

ALLYLSTANNATION

X *. STEREOCHEMICAL COURSE OF THE ADDITION REACTIONS OF (*E/Z*)- $\text{Bu}_3\text{SnCH}_2\text{CH}=\text{CHCH}_3$ WITH ALDEHYDES IN THE PRESENCE OF LEWIS ACIDS (Bu_2SnCl_2 , $\text{BF}_3 \cdot \text{Et}_2\text{O}$, AND TiCl_4)

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(Received August 4th, 1986)

Summary

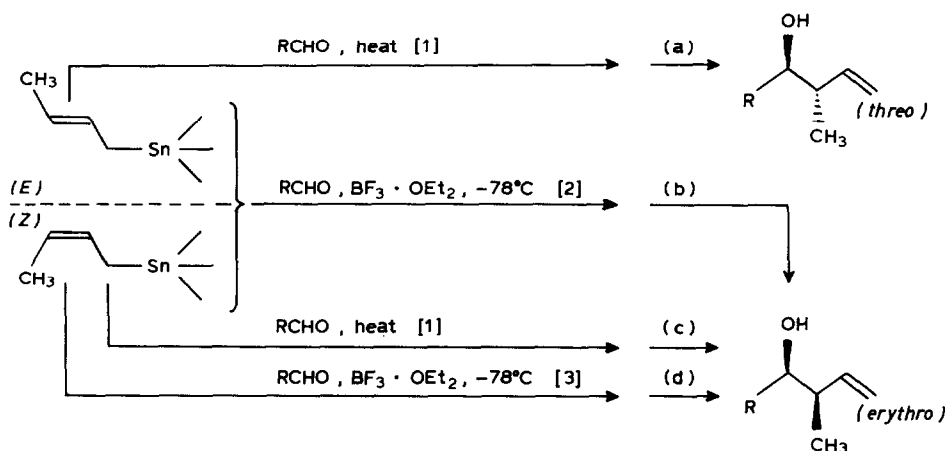
Reactions between (*E/Z*)- $\text{Bu}_3\text{SnCH}_2\text{CH}=\text{CHCH}_3$ and RCHO ($\text{R} = \text{CH}_3$, C_2H_5 , $n\text{-C}_3\text{H}_7$, $n\text{-C}_4\text{H}_9$, $n\text{-C}_5\text{H}_{11}$, $(\text{CH}_3)_2\text{CH}$, $(\text{CH}_3)_3\text{C}$, C_6H_5 , $\text{CH}_2=\text{CH}$, $\text{CH}_2=\text{C}(\text{CH}_3)$, (*E*)- $\text{CH}_3\text{CH}=\text{CH}$, (*E*)- $\text{C}_3\text{H}_7\text{CH}=\text{CH}$, (*E*)- $\text{C}_6\text{H}_5\text{CH}=\text{CH}$) have been carried out in the presence of Lewis acids such as Bu_2SnCl_2 , $\text{BF}_3 \cdot \text{Et}_2\text{O}$, and TiCl_4 . The stereochemical course of the reactions to give homoallylic alcohols does not necessarily depend on the formation of intermediate Lewis acid-aldehyde complexes, but rather upon the formation of allylmetal compounds (e.g., $\text{Bu}_2\text{ClSnCH}_2\text{CH}=\text{CHCH}_3$, $\text{Bu}_2\text{ClSnCH}(\text{CH}_3)\text{CH}=\text{CH}_2$, $\text{Cl}_3\text{TiCH}_2\text{CH}=\text{CHCH}_3$, etc.) which are the actual species which react with the carbonyl compounds. $\text{Bu}_3\text{SnCH}_2\text{CH}=\text{CHCH}_3$ does not undergo the reaction.

Introduction

Only a few addition reactions [1–3] with aldehydes involving 2-butenyltri-*n*-butyltin have been examined; they can be summarized as shown in Scheme 1.

Reactions a, c, and d have stereospecific courses; b is characterized by a high stereoselectivity, and the condensation seems to take place regardless of the geometry of the crotyl unit [2].

