

## Hydrated $\sigma$ -bonded organometallic cations in organic synthesis

### I. Allyl-, crotyl-, 1-methylallyl-, cyclohex-2-enyl-, and cinnamyl-stannation of carbonyl compounds in water \*

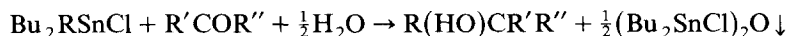
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#### Abstract

Homoallylic alcohols can be prepared in water by allyl-, crotyl-, 1-methylallyl-, cyclohex-2-enyl-, or cinnamyl-stannation of such carbonyl compounds as aldehydes, dialdehydes, and ketones, as well as acetals. The procedure is based on:

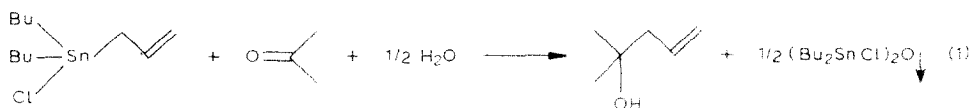


where R = allyl, crotyl, 1-methylallyl, cyclohex-2-enyl, or cinnamyl group, R' = H or alkyl group, R''  $\neq$  R' = alkyl group. In most cases, the reaction products are obtained rapidly in high yields (80–100%). Hydrated organometallic cations  $\text{Bu}_2\text{RSn}^+_{(\text{aq})}$  are partly involved. These results, together with those already published on 2-propynyl- and allenyl-stannation, indicate the value of this procedure.

#### Introduction

Allylations of carbonyl compounds in aqueous media have been recently developed using two different approaches: (i) reactions of allyltin mono- or di-chlorides ( $\text{Bu}_2\text{ClSnCH}_2\text{CH}=\text{CH}_2$  or  $\text{BuCl}_2\text{SnCH}_2\text{CH}=\text{CH}_2$ ) (eq. 1) [1], and (ii) tin- or zinc-mediated reactions of allyl halides (eq. 2) [2–7]. Where Z = H the reagents are

\* Dedicated to Professor Colin Eaborn in recognition of his important contributions to organometallic chemistry.



either Sn, Al and HBr in THF/H<sub>2</sub>O or Et<sub>2</sub>O/H<sub>2</sub>O [2], or Sn in THF/H<sub>2</sub>O [7]; where Z = OH or O<sub>2</sub>CMe, the reagents are Sn and HBr in Et<sub>2</sub>O/H<sub>2</sub>O [3]. Reaction 2, gives rise to satisfactory results only when allylic bromides are used: crotyl or 3,3-dimethylallyl bromides always react at the more substituted carbon atom [6], whereas cinnamyl bromide yields phenylpropene and 3-bromocyclohexene decomposes without formation of the expected homoallylic alcohol [7]. Therefore, reaction 2 has limited application [7] and its synthetic utility is restricted to the additions of allyl, and mono- and di-methylallyl derivatives. In contrast, reaction 1 has already been established as a useful route to 1-allenic and 2-acetylenic alcohols [1,8].

Here, we demonstrate that syntheses via reaction 1 can be extended to other organotin mono-chlorides having a 2,3-unsaturated organic group bound to the tin atom. Thus, Bu<sub>2</sub>(CH<sub>2</sub>=CHCH<sub>2</sub>)SnCl (1), (*E/Z*)-Bu<sub>2</sub>(CH<sub>3</sub>CH=CHCH<sub>2</sub>)SnCl (2), Bu<sub>2</sub>[CH<sub>2</sub>=CHCH(CH<sub>3</sub>)]SnCl (3), Bu<sub>2</sub>(cyclohex-2-enyl)SnCl (4), Bu<sub>2</sub>(Ph-CH=CHCH<sub>2</sub>)SnCl (5), and Bu<sub>2</sub>[CH<sub>2</sub>=CHCH(Ph)]SnCl (6) react with carbonyl compounds (aldehydes, dialdehydes, acetals, and ketones) to give homoallylic alcohols. Aqueated organometallic cations Bu<sub>2</sub>RSn<sup>+</sup><sub>(aq)</sub> (R = 2,3-unsaturated organic group) are involved, together with molecular species, Bu<sub>2</sub>RSnCl, in the addition process conducted in water.

The stereochemistry of the reactions has been evaluated and compared with that found for analogous reactions performed in a solvent-free mixture [9–11].

