a series of sharp intense bands at 344 m, 406 m, 447 s, 485 vs, 511 vs and 538 m $cm^{-1}$, which effectively blanket the $\nu$(Sn-C) region, and further series at 676 s, 695, 708, 733, 746 and 756 (all vs) $cm^{-1}$ hinders any study of the $CH_3$ rocking mode. Proton nmr studies of these diphos adducts were confounded by low solubility in the usual inert solvents. When dissolved in dimethylsulphoxide, the compound $(C_2H_5)_2SnI_2$. diphos decomposed by loss of diphos, which slowly (∿ 1 hr.) precipitated (identified by infrared spectrum). Evaporation of the resultant solution gave $(C_2H_5)_2SnI_2.2$dmso (Found I 46.0: ir confirms presence of dmso) which as before slowly lost dmso on standing. A similar experiment with acetonitrile yielded $(C_2H_5)_2SnI_2.2CH_3CN$ (Found I 48.7%:ir confirms presence of $CH_3CN$). It seems probable that the instability of the diphos complexes is the result of steric crowding around tin, produced by 2 P, 2 I and 2 C atoms, and relieved by substitution of phosphorus by either oxygen or nitrogen.

The electrochemical method described provides a rapid and efficient way of synthesising a wide variety of adducts of the dialkyl (or aryl) tin dihalides. In addition to the diphos complexes mentioned above, a new compound prepared by this route in good yield is the adduct of stannacyclopentane-1,1'-dibromide obtained by the direct reaction of tin and 1,4-dibromobutane. This appears to be the first such cyclic organotin dihalide to be reported, although molecules such as $\underline{c}$-$C_4H_8SnR_2$ (R =

$C_4H_9$, $(CH_3)_3CCH_2$) have been prepared via Grignard reagents [25].

## Reaction Mechanism

In the present work, as in related studies with cadmium [14,16] and nickel [26], the electrochemical reaction has a stoichiometry which corresponds to the oxidative insertion reaction

$$\underline{n}RX + M \longrightarrow R_{\underline{n}}MX_{\underline{n}} \qquad (7)$$

(M = Cd or Ni, $\underline{n} = 1$;  M = Sn, $\underline{n} = 2$).

The probable mechanism of the first step in this process in the present system, the formation of an $RSn^{II}X$ species, has been briefly investigated. The current efficiencies in the experiments reported in Table 1 were between 0.4 and 1.5 mol $F^{-1}$, based on weight of tin dissolved, but these values are not meaningful, since current may vary throughout the experiment, especially when insoluble adducts form on the tin anode. In short controlled experiments with methyl or ethyl iodides, we found that the loss of tin at 30 v corresponded to the dissolution of 3.2 ($CH_3I$) or 4.9 ($C_2H_5I$) mol(Sn)$F^{-1}$ values which suggest a chain reaction involving radical species in solution. In further experiments, the gas generated at the cathode was collected and analysed mass-spectrometrically; in addition to $CH_3I$ and ions derived therefrom, we identified masses of 30, 29 and 28, indicating the formation of $C_2H_6$ during the electrolysis. Gassing was not observed with ethyl or higher halides, presumably because the equivalent $R_2$ species are soluble in the reaction mixture.

The formation of radicals at the cathode in organic solvent electrolysis has been successfully postulated in earlier studies of the electrochemical synthesis of organotin compounds [10,11,12], and in work on the reduction of organic halides at a mercury cathode [27]. We propose the following mechanism cathode: $$RX + e^- \longrightarrow R^\cdot + X^- \tag{8a}$$

The formation of $R_2$ may proceed either by

$$2R^\cdot \longrightarrow R_2 \tag{8b}$$

<u>or</u>

$$R^\cdot + RX \longrightarrow R_2 + X^\cdot \tag{8c}$$

We did not observe significant quantities of $I_2$ or $Br_2$ formation at the cathode, and therefore neglect (8c) in subsequent discussion.

