Journal of Organometallic Chemistry, 231 (1982) 307—314
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

ALLYLSTANNATION

II *. A TOTAL "*cis*-PREFERENCE" IN THE ADDITION OF n-$Bu_2ClSnCH(CH_3)CH{=}CH_2$ TO ALDEHYDES

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(Received December 21st, 1981)

Summary

1-Buten-3-yldi-n-butylchlorotin, formed by redistribution of (*E*/*Z*)-2-butenyltri-n-butyltin and Bu_2SnCl_2, reacts readily with neat RCHO (R = C_2H_5, $C_2H_5(CH_3)CH$, $(CH_3)_2CH$, $(CH_3)_3C$ and C_6H_5) to give high yields (80—100%) of alcohols of the type $RCH(OH)CH_2CH{=}CHCH_3$ only in the *Z*-configuration. This appears to be the first example of total "*cis*-preference" in the addition of Grignard-like reagents to carbonyl compounds. The results are discussed in terms of steric requirements around the tin centre which is probably five-coordinate in the transition state.

Introduction

Additions of crotylmetal compounds to aldehydes are known to lead to "branched" carbinols, $RCH(OH)CH(CH_3)CH{=}CH_2$ (in the *erythro* and/or *threo* form), "linear" carbinols $RCH(OH)CH_2CH{=}CHCH_3$ (in the *E* and/or *Z* form) depending on the metal present in the reagent and on the experimental conditions [1].

Recently a high "*cis*-preference" [2] was demonstrated in the addition of 1-butenyl-3-boronic acid to aldehydes, which gave 2-butenyl-1-carbinols with a *Z*/*E* ratio varying between 3/1 and 2/1, the ratio varying with the steric require-

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* For Part I, see ref. 5.

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0022-328X/82/0000—0000/$02.75

ments of the organoboron species. Similar behaviour was observed when magnesium [3] or zinc [4] substrates were used.

The account given by Hoffmann and Weidmann [2] of the reaction mechanism when boron, magnesium and zinc substrates are involved, prompted us to examine related reactions involving allylstannation. We considered that a potentially five-coordinate tin centre would lead to a locally overcrowded transition state and thus to an increase of the Z/E ratio in the final products. We therefore studied the addition of $R'_2ClSnCH(CH_3)CH{=}CH_2$ ($R' = Me$, n-Bu, Ph), formed by redistribution reaction of (Z/E)-n-$Bu_3SnCH_2CH{=}CHCH_3$ and R'_2SnCl_2, to the aldehydes RCHO with R = Et, s-Bu, i-Pr, t-Bu and Ph.

Experimental

Details of the IR and NMR equipment and of the preparations of starting materials have been described previously [5—10].

Addition reactions

The general procedure was as follows: Equimolecular amounts (16—29 mmol) of (Z/E)-$Bu_3SnCH_2CH{=}CHCH_3$ (with various Z/E ratios) and RCHO were mixed. The mixture was added as quickly as possible to solid Bu_2SnCl_2 with a molar ratio $Bu_3SnCH_2CH{=}CHCH_3/Bu_2SnCl_2$ of 1/1.5. The solvent-free mixture was stirred at a constant temperature of 25°C. The progress of the reaction was then monitored by infrared spectroscopy using liquid cells (0.1 or 0.2 mm thickness, KBr optics). The complete disappearance of the carbonyl stretching band in the range 1750—1700 cm^{-1} marked the end of the reaction. Aqueous NH_4Cl was then added and the carbinol and the organotin compounds were extracted with ethyl ether. Subsequently the carbinol was separated by distillation in yields varying from 70 to 100%. In all cases only "linear" Z-crotylcarbinols were obtained together with small amounts of "branched" methylallylcarbinols.

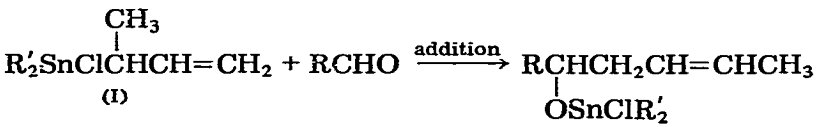
Assignments of the Z-configuration were made by IR spectroscopy (compare data of Table 1 with literature data [3,4,11]) and were confirmed by ^{13}C NMR spectroscopy. The NMR resonance lines of carbons 1, 2, 3 and 4 (cf. Table 1) of the *cis* form are found at higher field than those of the *trans* form, as is usual with olefinic systems [6,10,12]. Assignments and composition of the "branched" alcohols were made using the previously reported data [5].

In two runs (cf. runs 9 and 10 of Table 2) Me_2SnCl_2 and Ph_2SnCl_2 were used as scrambling reagents instead of Bu_2SnCl_2.

Variations in the procedures are indicated in Table 2.