## Results and discussion

**Allylstannation.** Results for dibutylallyltin chloride (system A) are listed in Table 1. This organotin substrate, as already reported [1], exhibits high reactivity towards aldehydes and acetals (runs 1–4, 9 and 10): the precipitation of the distannoxane (cf. reaction 1) is observed about 5 or 10 min after the mixing of the reactants. The times are shorter than those observed for reactions in a homogeneous solvent-free mixture [9]. Moreover, these reactions are complete in times shorter than those observed for eq. 2 [2,3,7].

Reaction times increase with di-aldehydes (runs 5 and 6) and ketones (runs 7 and 8); glyoxal results in the lowest yield (68%). This may be due to steric factors, because in this dialdehyde two adjacent carbonyl groups are involved. Reactions of this aldehyde with other (alk-2-enyl)tin substrates, such as crotyl and cyclohex-2-enyl-tin monochlorides, give low yields, or otherwise unsatisfactory results.

Run 10 is a remarkable example of the application of this approach: the yield of 1,5-hexadiene-3-ol is 98% in comparison with yields of 90, 75, and 74% for

(continued on p. 350)

Table 1

Allylstannation of aldehydes, dialdehydes, ketones and acetals by  $\text{Bu}_2(\text{CH}_2=\text{CHCH}_2)_2\text{SnCl}$  in water at  $20^\circ\text{C}$ <sup>a</sup>

Run	Carbonyl compound <sup>b</sup>	Reaction time <sup>c</sup>	Product	Yield	
				g	%
1	$\text{CH}_2\text{O}$ <sup>d</sup>	5 min	I, $\text{HOCH}_2\text{CH}_2\text{CH}=\text{CH}_2$	1.7	97
2	( <i>E,E</i> )- $\text{CH}_3\text{CH}=\text{CHCH}=\text{CHCHO}$	10 min	II, ( <i>E,E</i> )- $\text{Me}(\text{CH}=\text{CH})_2\text{CH}(\text{OH})\text{CH}_2\text{CH}=\text{CH}_2$	3.4	98
3	( <i>E,E</i> )- $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}=\text{CHCHO}$	10 min	III, ( <i>E,E</i> )- $\text{Et}(\text{CH}=\text{CH})_2\text{CH}(\text{OH})\text{CH}_2\text{CH}=\text{CH}_2$	3.6	94
4	(-)- $(\text{CH}_3)_2\text{CH}=\text{CHCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CHO}$	10 min	IV, (-)- $\text{Me}_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{CH}(\text{Me})\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}=\text{CH}_2$	4.3	88
5	$\text{CHOCHO}$ <sup>e</sup>	3 h	V, $[\text{CH}_2=\text{CHCH}_2\text{CH}(\text{OH})]_2$	2.4	68 <sup>h</sup>
6	$\text{CHOCH}_2\text{CH}_2\text{CH}_2\text{CHO}$ /	3 h	VI, $[\text{CH}_2=\text{CHCH}_2\text{CH}(\text{OH})\text{CH}_2]_2\text{CH}_2$	3.8	82 <sup>i</sup>
7	$\text{CH}_3\text{COCH}_2\text{CH}_2\text{OCOCH}_3$	12 h	VII, $\text{CH}_2=\text{CHCH}_2\text{C}(\text{OH})(\text{Me})\text{CH}_2\text{CH}_2\text{OC}(\text{O})\text{Me}$	3.9	90
8	$\text{CH}_3\text{COCH}(\text{OCH}_3)_2$ <sup>g</sup>	12 h	VIII, $\text{CH}_2=\text{CHCH}_2\text{C}(\text{OH})(\text{Me})\text{CH}(\text{OMe})_2$	2.3	59
			IX, $\text{CH}_2=\text{CHCH}_2\text{C}(\text{OH})(\text{Me})\text{CH}(\text{OH})\text{CH}_2\text{CH}=\text{CH}_2$	0.8	21 <sup>k</sup>
9	$\text{CH}_3\text{CH}(\text{OCH}_3)_2$	5 min	X, $\text{CH}_2=\text{CHCH}_2\text{CH}(\text{OH})\text{Me}$	2.1	98
10	$\text{CH}_2=\text{CHCH}(\text{OC}_2\text{H}_5)_2$	10 min	XI, $\text{CH}_2=\text{CHCH}(\text{OH})\text{CH}_2\text{CH}=\text{CH}_2$	2.4	98

