

# Wurtz-type reductive coupling reaction of primary alkyl iodides and haloorganotins in cosolvent/H<sub>2</sub>O(NH<sub>4</sub>Cl)/Zn media as a route to mixed alkylstannanes and hexaalkyldistannanes

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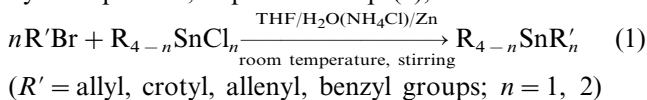
## Abstract

Mixed tetra-alkylstannanes R<sub>3</sub>SnR' (R = Et, *n*-Pr, *n*-Bu and R' = Me, Et, *n*-Pr, *n*-Bu, *n*-Pent) and R<sub>2</sub>SnR'<sub>2</sub> (R = *n*-Bu and R' = Me, Et, *n*-Pr, *n*-Bu) can be easily prepared in a one-pot synthesis via coupling reaction of alkyl iodides R'I with R<sub>3</sub>SnX (X = Cl, I) and R<sub>2</sub>SnCl<sub>2</sub> compounds in cosolvent–H<sub>2</sub>O(NH<sub>4</sub>Cl) medium mediated by zinc dust. Coupling also occurs with (Bu<sub>3</sub>Sn)<sub>2</sub>O. It has been verified that reactions are possible only with primary alkyl iodides; with secondary alkyl iodides the coupling reaction fails. When alkyl chlorides and bromides are used ditin compounds are obtained instead of the unsymmetrical tetra-alkylstannanes. This represents a route to hexaalkyldistannanes. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Alkyltin; Coupling; Distannane

## 1. Introduction

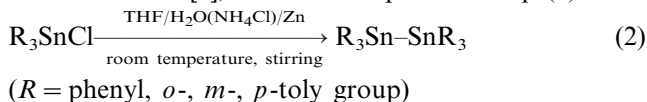
The Wurtz-type reductive coupling reaction mediated by zinc powder, depicted in Eq. (1),



has been successfully employed when R' = allyl, crotyl, allenyl and benzyl groups [1–4].

The stereochemical pathways of these reactions, together with those dealing with the allylation of aldehydes [5], seem to be determined by the structure of the radical anions [R'Br]<sup>•−</sup> adsorbed on the zinc particles, not on the geometry of the organic halides, cosolvents or salt [3,5].

This procedure has been adopted in Sn–Sn forming bond reactions [3], as well as depicted in Eq. (2):



This methodology has been now recognized to be useful for coupling reactions between saturated alkyl iodides and organotin halides in forming Sn–C<sub>alkyl</sub> bonds.

Thus, the work deals with the preparation of mixed alkyltin derivatives of the type R<sub>3</sub>SnR' or R<sub>2</sub>SnR'<sub>2</sub> (R = Et, *n*-Pr, *n*-Bu; R' = Me, Et, *n*-Pr, *n*-Bu, *n*-Pent), as well as of hexaalkylditins R<sub>3</sub>SnSnR<sub>3</sub> (R = Et, *n*-Pr, *n*-Bu).

## 2. Results and discussion

### 2.1. Coupling reactions of tri- and diorganotins and alkyl iodides

Table 1 shows the results obtained from reactions of mono- or dichloro alkyltins R<sub>3</sub>SnCl and R<sub>2</sub>SnCl<sub>2</sub> (R = Et, *n*-Pr, *n*-Bu) and tributyltin oxide, (Bu<sub>3</sub>Sn)<sub>2</sub>O, with primary alkyl iodides R'I, with R' = Me, Et, *n*-Pr, *n*-Bu and *n*-Pent.