Results and discussion

The main reactions are as follows:



$$\underset{\text{(I)}}{R'_2SnCl\overset{\overset{CH_3}{|}}{C}HCH{=}CH_2} + RCHO \xrightarrow{\text{addition}} R\underset{\underset{OSnClR'_2}{|}}{C}HCH_2CH{=}CHCH_3 \qquad (1)$$

(R' = Me, n-Bu, Ph)

(continued on p. 312)

TABLE 1

CARBON-13 NMR CHEMICAL SHIFTS [a] AND RELEVANT IR FREQUENCIES (cm^{-1}) OF THE PREPARED Z-CARBINOLS

Carbinols	Carbon atoms									$\nu(OH)$	$\nu(CH)$	$\nu(C{=}C)$
	1	2	3	4	5	6	6′	7	8			
1 2 3 4 5 6 7 $CH_3CH{=}CHCH_2CH(OH)CH_2CH_3$	13.0	125.4	127.5	35.1	73.0	29.9		10.3		3380 s	3015 m	1655 w
1 2 3 4 5 6 6′ 7 8 $CH_3CH{=}CHCH_2CH(OH)CH(CH_3)CH_2CH_3$ [b]	13.0 *s*	125.4	128.0	32.6 *s*	74.4 *s*	40.0 *s*	14.2 *s*	26.5 *s*	13.6	3400 s	3010 m	1652 w
	12.1	125.4	128.0	31.7	75.4	40.5	15.4	25.1	13.6			
1 2 3 4 5 6 6′ 7 $CH_3CH{=}CHCH_2CH(OH)CH(CH_3)CH_3$	13.0	125.3	128.0	32.4	76.3	33.5	17.5 [c]	19.3 [c]		3390s	3015 m	1655 w
1 2 3 4 5 6 7 $CH_3CH{=}CHCH_2CH(OH)C(CH_3)_3$	12.9	125.2	129.0	29.6	79.2	35.0		26.0		3450 s	3020 m	1652 w
1 2 3 4 5 6 $CH_3CH{=}CHCH_2CH(OH)C_6H_5$	12.8	*d*	*d*	36.9	74.0	144.4				3390s	3015 m	1650 w

[a] ppm from internal TMS of pure liquids. [b] The splitting in doublets of the resonance lines of each carbon is due to the presence of a diastereoisomeric mixture *erythro* and *threo* (carbon 5 and 6 are chiral centres). The two diastereoisomers are in the ratio 60/40. That presents in higher concentration is marked by *s* index. [c] These figures may be interchanged between carbon 7 and 6′. [d] Carbon 2 and 3 together with phenylic ones resonate in the same field range. However only three lines at 128.2, 127.2, 126.2 ppm were resolved, having intensity ratio 2/1/4, respectively.

TABLE 2

ADDITION REACTIONS OF (*Z*/*E*)2-BUTENYLTRI-n-BUTYLTIN AND ALDEHYDES IN THE PRESENCE OF R'_2SnCl_2 AT 25°C

Run no.	RCHO (R)	System A [a] (mmol) (*Z*/*E*) [b]	System B (mmol) (*Z*/*E*) [b]	Molar ratio $\frac{[R'_2SnCl_2]}{[Bu_3SnCrot]}$	Time [c] (h)	Alcohols (Total yield %)	Composition of the recovered alcohols mixture	
							(*Z*)-RCH(OH)-$CH_2CH{=}CHCH_3$ (%)	$\underset{OH}{RCH}-\underset{CH_3}{CH}CH{=}CH_2$ (%) (*Erythro*/*threo* ratio)
1	C_2H_5	$Bu_3SnCrot$ + RCHO (27) (27) (66/33)	Bu_2SnCl_2 (40.5)	1.5	0.25	94	87	13 (3/2)
2	C_2H_5	$Bu_3SnCrot$ + RCHO (29) (29) (66/33)	Bu_2SnCl_2 + Et_2O (4 ml) [h] (29)	1	3	92	89	11 (1/1)
3	C_2H_5	$Bu_3SnCrot$ + RHCO (16.2) (16.2) (66/33)	Bu_2SnCl_2 (15.9)	0.98	1.5	100	96	4
4	$C_2H_5(CH_3)CH$	$Bu_3SnCrot$ + RHCO (27.4) (27.4) (66/33)	Bu_2SnCl_2 (41.1)	1.5	1	82	80 [f]	20 (3/2)
5	$(CH_3)_2CH$	$Bu_3SnCrot$ + RCHO (26.9) (26.9) (66/33)	Bu_2SnCl_2 (38.8)	1.54	1.5	85	87	13 (1/1)
6	$(CH_3)_2CH$	Bu_2SnCl_2 + Et_2O (4 ml) [h] (26.2)	$Bu_3SnCrot$ + RCHO (23.2) (23.2) (44/56)	1.12	0.5 [d]	70	81	19 (1/1)