<sup>a</sup> Conditions as for system A. <sup>b</sup> 25 mmol. <sup>c</sup> This is the time between the mixing of the reactants and the appearance of the distannoxane precipitate. <sup>d</sup> From a 37 wt.% commercial aqueous solution; 60 mmol. <sup>e</sup> From a 40 wt.% commercial aqueous solution and 50 mmol of  $\text{Bu}_2(\text{CH}_2=\text{CHCH}_2)_2\text{SnCl}$ . <sup>f</sup> From a 25 wt.% commercial aqueous solution and 50 mmol of  $\text{Bu}_2(\text{CH}_2=\text{CHCH}_2)_2\text{SnCl}$ . <sup>g</sup> 50 mmol of  $\text{Bu}_2(\text{CH}_2=\text{CHCH}_2)_2\text{SnCl}$ . <sup>h</sup> Stereoisomeric ratio = 56/44. <sup>i</sup> Stereoisomeric ratio = 54/47. <sup>k</sup> *erythro/threo* ratio = 75/25.

Table 2

Crotylstannation of aldehydes and acetals by (*E/Z*)-Bu<sub>2</sub>(CH<sub>3</sub>CH=CHCH<sub>2</sub>)<sub>2</sub>SnCl<sup>a</sup> in water (15 cm<sup>3</sup>) at 20°C

Run	Carbonyl compound	Reaction time <sup>b</sup>	Product	Yield	Isomeric composition (%)	
					g	%
11	(CH <sub>3</sub> ) <sub>2</sub> CHCHO	30 min	XII, Me <sub>2</sub> CCH(OH)CH(Me)CH=CH <sub>2</sub>	2.2	85	78
12	(CH <sub>3</sub> ) <sub>3</sub> CCHO	30 min	XIII, Me <sub>3</sub> CCH(OH)CH(Me)CH=CH <sub>2</sub>	1.9	67	46
13	C <sub>6</sub> H <sub>5</sub> CHO	20 min	XIV, PhCH(OH)CH(Me)CH=CH <sub>2</sub>	2.1	85	61
14	( <i>E,E</i> )-CH <sub>3</sub> CH=CHCH=CHCHO	20 min	XV, ( <i>E,E</i> )-Me(CH=CH) <sub>2</sub> CH(OH)CH(Me)CH=CH <sub>2</sub>	2.3	76	50
15	(-)-(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> CHO	20 min	XVI, (-)-Me <sub>2</sub> C=CH(CH <sub>2</sub> ) <sub>2</sub> CH(Me)CH <sub>2</sub> CH(OH)CH(Me)CH=CH <sub>2</sub>	1.8	85	60
16	CH <sub>3</sub> CH(OCH <sub>3</sub> ) <sub>2</sub>	5 min	XVII, CH <sub>2</sub> =CHCH(Me)CH(OH)Me	2.0	98	45

<sup>a</sup> 20 mmol; *E/Z* = 60/40. <sup>b</sup> This is the time between the mixing of reactants and the appearance of the distannoxane precipitate.

Table 3

1-Methylallylstannation of aldehydes, dialdehydes, ketones and acetals by  $\text{Bu}_2[\text{CH}_2=\text{CH}-\text{CH}(\text{CH}_3)]\text{SnCl}_2^a$  in water (15  $\text{cm}^3$ ) at 20 °C.

Run	Carbonyl compound (15 mmol)	Reaction time <sup>b</sup>	Products	Total yield g	Isomeric composition (%)		Ratio ( <i>erythro</i> / <i>threo</i> )
					Z	<i>erythro</i> <i>threo</i>	
17	$\text{CH}_3\text{CHO}$	5 min	XVIII, $\text{MeCH}=\text{CHCH}_2\text{CH}(\text{OH})\text{Me}$ XVII, $\text{CH}_2=\text{CHCH}(\text{Me})\text{CH}(\text{OH})\text{Me}$	1.5	99	—	—
18	$(\text{CH}_3)_3\text{CCHO}$	1 h	XIX, $\text{MeCH}=\text{CHCH}_2\text{CH}(\text{OH})\text{CMe}_3$ XIII, $\text{CH}_2=\text{CHCH}(\text{Me})\text{CH}(\text{OH})\text{CMe}_3$	1.7	80	—	—
19	$\text{C}_6\text{H}_5\text{CHO}$	30 min	XX, $\text{PhCH}(\text{OH})\text{CH}_2\text{CH}=\text{CHMe}$ XIV, $\text{PhCH}(\text{OH})\text{CH}(\text{Me})\text{CH}=\text{CH}_2$	2.2	90	—	—
20	$(E)\text{-CH}_3\text{CH}=\text{CHCHO}$	10 min	XXI, $(E)\text{-MeCH}=\text{CHCH}(\text{OH})\text{CH}_2\text{CH}=\text{CHMe}$ XXII, $(E)\text{-MeCH}=\text{CHCH}(\text{OH})\text{CH}(\text{Me})\text{CH}=\text{CH}_2$	1.6	84	—	—
21	$(\text{CH}_3)_2\text{CHCOCH}_3$	2 d	XXIII, $\text{Me}_2\text{CHC}(\text{Me})\text{OHCH}_2\text{CH}=\text{CHMe}$ XXIV, $\text{Me}_2\text{CHC}(\text{Me})\text{OHCH}(\text{Me})\text{CH}=\text{CH}_2$	0.4	19	—	—
22	$(\text{CH}_3)_2\text{CHCOCH}_3^c$	3 d	XXIII XXIV	0.5	23	—	—
23	$\text{CH}_3\text{CH}(\text{OCH}_3)_2$	10 min	XVIII XVII	1.4	93	—	—
					72	—	—
					—	18.5	9.5
							66/34