* For Part IX, see ref. 16.



SCHEME 1

Stereoselectivity is encountered in many addition reactions in which Lewis acids are used, e.g. $\text{BF}_3 \cdot \text{OEt}_2$ [2–15], Et_2AlCl_2 [5], Et_2AlCl [8], MgCl_2 [9], MgBr_2 [4,8,9], MgI_2 [8], $\text{Mg}(\text{ClO}_4)_2$ [9], ZnBr_2 [8,9], ZnI_2 [4,8,9], ZrCl_4 [8], TiCl_4 [4,7–9], SnCl_4 [4,8,16], SnBr_4 [16], BuSnCl_3 [16,17], and R_2SnCl_2 ($\text{R} = \text{Me}$, Bu , and Ph) [18,19]: in such cases the relevant condensations occur very easily. In the absence of Lewis acids the substrates $\text{R}_3\text{SnCH}_2\text{CH}=\text{CHR}'$ ($\text{R}' = \text{H}$ or organic group) normally react only at elevated temperatures [1], and the reactions take place under mild conditions only when activated carbonyl compounds are used [1,3,25,26]. On the other hand, allylstannanes [16–20,23,24], which are examples of activated organotin substrates, react even under mild conditions.

The features of the Lewis-acid mediated reactions can be understood in terms of catalytic effects [2,3,21] involving activation of the carbonyl group via coordination of the Lewis acid with the oxygen atom or a reaction of the Lewis acid with the organotin substrate. In this latter case the actual compounds undergoing reaction with aldehyde are new species formed by redistribution of the system $\text{R}_3\text{SnCH}_2\text{CH}=\text{CHR}'/\text{Lewis acid}$, or are isomeric species subsequently formed under catalysis by the Lewis acid itself [27].

Allylbutyltin halides are the actual reactants in allylstannation, and formed from the systems:

$(E/Z)\text{-Bu}_3\text{SnCH}_2\text{CH}=\text{CHCH}_3$ (or $\text{Bu}_3\text{SnCH}_2\text{CH}=\text{CH}_2$)/ $\text{R}_{4-n}\text{SnX}_n/\text{RCHO}$ where $\text{X} = \text{halogen}$, $n = 2, 3$, and 4 [16–20,22–24]. A typical example from those previously reported involves the system $\text{Bu}_3\text{SnCH}_2\text{CH}=\text{CHCH}_3 + \text{RCHO} \searrow \text{Bu}_2\text{SnCl}_2$ *: in this case the addition of the non-reactive mixture $\text{Bu}_3\text{SnCH}_2\text{CH}=\text{CHCH}_3 + \text{RCHO}$ to neat Bu_2SnCl_2 at room temperature results in formation of homoallylic alcohols ($\text{RCH}(\text{OH})\text{CH}_2\text{CH}=\text{CHCH}_3$) with high *Z*-convergence because the actual reactant is $\text{Bu}_2\text{ClSnCH}(\text{CH}_3)\text{CH}=\text{CH}_2$ [19].

* The arrow indicates the mode of mixing; i.e., in this case the butene-aldehyde is added to the Bu_2SnCl_2 .

In extension of our work on allylstannation, we report here results for the systems:

$RCHO \searrow (E/Z)\text{-Bu}_3\text{SnCH}_2\text{CH=CHCH}_3 + \text{Bu}_2\text{SnCl}_2$, ($R = \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_3\text{H}_7, n\text{-C}_4\text{H}_9, n\text{-C}_5\text{H}_{11}, (\text{CH}_3)_2\text{CH}, (\text{CH}_3)_3\text{C}, \text{C}_6\text{H}_5, \text{CH}_2=\text{CH}, \text{CH}_2=\text{C}(\text{CH}_3), (E)\text{-CH}_3\text{CH=CH}, (E)\text{-C}_3\text{H}_7\text{CH=CH}, (E)\text{-C}_6\text{H}_5\text{CH=CH}$, and show that this kind of Lewis acid mediated reaction can involve *threo*- or *erythro*-selectivity. Results obtained by use of other Lewis acids, such as $\text{BF}_3 \cdot \text{Et}_2\text{O}$ and TiCl_4 are also presented.