The feasibility of these reactions is the same as those previously reported for the formation of the Sn–C<sub>alkyl</sub> bond [1] where both organotin chlorides and oxide have been used. Nevertheless, in the present cases, a different

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Table 1

Preparation of mixed alkylstannanes from tri- and diorganotin derivatives and alkyl iodides in H<sub>2</sub>O(NH<sub>4</sub>Cl)/THF/Zn medium

Entry no.	Reagent					Amount of H <sub>2</sub> O <sup>b</sup> /THF (ml)	Reaction time <sup>c</sup> (h)	Product	Amount of product (g (yield%))
	Organotin	Amount (g (mmol))	Alkyl iodide	Amount (g (mmol))	Amount Zn (mmol) <sup>a</sup>				
1	Et <sub>3</sub> SnCl	7.3 (30.1)	MeI	17.1 (120.5)	8.0 (122.4)	50/25	1.5	Et <sub>3</sub> SnMe	4.9 (74)
2	Et <sub>3</sub> SnCl	7.4 (30.5)	<i>n</i> -BuI	22.6 (119.9)	8.5 (130.2)	50/25	1.0	Et <sub>3</sub> Sn( <i>n</i> -Bu)	6.8 (85)
3	<i>n</i> -Pr <sub>3</sub> SnCl	5.6 (19.8)	MeI	8.5 (59.9)	4.0 (61.2)	50/25	0.5	<i>n</i> -Pr <sub>3</sub> SnMe	3.9 (75)
4	<i>n</i> -Pr <sub>3</sub> SnCl	6.0 (21.0)	EtI	9.5 (60.6)	4.2 (61.8)	50/25	1.0	<i>n</i> -Pr <sub>3</sub> SnEt	4.7 (82)
5	<i>n</i> -Pr <sub>3</sub> SnCl	5.2 (18.4)	<i>n</i> -PrI	10.1 (60.6)	4.2 (61.8)	50/25	1.0	<i>n</i> -Pr <sub>3</sub> Sn( <i>n</i> -Pr)	4.2 (79)
6	<i>n</i> -Bu <sub>3</sub> SnCl	9.8 (30.2)	MeI	17.1 (120.5)	7.9 (121.2)	50/25	1.0	<i>n</i> -Bu <sub>3</sub> SnMe	7.7 (84)
7	<i>n</i> -Bu <sub>3</sub> SnCl	9.8 (30.2)	EtI	18.7 (120.0)	8.1 (123.7)	50/25	1.5	<i>n</i> -Bu <sub>3</sub> SnEt	7.6 (79)
8	<i>n</i> -Bu <sub>3</sub> SnCl	9.8 (30.2)	<i>n</i> -PrI	20.2 (120.0)	8.0 (122.4)	50/25	1.5	<i>n</i> -Bu <sub>3</sub> Sn( <i>n</i> -Pr)	6.8 (68) <sup>d</sup>
9	<i>n</i> -Bu <sub>3</sub> SnCl	9.8 (30.2)	<i>n</i> -BuI <sup>e</sup>	22.1 (120.0)	8.0 (122.4)	50/25	3.0	<i>n</i> -Bu <sub>3</sub> Sn( <i>n</i> -Bu)	4.8 (46) <sup>d</sup>
10	<i>n</i> -Bu <sub>3</sub> SnCl	9.9 (30.5)	<i>n</i> -PentI <sup>e</sup>	23.8 (120.3)	8.5 (129.9)	50/25	5.0	<i>n</i> -Bu <sub>3</sub> Sn( <i>n</i> -Pent)	4.8 (44) <sup>d</sup>
11	( <i>n</i> -Bu <sub>3</sub> Sn) <sub>2</sub> O	11.9 (20.0)	MeI	22.7 (160.0)	10.5 (160.0)	100/50	1.5	<i>n</i> -Bu <sub>3</sub> SnMe	11.9 (88)
12	( <i>n</i> -Bu <sub>3</sub> Sn) <sub>2</sub> O	11.9 (20.0)	EtI	24.9 (160.0)	10.5 (160.0)	100/50	1.5	<i>n</i> -Bu <sub>3</sub> SnEt	12.8 (80)
13	( <i>n</i> -Bu <sub>3</sub> Sn) <sub>2</sub> O	11.9 (20.0)	<i>n</i> -BuI	29.4 (160.0)	10.5 (160.0)	100/50	5.5	<i>n</i> -Bu <sub>3</sub> Sn( <i>n</i> -Bu)	6.9 (50) <sup>d</sup>
14	( <i>n</i> -Bu <sub>3</sub> Sn) <sub>2</sub> O	11.9 (20.0)	<i>n</i> -PentI	31.7 (160.0)	10.5 (160.0)	100/50	4.5	<i>n</i> -Bu <sub>3</sub> Sn( <i>n</i> -Pent)	5.4 (37) <sup>d</sup>
15	<i>n</i> -Bu <sub>2</sub> SnCl <sub>2</sub>	4.5 (14.9)	MeI	17.1 (120.5)	7.8 (119.6)	50/25	1.0	<i>n</i> -Bu <sub>2</sub> SnMe <sub>2</sub>	2.5 (64)
16	<i>n</i> -Bu <sub>2</sub> SnCl <sub>2</sub>	9.2 (30.3)	MeI	34.1 (240.1)	15.8 (241.9)	100/50	1.0	<i>n</i> -Bu <sub>2</sub> SnMe <sub>2</sub>	5.0 (62)
17	<i>n</i> -Bu <sub>2</sub> SnCl <sub>2</sub>	9.1 (30.0)	EtI	39.2 (251.0)	16.4 (250.2)	100/50	1.0	<i>n</i> -Bu <sub>2</sub> SnEt <sub>2</sub>	4.8 (55)
18	<i>n</i> -Bu <sub>2</sub> SnCl <sub>2</sub>	9.1 (30.0)	<i>n</i> -PrI	40.8 (240.0)	15.7 (240.0)	100/50	3.5	<i>n</i> -Bu <sub>2</sub> Sn( <i>n</i> -Bu) <sub>2</sub>	5.1 (52) <sup>d</sup>
19	<i>n</i> -Bu <sub>2</sub> SnCl <sub>2</sub>	9.1 (30.0)	<i>n</i> -BuI	44.2 (240.0)	15.7 (249.0)	100/50	3.5	<i>n</i> -Bu <sub>2</sub> Sn( <i>n</i> -Pent) <sub>2</sub>	4.4 (42) <sup>d</sup>