<sup>a</sup> Prepared in situ by redistribution of  $\text{Bu}_3\text{SnCH}_2\text{CH}=\text{CHCH}_3$  (15 mmol) and  $\text{Bu}_2\text{SnCl}_2$  (15 mmol). <sup>b</sup> This is the time between the mixing of the reactants and the appearance of the distannoxane precipitate. <sup>c</sup> Ratio  $[\text{Bu}_2\text{SnCl}_2]/[\text{Bu}_3\text{SnCH}_2\text{CH}=\text{CHCH}_3] = 1.2$ .

allylstannation in solvent-free conditions [12], by allylboration [13] and from reaction of allylmagnesium bromide with acrolein [14], respectively.

Allylstannation of the two functionalized ketones (run 7 and 8) gives high yields of products. Reactions of ketones with allyltin chlorides are known to give unsatisfactory results either in a solvent-free or organic solvent system [9]. This is due to the reversibility of the allylstannation process in such media [15–18]. In contrast, allylstannation in water is irreversible owing to precipitation of the distannoxane (cf. eq. 1).

Spectroscopic data indicate that the reaction involved in run 8 is stereochemically controlled: the *erythro*/*threo* ratio of the two diastereoisomers IX is 3/1.

**Crotylstannation.** Table 2 summarizes the results obtained from the reactions of (*E/Z*)- $\text{Bu}_2(\text{CH}_3\text{CH}=\text{CHCH}_2)\text{SnCl}$  (*E/Z* = 60/40) with aldehydes and with one acetal (system B). The reaction times are short and the observed yields are in the range 68–98%. A low *threo*-selectivity is favoured; such stereocontrol is in some cases higher than that previously found for the same reagents in a solvent-free mixture [9,10]. The slight increase in the *threo*-selectivity is considered to arise from the involvement of aquo-organotin species (see below). Furthermore, the observed *threo*-control is opposite to that found in reaction 2 [2].

**1-Methylallylstannation.** The results of system C, involving aldehydes, acetals, and ketones, are listed in Table 3. These results can be compared with our previous findings [19] using  $\text{Bu}_3\text{SnCH}_2\text{CH}=\text{CHCH}_3/\text{Bu}_2\text{SnCl}_2$  in a solvent-free mixture. Such systems in water can generate mixtures of linear (L) and branched (B) alcohols\*. Linear alcohols have the *Z*-configuration, whilst the branched alcohols are mixtures of *erythro* and *threo* isomers.

Comparison of the present data with those previously obtained under solvent-free conditions shows that the *Z*-configuration is still maintained, albeit at a low level. Here, the maximum value is 77% (see run 17) against 80–100% found in ref. 19. Mixtures of branched alcohols from aldehydes (runs 17–20) and the acetal (run 23) contain a large amount of the *erythro*-isomer (66–87%). The result from ethanal (run 17) is identical to that from the corresponding acetal (run 23).

Both runs 21 and 22, performed with methyl isopropyl ketone, are characterized by low yields (19% and 23%, respectively), after 2 and 3 days, respectively. The *Z*-configuration is still favoured, but no *stereo*-selectivity is observed: the *erythro*/*threo* ratio is about 1/1.