Experimental

Details of the IR and NMR apparatus and of the preparation of starting materials have been presented previously [16–20,22–24]. The ^1H , ^{13}C , and ^{119}Sn NMR spectra were recorded with a Jeol FX90Q Fourier transform NMR spectrometer.

Addition systems

System A: $RCHO \searrow (E/Z)\text{-Bu}_3\text{SnCH}_2\text{CH=CHCH}_3$ (**1**) + Bu_2SnCl_2 (**2**). Compounds **1** (20 mmol) and **2** (30 mmol) were mixed (neat) with stirring. After 150 min, or 10 d, or “infinite” time (about 50 d) the appropriate aldehyde (20 mmol) was added at such a rate that the temperature could be maintained at 25°C , the addition taking about 5 min. The progress of the reaction was then monitored by infrared spectroscopy as described previously [19]. At the end of the reaction aqueous NH_4Cl was added, and the carbinol and the organotin compounds were extracted with ethyl ether and subsequently isolated by distillation.

System B: $(E/Z)\text{-Bu}_3\text{SnCH}_2\text{CH=CHCH}_3 \searrow RCHO + \text{BF}_3 \cdot \text{Et}_2\text{O}$. The procedure was the same as that described in ref. 2. The tin compound (20 mmol) was added to a solution of $RCHO$ (20 mmol) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (40 mmol) in 40 ml of CH_2Cl_2 at -78°C , and the mixture was allowed to warm slowly to room temperature, then treated as above.

System C: $(\text{CH}_3)_2\text{CHCHO} \searrow (E/Z)\text{-Bu}_3\text{SnCH}_2\text{CH=CHCH}_3 + \text{BF}_3 \cdot \text{Et}_2\text{O}$. The amounts of reagents and the final work-up were as described above. It should be noted that the aldehyde was added to the CH_2Cl_2 solution prepared from Lewis acid and **1**.

System D: $(E/Z)\text{-Bu}_2\text{ClSnCH}_2\text{CH=CHCH}_3$ (**3**) $\searrow (\text{CH}_3)_2\text{CHCHO} + \text{BF}_3 \cdot \text{Et}_2\text{O}$. Compound **3** was added to a mixture of $(\text{CH}_3)_2\text{CHCHO}$ (20 mmol) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (40 mmol) at -78°C in 40 ml of CH_2Cl_2 . The mixture was allowed to warm to room temperature then worked up as before.

System E: $(E/Z)\text{-Bu}_2\text{ClSnCH}_2\text{CH=CHCH}_3 \searrow (\text{CH}_3)_2\text{CHCHO} + \text{TiCl}_4$. Compound **3** (20 mmol) was added to a mixture of $(\text{CH}_3)_2\text{CHCHO}$ (20 mmol) and TiCl_4 (20 mmol) at -78°C in 40 ml of CH_2Cl_2 . The mixture was allowed to warm to room temperature and then worked up as before.

Analysis of the redistributed compounds in the system $(E/Z)\text{-Bu}_3\text{SnCH}_2\text{CH=CHCH}_3/\text{Bu}_2\text{SnCl}_2$ (1/1.5 ratio, 25°C)

A mixture of $(E/Z)\text{-Bu}_3\text{SnCH}_2\text{CH=CHCH}_3$ (25 mmol) and Bu_2SnCl_2 (37.5 mmol) was allowed to react for the specified time at 25°C . Analysis of the mixture was by ^{119}Sn NMR spectroscopy, using the chemical shift data given in Table 1. The composition of the isomeric organotin mixtures as function of time is shown in Table 2.