<sup>a</sup> Zinc dust, <10 μm.<sup>b</sup> Deionized water saturated with NH<sub>4</sub>Cl.<sup>c</sup> This time has been evaluated looking at the disappearance of the <sup>119</sup>Sn-NMR or GLC signals of the starting organotin. In some cases, two identical gas-chromatographic profiles in two consecutive GLC tests marked the end of the reaction.<sup>d</sup> Yield was calculated with reference to the product obtained by elution through a chromatographic column (see Section 4).<sup>e</sup> In this case, after 1.5 h, a further addition of 15 mmol of alkyl iodide was carried out.

Table 2  
Halogen and solvent effect <sup>a</sup>

Entry no.	Reagent					Cosolvent	Reaction time <sup>c</sup> (h)	Product	Amount of product (g (yield%))
	Organotin	Amount (g (mmol))	Alkyl iodide	Amount (g (mmol))	Amount Zn (g (mmol)) <sup>b</sup>				
20	<i>n</i> -Bu <sub>3</sub> SnI	12.5 (30.0)	MeI	17.0 (120.0)	8.0 (122.4)	THF	1.0	<i>n</i> -Bu <sub>3</sub> SnMe	7.8 (85)
21	<i>n</i> -Bu <sub>3</sub> SnCl	9.4 (29.0)	MeI	17.1 (120.5)	8.1(123.1)	THF	1.0	<i>n</i> -Bu <sub>3</sub> SnMe	7.3 (82)
22	<i>n</i> -Bu <sub>3</sub> SnI	12.5 (30.0)	MeI	17.3 (120.7)	8.0 (122.4)	Cyclohexane	1.0	<i>n</i> -Bu <sub>3</sub> SnMe	7.1 (77)
23	<i>n</i> -Bu <sub>3</sub> SnCl	11.1 (34.2)	MeI	17.3 (120.7)	8.0 (122.4)	Cyclohexane	3.0	<i>n</i> -Bu <sub>3</sub> SnMe	5.4 (52) <sup>d</sup>
24	<i>n</i> -Bu <sub>3</sub> SnI	12.5 (30.0)	<i>n</i> -BuI	22.1 (120.0)	8.0 (122.4)	THF	1.0	<i>n</i> -Bu <sub>3</sub> Sn( <i>n</i> -Bu)	7.3 (70)
25	<i>n</i> -Bu <sub>3</sub> SnCl	10.0 (30.8)	<i>n</i> -BuI	22.3 (120.0)	8.1 (123.1)	THF	3.5	<i>n</i> -Bu <sub>3</sub> Sn( <i>n</i> -Bu)	5.2 (48) <sup>d</sup>

<sup>a</sup> Comparison between the results obtained using tributyltin chloride and tributyltin iodide in coupling reactions with alkyl iodides in H<sub>2</sub>O(NH<sub>4</sub>Cl)/cosolvent/Zn medium. All runs were performed using 50 ml of deionized water saturated with NH<sub>4</sub>Cl and 25 ml of cosolvent.