anode: $$X^- \longrightarrow X^\cdot + e^- \tag{8d}$$

$$X^\cdot + Sn \longrightarrow SnX \tag{8e}$$

$$SnX + RX \longrightarrow RSnX + X^\cdot \tag{8f}$$

Reactions (8d) - (8f) explain the high current efficiencies, since X. acts as a chain carrier whose existence can be terminated by

$$X^\cdot + RX \longrightarrow X_2 + R^\cdot \tag{8g}$$

or $$X^\cdot + SnX \longrightarrow SnX_2 \tag{8L}$$

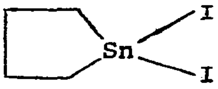
or $$X^\cdot + \text{ligand} \longrightarrow \text{products} \tag{8i}$$

The overall mechanism for the formation of RSnX is similar to that established by Mottus and Ort [28] in work on the electrochemical dissolution of aluminum in dichloromethane.

Organotin(II) species are unstable, and will react by

$$RSnX + RX \longrightarrow R_2SnX_2 \tag{9}$$

thus explaining the unique formation of the diorganotin dihalides in this synthetic method. The reaction sequence (8) and (9) also explains the ready formation of the tin heterocycle obtained as the diphos adduct, since the formation of a $-CH_2SnBr$ unit at one end of $1,4-C_4H_8Br_2$ would be followed by reaction at the other C-Br group to give ring closure. The mechanism is thus compatible with the experimental results on this and related systems, even though in our view the main conclusion of the present work lies in the advantages of the synthetic method for preparing $R_2SnX_2$ compounds.



## Tetramethyltin

The proton nmr spectrum of a sample of electrochemically prepared tetramethyltin (in carbon tetrachloride) was in good agreement with the literature values [29], showing a sharp singlet at $\tau = 9.90$, with $^{117}Sn$ and $^{119}Sn$ satellites ($J = 54.0$ and 51.0 Hz respectively). There was no evidence of the presence of any other protonic species in the distillate.

The stoichiometry of the formation of $Sn(CH_3)_4$ from $(CH_3)_2SnI_2$ by reaction with $CH_3I$ and anodic cadmium has been established (see Experimental). In terms of eq(7), the initial reaction presumably leads to the formation of $CH_3CdI$, a product identified in earlier work [14], followed by successive reaction of $CH_3CdI$ at the Sn–I bond of the organotin dihalide. The reaction between $(CH_3)_2SnI_2$ and anodic cadmium in the absence of $CH_3I$ may also involve insertion to give $(CH_3)_2Sn(I)CdI$, which could decompose to $CdI_2$ and $(CH_3)_2Sn$; two dimethyltin(II) species would yield $Sn(CH_3)_4$ and Sn. The tin-cadmium bonded species is related to compounds such as $R_3Sn(L)CdX$ (L = N,N,N',N'-tetramethylethylenediamine, reported by Noltes and co-workers [30,31], who find that reaction with R'X leads to the formation of $R_3R'Sn$, so that an alternate route to $(CH_3)_4Sn$ would involve the reaction of $(CH_3)_2Sn(I)CdI$ with $CH_3I$. Work on this problem, and on the electrochemical synthesis of compounds such as $Ph_3SnCdX$ is proceeding.

In general, this electrochemical preparation of $(CH_3)_4Sn$ appears to have some advantage over existing methods, in particular in the ability to work at room temperature, the ready availability of easily handled starting materials, and the simplicity of the apparatus. The method should be capable of adoption to continuous generation of $Me_4Sn$, which could be removed in a stream of carrier gas.

## Hexamethyl- and hexaphenylditin

Halide abstraction from $R_3SnX$ compounds by reaction with sodium [32] or lithium [33] is an established route to ditin compounds, which also result from the polarographic reduction of $(C_6H_5)_3SnX$ (X = F [34] or Cl [35,36]. The use of anodic cadmium in an electrochemical cell provides a convenient alternative mode of carrying out such halide abstraction reactions, and the stoichiometric analogy with the Wurtz reaction

i.e. $$2R_3SnX + Cd \longrightarrow R_6Sn_2 + CdX_2 \qquad (10)$$

has lead to a number of other synthetically useful coupling reactions [16].

## General

Electrochemical reactions involving either tin or cadmium as the sacrificial anode offer clean and rapid synthetic routes to a variety of organotin compounds. The reactions can be carried out at room temperature, and the product yields are high. Work on related elements has been initiated.

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