TABLE 1

^{119}Sn NMR CHEMICAL SHIFTS (δ ppm) ^{a,b} FOR COMPOUNDS OF THE TYPE $\text{Bu}_{3-n}\text{X}_n\text{-Sn}(\text{C}_4\text{H}_7)$ ^c, WHERE $\text{X} = \text{Cl}$ AND $n = 0, 1$ (298 K)

Compound	Isomer		
	Z	E	α -Methallyl
$\text{Bu}_3\text{Sn}(\text{C}_4\text{H}_7)$	-19.4	-15.3	-
$\text{Bu}_2\text{ClSn}(\text{C}_4\text{H}_7)$	+119.9	+117.6	+110.7

^a Positive values denote high frequency shifts from the reference $(\text{CH}_3)_4\text{Sn}$. ^b The measurements were carried out on neat liquids directly from the reaction mixture. ^c C_4H_7 refers to all three isomeric forms: Z-crotyl, E-crotyl, and α -methallyl.

TABLE 2

CHANGE IN THE COMPOSITION OF THE MIXTURES OF ISOMERIC ORGANOTIN COMPOUNDS WITH TIME FOR THE SYSTEM (*E/Z*)- $\text{Bu}_3\text{SnCH}_2\text{CH}=\text{CHCH}_3$, Bu_2SnCl_2 IN 1/1.5 RATIO AT 25°C

Time	Composition of the mixture of isomers of $\text{Bu}_2\text{ClSn}(\text{C}_4\text{H}_7)$			Z/E ratio
	Z (%)	E (%)	α -Meth (%)	
20 min	70	5	25	14.0/1
70 min	72	10	18	7.2/1
120 min	73	13	15	5.6/1
150 min	74	14	12	5.3/1 ^b
7 h	75	15	10	5.0/1
24 h	79	17	4	4.6/1
27 h	82	18	-	4.5/1
4 d	62	38	-	1.6/1
10 d	55	45	-	1.2/1 ^b
19 d	50	50	-	1.0/1
26 d	48	52	-	0.9/1
∞ ^a	40	60	-	0.7/1 ^b

^a ≥ 50 days. ^b Mixtures used in the addition reactions.

Determination of the isomeric composition of the recovered alcohol mixtures by ^{13}C NMR spectroscopy

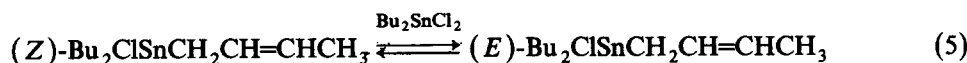
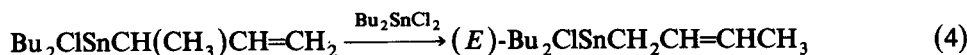
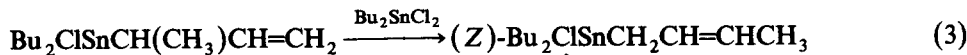
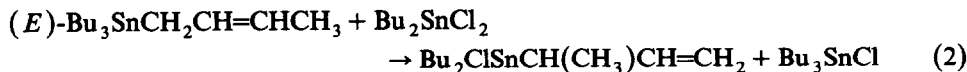
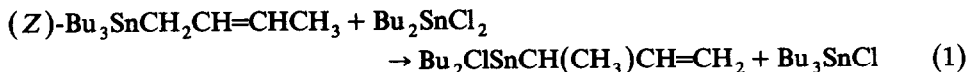
Characterization of the produced alcohols and analysis of the recovered mixtures was by ^{13}C NMR and IR spectroscopy and GLC analysis, as described previously [27,28]. For quantitative determinations the ^{13}C NMR spectra were recorded using sufficiently long pulse intervals to avoid saturation of the nuclear spins (at least 25 s) and the nuclear Overhauser effect (NOE) was suppressed by gated decoupling [29].

Results and discussion

The results for the system (*E/Z*)- $\text{Bu}_3\text{SnCH}_2\text{CH}=\text{CHCH}_3/\text{Bu}_2\text{SnCl}_2$ (in 1/1.5 ratio at 25°C) are shown in Table 2 *.

* They should be compared with results described in ref. 30.