**Cyclohex-2-enylstannation.** Table 4 lists the results of the reactions of dibutylcyclohex-2-enyltin monochloride with aldehydes and acetals (system D). We stress that the sonification method [7] is unsuccessful with 3-bromocyclohexene.

As for the stereochemical assignments of the alcohols, we have adopted the criteria given in ref. 20. The *erythro*-isomer is the major isomer present in the alcohol mixtures (from 68% for run 27 to 100% for run 28). As with crotylstannation, the stereo-selectivity in water (here in terms of *erythro*-selectivity) is slightly increased compared to reactions in a solvent-free mixture [21].

**Phenylallylstannation.** Both 3-phenylallyldibutyltin and 1-phenylallyldibutyltin monochlorides react in water with propanal and ethanal dimethyl acetal (see Table

\* Alcohols having a crotyl moiety are termed linear, those having a 1-methylallyl moiety are named branched.

Table 4

Cyclohex-2-enylstannation of aldehydes and acetals by  $\text{Bu}_2\text{RSnCl}$  ( $\text{R}$  = cyclohex-2-enyl) <sup>a</sup> in water (15 ml) at 20 °C

Run	Carbonyl compound	Reaction time <sup>b</sup>	Product ( $\text{R}$ = cyclohex-2-enyl)	Total yield		Isomeric composition (%) <sup>c</sup>	
				g	%	erythro	threo
24	$\text{CH}_2\text{O}$ <sup>d,e</sup>	20 min	XXV, $\text{RCH}_2\text{OH}$	1.8	80	—	—
25	$\text{CH}_3\text{CHO}$ <sup>e</sup>	20 min	XXVI, $\text{RCH}(\text{Me})\text{OH}$	1.9	75	65	35
26	$\text{C}_2\text{H}_5\text{CHO}$ <sup>f</sup>	20 min	XXVII, $\text{RCH}(\text{Et})\text{OH}$	2.3	83	75	25
27	$(\text{CH}_3)_2\text{CHCHO}$ <sup>f</sup>	30 min	XXVIII, $\text{Me}_2\text{CHCH}(\text{OH})\text{R}$	2.1	68	78	22
28	$(E)\text{-CH}_3\text{CH}=\text{CHCHO}$ <sup>f</sup>	40 min	XXIX, $(E)\text{-MeCH}=\text{CHCH}(\text{OH})\text{R}$	1.6	53	100	—
29	$\text{CH}_3\text{CH}(\text{OCH}_3)_2$ <sup>f</sup>	20 min	XXVI	2.1	85	62	38
30	$\text{C}_2\text{H}_5\text{CH}(\text{OC}_2\text{H}_5)_2$ <sup>f</sup>	20 min	XXVII	2.3	82	67	33

<sup>a</sup> Prepared in situ by redistribution of  $\text{Bu}_3\text{SnR}$  (20 mmol) and  $\text{Bu}_2\text{SnCl}_2$  (20 mmol). <sup>b</sup> This is the time between the mixing of the reactants and the appearance of the distannoxane precipitate. <sup>c</sup> From GLC measurements. <sup>d</sup> From a 37 wt.% commercially available aqueous solution. <sup>e</sup> 60 mmol. <sup>f</sup> 20 mmol.

5; obtained from  $\text{Bu}_3\text{SnCH}_2\text{CH}=\text{CHC}_6\text{H}_5/\text{Bu}_2\text{SnCl}_2$ ). Mixtures of linear and branched alcohols are formed in the case of propanal whereas the linear alcohol is the only product from the acetal (run 34). Both Systems E and F are characterized by low reactivity and low yields. The sonification method [7] does not work.