<sup>b</sup> Zinc dust, < 10 μm.

<sup>c</sup> This time has been evaluated looking at the disappearance of the <sup>119</sup>Sn-NMR or GLC signals of the starting organotin. In some cases, two identical gas-chromatographic profiles in two consecutive GLC tests marked the end of the reaction.

<sup>d</sup> Yield was calculated with reference to the product obtained by elution through a chromatographic column (see Section 4).

Table 3

Preparation of hexaalkyldistannanes from trialkyltin halides in H<sub>2</sub>O(NH<sub>4</sub>Cl)/THF/Zn medium<sup>a</sup>

Entry no.	Reagent		Reaction time <sup>c</sup> (h)	Amount of product (g (yield%))
	Amount organotin (g (mmol))	Amount Zn (g (mmol)) <sup>b</sup>		
26	Et <sub>3</sub> SnCl 10.9 (45.0)	5.8 (90.0)	17	(Et <sub>3</sub> Sn) <sub>2</sub> 5.0 (54)
27	<i>n</i> -Pr <sub>3</sub> SnCl 11.8 (41.3)	5.5 (83.6)	24	( <i>n</i> -Pr <sub>3</sub> Sn) <sub>2</sub> 6.0 (58)
28	<i>n</i> -Bu <sub>3</sub> SnCl 9.8 (30.0)	3.9 (60.2)	22	( <i>n</i> -Bu <sub>3</sub> Sn) <sub>2</sub> 3.9 (45)
29	<i>n</i> -Bu <sub>3</sub> SnI 25.0 (60.0)	7.8 (120.0)	20	( <i>n</i> -Bu <sub>3</sub> Sn) <sub>2</sub> 8.1 (47)
30	<i>n</i> -Pr <sub>3</sub> SnCl, <i>n</i> -Bu <sub>3</sub> SnCl 8.5 (30.0) 9.8 (30.0)	7.8 (120.0)	22	( <i>n</i> -Pr <sub>3</sub> Sn) <sub>2</sub> , ( <i>n</i> -Pr <sub>3</sub> )Sn-Sn( <i>n</i> -Bu <sub>3</sub> ), ( <i>n</i> -Bu <sub>3</sub> Sn) <sub>2</sub> <sup>d</sup> 2.2 (15) 4.5 (28) 2.3 (13)

<sup>a</sup> All runs were performed under nitrogen flow using 50 ml of deionized water saturated with NH<sub>4</sub>Cl and 25 ml of THF.<sup>b</sup> Zinc dust, <10 μm.<sup>c</sup> This time has been evaluated looking at the disappearance of the <sup>119</sup>Sn-NMR or GLC signals of the starting organotin halide.<sup>d</sup> The composition of the mixture of the three distannanes was calculated by integration of the corresponding <sup>119</sup>Sn-NMR resonance lines.

behavior is observed, because coupling is only possible when organic iodides are employed: the use of alkyl chlorides and bromides give rise to ditin compounds (see below).

Yields fall in the range 42–88%, and many reactions are characterized by high exothermicity (entries 1–7, 11, 12 and 15–17); the end of the reactions is reached in 0.5–5.5 h. These reactions seem to be affected by steric hindrance from both R and R' groups; the larger is the bulkiness of the alkyl group the lower is the yield: e.g. see on passing from methyl to *n*-pentyl iodides (entries 6–10), or from Et<sub>3</sub>SnCl to *n*-Bu<sub>3</sub>SnCl (entries 2, 5 and 9). This behavior is similar to that found for the nucleophilic electrochemical alkylation of Bu<sub>3</sub>SnCl with MeI, EtI and *n*-PrI to form Bu<sub>3</sub>SnMe, Bu<sub>3</sub>SnEt and Bu<sub>3</sub>SnPr [6]: the corresponding yields are 100, 82 and 40% respectively. Steric effects have also been found to be important in related coupling reactions between R<sub>3</sub>SnCl derivatives (R = Et, *n*-Pr, *n*-Bu) and benzyl bromides [3]. In the coupling reactions between Bu<sub>2</sub>SnCl<sub>2</sub> and alkyl iodides (see Table 1 entries 15–19), steric effects are also operating.