The following reactions must be considered:



The $\text{Bu}_2\text{ClSnCH(CH}_3\text{)CH=CH}_2$ initially produced in reactions 1 and 2 isomerizes to yield mixtures of *Z*- and *E*- $\text{Bu}_2\text{ClSnCH}_2\text{CH=CHCH}_3$ of variable composition (reaction 3 and 4). Formation of the *Z*-isomer (see Table 2) is kinetically favoured even though thermodynamic factors lead subsequently to formation of the *E*-isomer (reaction 5), which has a higher configurational stability, like other *E*-crotyltins [31,32]. The reaction rates for formation of *Z*-isomers (reactions 1 and 3) are higher than those for formation of *E*-isomers (reactions 2 and 4); the rate constant for the isomerization $Z \rightarrow E$ depicted in equation 5 is ca. $2 \times 10^{-6} \text{ sec}^{-1}$ at 25°C .

Addition of aldehydes to chloroorganotin compounds could be brought about by use of mixtures of appropriate isomeric composition used at a specific time after mixing of $\text{Bu}_3\text{SnCH}_2\text{CH=CHCH}_3$ and Bu_2SnCl_2 . Table 3 lists the results obtained for three different mixtures of chloroorganotin compounds taken after 150 min, 10 days, and "infinite" time: Table 2 shows the corresponding *Z/E* ratios (marked ^b).

It can be seen from the results for reactions of group 1 (cf. Table 3) that addition of non-reactive mixtures of (*E/Z*)- $\text{Bu}_3\text{SnCH}_2\text{CH=CHCH}_3$ and RCHO to Bu_2SnCl_2 leads to formation of *Z*-homoallylic alcohols from the $\text{Bu}_2\text{ClSnCH(CH}_3\text{)CH=CH}_2$ species rapidly produced via reactions 1 and 2 [19].

In contrast reactions of group 2, 3, and 4, involve additions of the appropriate aldehyde to chloroorganotin mixtures in which the α -methylallylchlorotin isomer is present in smaller amount or totally absent. The *erythro/threo* ratios of the recovered homoallylic alcohols can be roughly related to the *Z/E* isomer ratios for the chloroorganotins (cf. Table 3).

The change in stereoselectivity on going from organotin mixtures in which the *Z*-isomer predominates (group 2) to the equilibrated thermodynamic mixture in which the *E*-isomer predominates (group 4), can be accounted for many runs in terms of the stereospecificities of the reactions.

It must be emphasized that the change in stereoselectivity occurs in a system in which the presence of a Lewis acid such as Bu_2SnCl_2 leads to formation of new reactants. The observations are not surprising, since stereoselectivity is encountered in many "Lewis acid mediated reactions" of triorganocrotyltins and carbonyl compounds [2-19].

The important question thus arises of whether the stereoselectivity arises from catalytic effects, by activation of the aldehyde, or by the formation of new species through processes involving the triorganoallyltin substrates and Lewis acids. The

TABLE 3

RESULTS OF THE ADDITION REACTIONS FOR SYSTEMS A ($\text{RCHO} \searrow \text{Bu}_3\text{SnCH}_2\text{CH}=\text{CHCH}_3$ + Bu_2SnCl_2) AND PREVIOUS SYSTEMS ^a $\text{Bu}_3\text{SnCH}_2\text{CH}=\text{CHCH}_3$ + $\text{RCHO} \searrow \text{Bu}_2\text{SnCl}_2$, USED NEAT AT 25°C