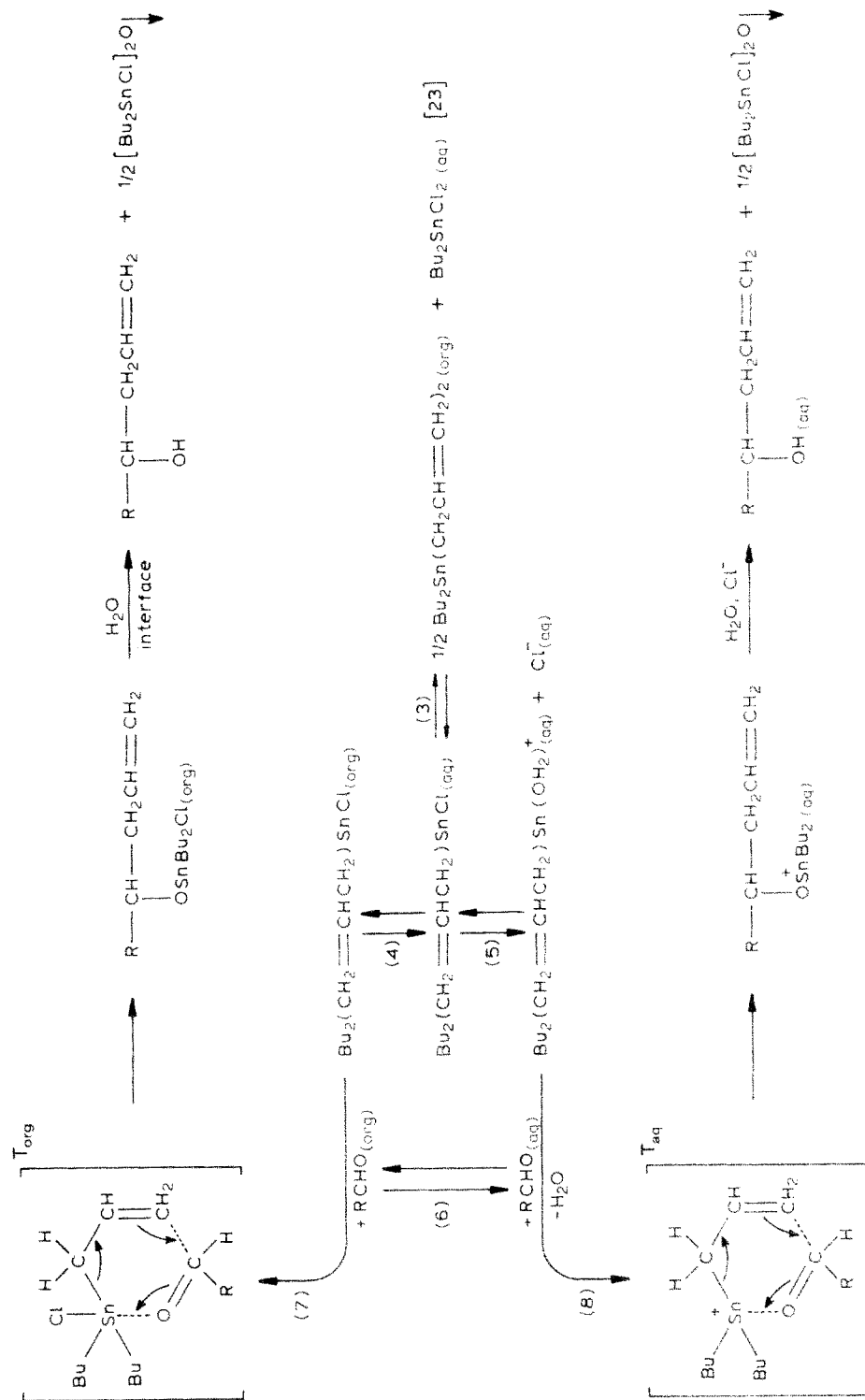
*General comments.* The present procedure consists of the following features: (1) The reactions are one-pot syntheses and yields are generally high. (2) Reaction times for the addition of allyl-, crotyl-, and cyclohex-2-enyl-tin monochlorides are generally so short that the procedure is much more convenient than other methods

Table 5

Cinnamylstannation of propanal and ethanal dimethyl acetal by  $\text{Bu}_2(\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2)\text{SnCl}$  (20 mmol) in water (15  $\text{cm}^3$ ) at 20 °C

Run	Carbonyl compound <sup>a</sup>	Time	Products	Total yield		Isomeric composition (%)	
				g	%	L <sup>b</sup>	B <sup>b</sup>
31 <sup>c</sup>	$\text{C}_2\text{H}_5\text{CHO}$	4 d	XXX, $\text{C}_2\text{H}_5\text{CH}(\text{OH})\text{CH}_2\text{CH}=\text{CHC}_6\text{H}_5$ (L) XXXI, $\text{C}_2\text{H}_5\text{CH}(\text{OH})\text{CH}(\text{C}_6\text{H}_5)\text{CH}=\text{CH}_2$ (B)	1.5	42	70	30
32 <sup>d</sup>	$\text{C}_2\text{H}_5\text{CHO}$	2 d	XXX,	1.3	37	85	15
33 <sup>d</sup>	$\text{C}_2\text{H}_5\text{CHO}$	4 d	XXXI,	1.4	40	66	34
34 <sup>d</sup>	$\text{CH}_3\text{CH}(\text{OCH}_3)_2$	1 d	XXXII, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}=\text{CHC}_6\text{H}_5$ (L)	0.9	28	100	—

<sup>a</sup> 20 mmol. <sup>b</sup> L = linear alcohol; B = branched alcohol. <sup>c</sup> Work up as system E. <sup>d</sup> Work up as system F.