Reactions performed using (*n*-Bu<sub>3</sub>Sn)<sub>2</sub>O yield the same results as those obtained using (*n*-Bu<sub>3</sub>SnCl (compare entries 6–10 with entries 11–14).

The small amount of organic solvent used, the short reactions time and the fairly good yields obtained in many cases, have the adopted procedure offers some advantages with respect to those based for instance on the Grignard reagent [7,8] or on the use of organostannylmetal [9] and organostannyl hydrides substrates [7].

Attempts to carry out coupling reactions between *n*-Bu<sub>3</sub>SnCl and secondary organic iodides RI (R = *i*-propyl, *sec*-butyl, cyclohexyl) or *i*-PrBr or *n*-BuCl (a primary organic halide) failed. The secondary iodides

are highly reactive compounds in Zn/THF/H<sub>2</sub>O (NH<sub>4</sub>Cl) medium: the main reaction is the reduction of the iodides by zinc and, under these conditions, *n*-Bu<sub>3</sub>SnCl is converted in *n*-Bu<sub>3</sub>SnI (61–87%). The formation of *n*-Bu<sub>3</sub>SnI is due to an exchange reaction between *n*-Bu<sub>3</sub>SnCl and the iodide ions<sup>1</sup>. By contrast, in the runs performed with *i*-PrBr or *n*-BuCl, the reduction of organic halides has been never observed and the main reaction is the coupling of [Bu<sub>3</sub>SnX]<sup>•-</sup> with Bu<sub>3</sub>SnX to form hexabutyliditin.

## 2.2. Halogen and solvent effects

Table 2 shows the results obtained using Bu<sub>3</sub>SnI in comparison with those obtained with Bu<sub>3</sub>SnCl. Comparison must be made inside the pair of runs of entries 20–21, 22–23 and 24–25 respectively, where the same cosolvent has been employed.

Yields are in the range 48–85% and the best results have been obtained, independent of the employed cosolvent (THF or cyclohexane), when *n*-Bu<sub>3</sub>SnI is used instead of *n*-Bu<sub>3</sub>SnCl. This result may be explained by two factors: (i) owing to the lesser polarity of the Sn–I bond with respect of that of Sn–Cl bond [11], *n*-Bu<sub>3</sub>SnI will be present in the organic phase at higher concentrations than *n*-Bu<sub>3</sub>SnCl, so that the trapping of the

<sup>1</sup> The formation of Bu<sub>3</sub>SnI has been verified to occur when Bu<sub>3</sub>SnCl is allowed to react in H<sub>2</sub>O/THF in the presence of the sole NH<sub>4</sub>I. On the contrary, a metathetic reaction was not observed when equimolar amounts of Bu<sub>3</sub>SnCl and organic iodide were allowed to react in H<sub>2</sub>O(NH<sub>4</sub>Cl)/THF medium in the absence of zinc. Indeed, an exchange reaction between Bu<sub>3</sub>SnCl and RI in an organic medium is only possible at high temperature in the presence of catalysts [10].

radicals ions  $[R'I]^{*-}$  by  $n\text{-Bu}_3\text{SnI}$  species will be favored<sup>2</sup>; (II) the iodide is a better leaving group than chloride in nucleophilic substitution reactions [12].

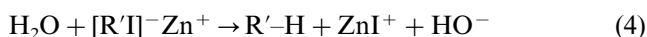
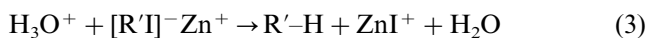
### 2.3. Preparation of hexa-alkyldistannanes

So far, this methodology has been applied in the past [3,4] only for the preparation of hexaaryldistannanes, because these compounds are fairly stable in water and towards the oxygen of the air. The same conditions can not be adopted for the preparation of hexaalkyldistannanes, because, as it is known, these are oxidized in air to give the oxide,  $(R_3\text{Sn})_2\text{O}$  [13]. We succeeded in preparing some hexa-alkyldistannanes (see Table 3) by working under nitrogen atmosphere.