Group	Run	Time of mixing (Z/E) ^b	RCHO R =	Total yield (%)	Homoallylic alcohols isomeric composition (%)				erythro/ threo ratio
					erythro	threo	Z	E	
1 ^a	1		C_2H_5	94	8	5	87	—	—
	2		$\text{C}_2\text{H}_5(\text{CH}_3)\text{CH}$	82	12	8	80	—	—
	3		$(\text{CH}_3)_2\text{CH}$	85	7	6	87	—	—
	4		$(\text{CH}_3)_3\text{C}$	82	—	—	100	—	—
	5		C_6H_5	95	—	—	100	—	—
2	6	150 min	CH_3	78	55	30	15	—	1.8/1
	7	(5.3/1)	C_2H_5	70	56	32	12	—	1.7/1
	8		$(\text{CH}_3)_2\text{CH}$	80	50	37	13	—	1.3/1
	9		$(\text{CH}_3)_2\text{CH}$	78	52	40	8	—	1.3/1
	10		$(\text{CH}_3)_3\text{C}$	70	77	15	8	—	5.1/1
	11		C_6H_5	72	77	15	8	—	5.1/1
	12		$\text{CH}_2=\text{CH}$	83	73	16	11	—	4.6/1
	13		$\text{CH}_2=\text{C}(\text{CH}_3)$	82	75	12	13	—	6.2/1
	14		$\text{CH}_2=\text{C}(\text{CH}_3)$	80	72	14	14	—	5.1/1
	15		(E)- $\text{CH}_3\text{CH}=\text{CH}$	71	67	20	13	—	3.3/1
	16		(E)- $\text{C}_3\text{H}_7\text{CH}=\text{CH}$	76	71	18	11	—	3.9/1
3	17	10 ^d	C_2H_5	97	55	45	—	—	1.2/1
	18	(1.2/1)	C_3H_7	75	54	46	—	—	1.2/1
	19		$(\text{CH}_3)_2\text{CH}$	80	33	66	—	—	0.5/1
	20		$\text{CH}_2=\text{CH}$	93	60	40	—	—	1.5/1
	21		$\text{CH}_2=\text{C}(\text{CH}_3)$	78	55	45	—	—	1.2/1
	22		(E)- $\text{CH}_3\text{CH}=\text{CH}$	75	56	44	—	—	1.3/1
	23		(E)- $\text{C}_3\text{H}_7\text{CH}=\text{CH}$	78	54	46	—	—	1.2/1
	24		$\text{C}_6\text{H}_5\text{CH}=\text{CH}$	80	55	45	—	—	1.2/1
	25		C_6H_5	78	54	46	—	—	1.2/1
4	26	∞	C_2H_5	80	38	62	—	—	0.6/1
	27	(0.7/1)	n- C_4H_9	72	45	55	—	—	0.8/1
	28		n- C_5H_{11}	79	45	55	—	—	0.8/1
	29		$(\text{CH}_3)_2\text{CH}$	82	35	65	—	—	0.5/1
	30		$(\text{CH}_3)_2\text{CH}$	79	42	58	—	—	0.7/1
	31		$\text{CH}_2=\text{CH}$	80	44	56	—	—	0.8/1
	32		$\text{CH}_2=\text{C}(\text{CH}_3)$	75	37	63	—	—	0.6/1
	33		(E)- $\text{CH}_3\text{CH}=\text{CH}$	70	44	56	—	—	0.8/1
	34		(E)- $\text{C}_3\text{H}_7\text{CH}=\text{CH}$	85	45	55	—	—	0.8/1
	35		C_6H_5	75	44	56	—	—	0.8/1

^a Previous data; see ref. 19. ^b (Z/E) ratio of $\text{Bu}_2\text{ClSnCH}_2\text{CH}=\text{CHCH}_3$.

results in Tables 3 and 4 confirm that the stereoselectivity in these "mediated reactions" arises from the interaction of aldehydes with new species formed in the reaction between $\text{Bu}_3\text{SnCH}_2\text{CH}=\text{CHCH}_3$ and the Lewis acid.

Runs for system B of Table 4 show that work-up in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$, such as was used previously [2] *, leads to a mixture of three isomeric alcohols when

* The sole difference was the use of 20 mmol of organotin instead of 2 mmol.