Scheme 1



described in the literature. (3) Commercially available aqueous solutions of carbonyl compounds can be used. (4) The method can be extended to other organotin monochlorides having 2,3-unsaturated groups and shows wider applications than those reported in refs. 2 and 7.

Nevertheless, our procedure has limited success when applied to compounds with bulky groups, e.g. ketones. It is our hope to overcome this limitation by using the more reactive alk-2-enyltin di- and tri-halides [1,2].

The reactive organotin species are the aqueous organometallic cations  $\text{Bu}_2\text{RSn}^+_{(\text{aq})}$  [22] (R = 2,3-unsaturated organic group) and the molecular species,  $\text{Bu}_2\text{RSnCl}$ . The former species react in the aqueous phase (aq), whereas the latter will act in the organometallic phase (org). Evidence for the involvement of the cations was formed from runs carried out in homogeneous aqueous solutions of allyltin monochloride and carbonyl compounds at low concentrations. Under such conditions, precipitation of the distannoxane is practically instantaneous and the reactions occur quantitatively.

Reaction 1 does not represent the total process: an exhaustive interpretation of the overall process must take into account the partition between the two layers and reactions occurring in each phase. On the basis of our findings [23], we propose the reactions shown in Scheme 1.

Reaction 7 has been shown to occur through an hexacyclic transition state [9,11] in the organometallic phase ( $T_{\text{org}}$ ). The observed allylic rearrangements, together with the stereocontrols (similar to those found in a solvent-free system), suggest that a cyclic transition state is also probable in water ( $T_{\text{aq}}$ ).

The occurrence of reactions 7 and 9 depends upon the heterogeneous, equilibria 4 and 6 and the solvolytic equilibrium 5 [22]. The two addition processes 7 and 8, are substantially different: in  $T_{\text{org}}$ , the tin centre is penta-coordinate; in  $T_{\text{aq}}$ , the tin centre is tetra-coordinate. Thus, the addition process 8 may proceed through a coordination step forming the ionic adduct  $\text{Bu}_2\text{Sn}^+\text{OCH(R)CH}_2\text{CH=CH}_{2(\text{aq})}$ ; the cyclic transition state,  $T_{\text{aq}}$ , forms next with a probable higher degree of stereocontrol than  $T_{\text{org}}$ . In fact, we have observed that the stereoselectivity, although still poor, increases with respect to that found in a solvent-free mixture [9,10]. Further work is in progress in our laboratories on the stereochemistry of these reactions in water and their practical applications.

## Experimental

Allyldibutyltin chloride (1), 3-methylallyltributyltin (7), crotyldibutyltin chloride (2), 3-phenylallyltributyltin (8), cyclohex-2-enyltributyltin (9) and dibutyltin dichloride (10) were prepared as previously described [10,24–27].

Commercial samples of the organic substrates were distilled before use. Commercially available aqueous solutions of aldehydes were used as received.

The products were characterized by their IR,  $^1\text{H}$ , and  $^{13}\text{C}$  NMR spectra, recorded on a Perkin–Elmer Model 599B spectrophotometer and a Jeol FX90Q FT NMR spectrometer, respectively.

The isomeric compositions of the product mixtures were determined by  $^{13}\text{C}$  NMR spectroscopy and GLC analysis [28,29].  $^{13}\text{C}$  NMR spectra were recorded using sufficiently long pulse intervals to avoid saturation of the nuclear spins (at

least 25 s), and the nuclear Overhauser effect (NOE) was suppressed by gated decoupling [30].

*System A: Reactions of 1.* A solution of organic substrate (25 mmol) in water (15 cm<sup>3</sup>) was added to an equimolar amount of **1**, with stirring, at 20°C. After an appropriate time, estimated by the appearance of a white precipitate of tetrabutyl-1,3-dichlorodistannoxane (cf. eq. 1), the mixture was worked-up as previously described [1]; the results are given in Table 1.

*System B: Reactions of 2.* Runs were performed as above, using equimolar amounts of organic substrate and compound **2** (20 mmol); the results are given in Table 2.