Even though the yields are not high (45–58%), this very simple methodology may be preferred to other procedures that give higher yields but need long work-up [14–16].

### 3. General comments

Exhaustive explanation of the obtained results requires recognition that competitive reactions occur into the system together with the main reaction (Eq. (1)). The following reactions deal with the reduction (mediated by zinc) of alkyl iodides to alkanes<sup>3</sup>.



Reaction 4 is especially important for secondary and tertiary alkyl halides which react with water more rapidly than their primary counterparts [17].

Finally, the coupling reaction:



dealing with the formation of the tin-tin bond [2–5] must be considered.

Only when primary alkyl iodides are used, the trapping of the radical ions  $[R'I]^{*-}$  by the organotin species occurs to form of Sn–C bond in competition with reactions 3 and 4. Since the coupling reaction seems to be greatly affected by steric effects, the reduction of the organic iodides (Eqs. (3) and (4)) became prevalent as the steric hindrance of both R and R' groups increases (see Table 1, compare entry 2 with entries 9 and entries 6–10). Indeed, with secondary organic iodides the sole

reaction observed is the reduction of the organic iodides (Eqs. (3) and (4)). When organic bromides or chlorides are used, the main reaction is the formation of ditin compounds (Eq. (5)). Formation of Sn–C<sub>alkyl</sub> bonds may be carried out only by employing primary alkyl iodides.

The formation of radical ions  $[R'X]^{*-}$  on a metal surface seems to be characterized by two reaction steps [17]: (i) a molecular absorption occurs with the initial attachment of the halogen atom to the metal surface; (ii) the adsorbed halide can simply desorb (released unchanged) or undergo dissociation of the carbon-halogen bond. Thus, the formation of these ion radicals depends both on the nature of the organic group, which can allocate the unpaired electron or upon the tendency of the carbon-halogen bond to dissociate. This is in the order  $\text{I} \gg \text{Br} > \text{Cl}$ , as it can be formulated on taking into account for the electron affinities of the organic halides [18]. Analogously, the formation of the ion radicals  $[R_3\text{SnX}]^{*-}$  still depends upon the tendency of the tin-halogen bond to dissociate. This is in the order  $R_3\text{SnI} > R_3\text{SnBr} > R_3\text{SnCl}$  as it can be argue from the electrochemical potential reduction of these substrates, which are more negative in the order  $R_3\text{SnCl} > R_3\text{SnBr} > R_3\text{SnI}$  [19].

### 4. Experimental

All manipulations were carried out under air atmosphere at room temperature. Nitrogen atmosphere was only used for preparations of distannanes. THF was distilled before use; other solvents, salts and zinc dust ( $< 10 \mu\text{m}$ ), commercially available, were used as received.

Tripropyltin chloride, tributyltin chloride, tributyltin iodide and bis(tributyltin) oxide, commercially available (Aldrich), were distilled under vacuum before use. Triethyltin chloride was prepared by redistribution reaction between tetraethylstannane and tin tetrachloride [20].  $\text{Bu}_2\text{SnCl}_2$  was recrystallized before use. All the alkyl iodides, commercially available, were employed as received.

Boiling points, infrared spectra [21], as well as  $^{13}\text{C}$ - and  $^{119}\text{Sn}$ -NMR [8,22–26] were in agreement with those reported in literature. Infrared spectra were registered as pure liquid (CsI optics) using a Perkin–Elmer 599B spectrophotometer. The NMR spectra, registered as pure liquid using  $\text{Me}_4\text{Sn}$  and  $\text{Me}_4\text{Si}$  as external and internal standard respectively, were obtained with a JEOL FX90Q instrument Fourier Transform NMR spectrometer. GLC analyses were made using a Perkin–Elmer gas-chromatograph model 8310 equipped with a flame-ionization detector (DB1 non-polar column, 15 m, 0,25 mm i.d.,  $T_i = 200^\circ\text{C}$ ,  $T_d = 320^\circ\text{C}$ ,  $T_c = 80\text{–}300^\circ\text{C}$ ,  $10^\circ\text{C min}^{-1}$ , nitrogen as carrier

<sup>2</sup> For our previous mechanistic considerations about these reactions see Ref. [2].