TABLE 4
RESULTS OF THE ADDITION REACTIONS FOR SYSTEMS B, C, D AND E

System	Run	Lewis Acid	Organotin	E/Z ratio	RCHO R =	Total yield (%)	Homocyclic alcohols isomeric composition (%)			erythro/threo ratio
							erythro	threo	Z	E
B	36	BF ₃ ·Et ₂ O	(E/Z)-Bu ₃ SnCH ₂ CH=CHCH ₃	70/30	(CH ₃) ₂ CH	88	55	9	36	-
	37	BF ₃ ·Et ₂ O	(E/Z)-Bu ₃ SnCH ₂ CH=CHCH ₃	36/64	(CH ₃) ₃ C	70	59	9	4	28
C	38	BF ₃ ·Et ₂ O	(E/Z)-Bu ₃ SnCH ₂ CH=CHCH ₃	52/48	(CH ₃) ₂ CH	89	54	11	5	30
D	39	BF ₃ ·Et ₂ O	(E/Z)-Bu ₂ ClSnCH ₂ CH=CHCH ₃	46/54	(CH ₃) ₂ CH	75	33	66	-	-
	40	BF ₃ ·Et ₂ O	(E/Z)-Bu ₂ ClSnCH ₂ CH=CHCH ₃	46/54	(CH ₃) ₂ CH	72	33	66	-	-
E	41	TiCl ₄	(E/Z)-Bu ₂ ClSnCH ₂ CH=CHCH ₃	46/54	(CH ₃) ₂ CH	80	74	26	-	-

$R = (CH_3)_2CH$ (run 36) and four isomeric alcohols when $R = (CH_3)_3C$ (run 37). The previously observed [2] *erythro*-selectivity is maintained, but the isolation of *Z*- and *E*-homoallylic alcohols suggests that these come from reactions of the aldehyde with substrates containing an α -methylallyl group, presumably an intermediate formed from the initial organotin substrate and the added $BF_3 \cdot Et_2O$ Lewis acid. These results are rather similar to those for reactions of group 2 in Table 3. When inverse addition is used in procedure C, the aldehyde added to the mixture of $Bu_3SnCH_2CH=CHCH_3/BF_3 \cdot Et_2O$ actually reacts with a mixture of new allylmetal substrates, the composition of which is different from that in run 36, as revealed by the different proportions of isolated isomer alcohols. The results for system D are significant in that the presence of $BF_3 \cdot Et_2O$ does not affect the reaction between the chloroallyltin substrate and the aldehyde: the *threo*-selectivity results are the same (*erythro*/*threo* ratio 1/2) as that for reaction in the absence of the Lewis acid [22]. In this case $BF_3 \cdot Et_2O$ is inactive towards the chloroorganotin substrate (the Lewis-acid strength of $Bu_2ClSnCH_2CH=CHCH_3$ is greater than that of $Bu_3SnCH_2CH=CHCH_3$) and towards the aldehyde.

Work-up, involving adducts of $TiCl_4$ (system E), leads to an *erythro*-selectivity which can be explained only in terms of a reaction of titanium-organometallic species formed by redistribution in the system $Bu_2ClSnCH_2CH=CHCH_3/TiCl_4$ as previously reported [4,7] for the case of the $Bu_3SnCH_2CH=CHCH_3$ substrate. It is again necessary to emphasize that the Lewis acid strength of $TiCl_4$ is greater than that of $Bu_2ClSnCH_2CH=CHCH_3$, and consequently than that of $Bu_3SnCH_2CH=CHCH_3$.

The present results together with those previously presented show that tri-organoallyltin species can react under mild conditions with carbonyl compounds only in the presence of a Lewis acid. Previously presented mechanistic reasoning indicates that the formed $RR'C=O \rightarrow$ Lewis-acid adducts are involved in the reactions and are responsible for the stereochemical outcome. Such a conclusion seems to conflict with the observation that in the Lewis acid mediated reactions new species are formed by reaction between the organotin compounds and the Lewis acid itself, and that these species determine the stereochemical course of the reactions. The results of investigation of the systems described here and those for systems previously considered [16,20,33] support this conclusion: correct interpretation can only be made if the results for $R_3SnCH_2CH=CHCH_3$ /Lewis-acid systems are carefully examined in order to specify the actual species involved in the addition reactions.

Acknowledgement

We thank the C.N.R., for financial support under the "Progetto Finalizzato del CNR per la Chimica Fine e Secondaria" and the Ministero della Pubblica Istruzione, Roma, for financing the purchase of apparatus.

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