*System C: Reactions of 3 (generated from 7 and 10).* A solution of organic substrate (15 mmol) in water (15 cm<sup>3</sup>) was added to an equimolar amount of solid Bu<sub>3</sub>SnCl<sub>2</sub> (15 mmol) with stirring at 20°C. Then compound **7** (15 mmol) was quickly added. The mixing procedure allows the preparation in situ of compound **3** in an aqueous medium, at the same initial stage of the addition reaction [19,23]. After an appropriate time (precipitation of the distannoxane), the mixture was worked-up as above; the results are given in Table 3.

*System D: Reactions of 4 (generated from 9 and 10).* Equimolar amounts (20 mmol) of compounds **9** and **10** were mixed at 0°C. The solvent-free mixture was stirred, and allowed to reach 20°C. After 1 h \*, solution of organic substrate (20 mmol) in water (15 cm<sup>3</sup>) was added with stirring. Work-up of the mixture was as above, after the appearance of the distannoxane precipitate; the results are given in Table 4.

*System E: Reactions of 5 (generated from 8 and 10).* Equimolar amounts (20 mmol) of compounds **8** and **10** were mixed, with stirring, at 20°C. After 1 h \*\*, a solution of organic substrate (20 mmol) in water (15 cm<sup>3</sup>) was added, and work-up of the mixture was made as above.

*System F: Reactions of 6 (generated from 8 and 10).* A solution of organic substrate (20 mmol) in water (15 cm<sup>3</sup>) was added to solid **10** (20 mmol) with stirring at 20°C. Then compound **8** (20 mmol) was quickly added. After an appropriate time, the mixture was worked-up as above. The procedure used is similar to that of system C: in such a case **6** can be prepared in situ at the initial stage of the addition reaction.

#### *Characterization of the prepared alcohols*

The physical properties of the following alcohols were in agreement with literature values:

Compounds: I, 3-butene-1-ol [31]; II, 1,5,7-nonatriene-4-ol [32]; VII, 1-acetoxy-3-methyl-5-hexene-4-ol [33]; XI, 1,5-hexadiene-3-ol [12]; XII, 3,5-dimethyl-1-hexene-4-ol [10]; XIII, 3,5,5-trimethyl-1-hexene-4-ol [10]; XIV, 1-phenyl-2-methyl-3-butene-1-ol [10]; XVII, 3-methyl-1-pentene-4-ol [10]; XVIII, (Z)-4-hexene-2-ol [19]; XIX, (Z)-2,3-dimethyl-5-heptene-3-ol [19]; XX, (Z)-1-phenyl-3-pentene-1-ol [19]; XXI, (Z)-2,6-octadiene-4-ol [34]; XXIII, (Z)-2,3-dimethyl-5-heptene-3-ol [19]; XXIV, 2,3,4-trimethyl-5-hexene-3-ol [17]; XXVI, 1-(1'-hydroxyethyl)cyclohex-2-ene

\* This time (see ref. 27) allows for the preparation in situ of **4**, along with Bu<sub>3</sub>SnCl.

\*\* This time is necessary to allow for the generation in situ of compound **5**.

[20,35]; XXVIII, 1-(1'-hydroxy-2'-methylpropyl)cyclohex-2-ene [20]; XXX, 1-phenyl-1-hexene-4-ol; XXXI, 3-phenyl-1-hexene-4-ol; and XXXII, 1-phenyl-1-pentene-4-ol [36,37].

Details of the IR and  $^{13}\text{C}$  NMR data of the following compounds are available from the authors: III, 1,5,7-decatriene-4-ol; IV, (–)-6,10-dimethyl-1,9-undecadiene-4-ol [38]; V, 1,7-octadiene-4,5-diol [7]; VI, 1,10-undecadiene-4,8-diol [7]; VIII, 1,1-dimethoxy-2-methyl-4-pentene-2-ol [7,36]; IX, 4-methyl-1,7-octadiene-4,5-diol [7]; X, 4-pentene-2-ol [37]; XV, 3-methyl-1,5,7-nonatriene-4-ol; XVI, (–)-3,6,10-trimethyl-1,9-undecadiene-4-ol; XXII, 3-methyl-1,5-heptadiene-4-ol; XXV, 1-(1'-hydroxymethyl)cyclohex-2-ene; XXVII, 1-(1'-hydroxypropyl)cyclohex-2-ene; and XXIX, 1-(1'-hydroxybut-2'-enyl)cyclohex-2-ene.

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