<sup>3</sup> Reactions 3 and 4 are prevalent with respect to both dimerization and dismutation reactions. Indeed, the reaction between the sole  $n$ -pentyl iodide and zinc in  $\text{H}_2\text{O}(\text{NH}_4\text{Cl})/\text{THF}$  medium gives rise only  $n$ -pentane with traces of  $n$ -decane. Formation of 3,4-dimethyloctane is not observed.

gas at 10 psi, 1/35 split). Additional GC–MS characterization of the products was made using a Carlo Erba gas-chromatograph model HRGC 800 EC-WAX column, 30 m, 0.25 mm i.d.,  $T_i = 250^\circ\text{C}$ , helium as carrier gas at 1 ml  $\text{min}^{-1}$ , 1/30 split) combined with a Fisons mass spectrometer model 800 equipped with an electron impact ionization source ( $-70$  eV) and a quadrupole mass analyzer.

The progress of the reactions was monitored by means of  $^{119}\text{Sn}$ -NMR or GLC. The complete disappearance of the related signals (or peaks) or their standing at a constant value marked the end of the reactions. In such a way, we have had the possibility to make a rough comparison between the rates of the various processes here considered.

#### 4.1. Preparation of $R_3\text{SnR}'$ and $R_2\text{SnR}'_2$ compounds (entries 1–25)

In a round bottom two-necked flask (100 ml) equipped with a condenser and dropping funnel and magnetic stirrer, the appropriate alkyl tin halide was added at room temperature into the system organic cosolvent/ $\text{H}_2\text{O}$  ( $\text{NH}_4\text{Cl}$  saturated)/Zn dust (the quantities are given in Table 1). Under stirring, the appropriate alkyl iodide (generally in 1:1 stoichiometric ratio with respect to the zinc) was added dropwise over about 15 min, a rate sufficient to maintain a gentle reflux due to the exothermicity of many reactions. At the end of the reaction, the unreacted zinc was filtered off and the aqueous phase was extracted three times with *n*-pentane (10 ml each). The separated organic layer was washed with saturated aqueous NaCl solution and dried over  $\text{MgSO}_4$ . Removal of the solvent left a crude oil, which was distilled under vacuum to afford the pure alkyltin compound. In a few cases (see Table 1, entries 8–10, 13, 14, 18 and 19) the distilled product contained unreacted starting organotin halide. A further purification by elution on a chromatographic column (22 cm length, filled with silica gel 70–230 mesh) using *n*-hexane as eluent was carried out to ensure a pure compound. Yields, listed in Table 1, were calculated from the amount of pure compound.

Table 2 compares the results obtained using  $\text{Bu}_3\text{SnI}$  with those obtained using  $\text{Bu}_3\text{SnCl}$  with different organic cosolvents.

#### 4.2. Preparation of hexa-alkyldistannanes (entries 26–30)

In a round bottom two-necked flask (100 ml), an appropriate amount of zinc powder was added under stirring to 25 ml of THF and 50 ml of a solution saturated with  $\text{NH}_4\text{Cl}$ , kept under nitrogen atmosphere. Then, the trialkyltin halide (the quantities are indicated in Table 3) was added. In order to avoid the presence of

air, the system was always maintained under nitrogen flow. Reactions required 17–22 h for completion. After this time, the unreacted zinc was removed by filtration and the aqueous phase was extracted with *n*-pentane. Removal of the solvent left a slurry residue, which was distilled under vacuum to afford pure ditin compounds.

Entry 30 of Table 3 deals with the attempt to prepare the mixed ditin  $\text{Pr}_3\text{SnSnBu}_3$ . Its  $^{119}\text{Sn}$ - and  $^{13}\text{C}$ -NMR chemical shifts are as follows:

$\delta (^{119}\text{Sn})$	C—C—C—Sn—Sn—C—C—C—C	-89.2 -83.1
$\delta (^{13}\text{C})$	19.2 22.0 13.3	10.3 31.0 27.8 13.7

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