7	$(CH_3)_2CH$	$Bu_3SnCrot$ (25.9) (44/56)	Bu_2SnCl_2 + RCHO (38.8) (25.9)	1.5	1	76	82	18 (1/1)
8 [e]	$(CH_3)_2CH$	$Bu_3SnCrot$ + RCHO (20.8) (20.8) (45/55)	Bu_2SnCl_2 + Et_2O (3 ml) [h] (31.2)	1.5	3.5	87	93	7 (1/1)
9	$(CH_3)_2CH$	$Bu_3SnCrot$ + RCHO (21.7) (21.7) (45/55)	Ph_2SnCl_2 + Et_2O (2 ml) [h] (32.6)	1.5	0.1	90	87	13 (3/2)
10	$(CH_3)_2CH$	$Bu_3SnCrot$ + RCHO (21.7) (21.7) (45/55)	Me_2SnCl_2 + Et_2O (6 ml) [h] (32.6)	1.5	0.4	86	87	13 (2/3)
11	$(CH_3)_3C$	$Bu_3SnCrot$ + RCHO (27.5) (27.5) (66/33)	Bu_2SnCl_2 (44.3)	1.5	24	82	100	traces
12	$(CH_3)_3C$	$Bu_3SnCrot$ + RCHO (29) (29) (66/33)	Bu_2SnCl_2 + Et_2O (4 ml) [h] (29)	1	24	96	100	traces
13	C_6H_5	$Bu_3SnCrot$ + RCHO (27.6) (27.6) (66/33)	Bu_2SnCl_2 (41.3)	1.5	3	95	100	traces

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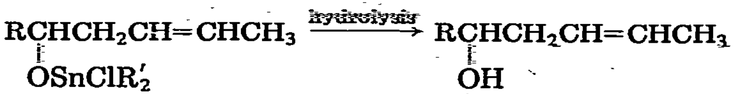
[a] System A was added to system B as quickly as possible. [b] Compositions were determined from the relative integrations of the ^{13}C NMR resonances. [c] The figures in this column represent the time necessary to have complete reaction as determined by the complete disappearance of the carbonyl stretching band in the range 1750–1700 cm^{-1}. [d] Time of addition of system A to system B. [e] Temperature 0°C. [f] Mixture of two configurational isomers *erythro threo.* [g] The use of the terms *erythro* and *threo* in this case must be considered in the light of the discussion in ref. 5. [h] Runs performed in the presence of Et_2O. In parentheses is shown the minimum volume of Et_2O added to dissolve the R'_2SnCl_2 compounds.



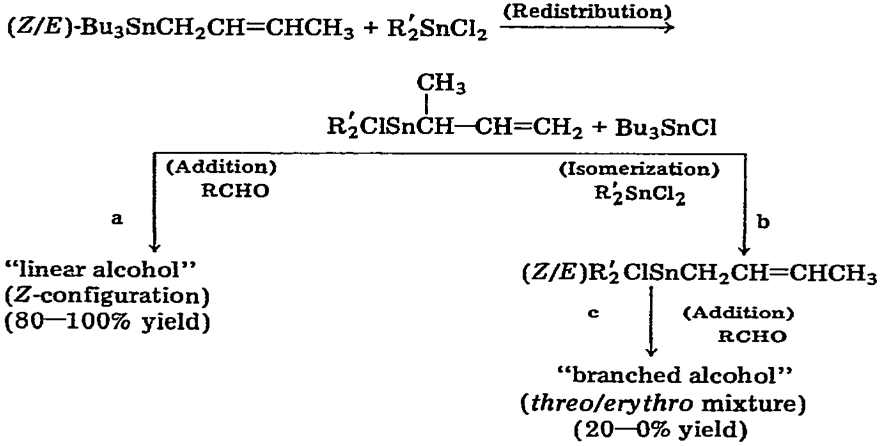
$$\underset{\displaystyle OSnClR'_2}{RCHCH_2CH{=}CHCH_3} \xrightarrow{\text{hydrolysis}} \underset{\displaystyle OH}{RCHCH_2CH{=}CHCH_3} \qquad (2)$$

Compounds such as I do not exist as pure species. We avoided preparing these compounds separately since it is possible to obtain them "in situ" by redistribution reactions of (*Z*/*E*)-$Bu_3SnCH_2CH{=}CHCH_3$ and R'_2SnCl_2 (R' = Me, n-Bu and Ph); the system having R' = n-Bu has been extensively described [10]. Thus we used a one-pot reaction (cf. Table 2). We assumed that the rate of the addition reaction is equal or slightly lower than that of the redistribution processes [10]. The aldehydes under these conditions do not add to $Bu_3SnCH_2CH{=}CHCH_3$ [5,6,13] and the rate of addition of an allyl moiety is higher than that of a crotyl species [7].

The results are shown in Table 2. In all cases, independent of the procedure used, *Z*-2-butenyl-1-carbinols are the main products. Yields of 100% were found for RCHO with R = t-Bu or Ph (cf. runs 11—13 of Table 2).

We point out that: (i) the addition occurs with complete allylic rearrangement, (ii) no side-reactions occur, except that leading to "branched" alcohols (the formation of these alcohols is explained by the addition of the isomerized product to the RCHO, as can be seen from Scheme 1, steps *b* and *c*), (iii) as we have previously noted [7,14], the rate of the addition reaction depends on the acceptor ability of the $R'_2ClSnCH(CH_3)CH{=}CH_2$ compounds used; we found the following sequence of reactivity (cf. Table 2, runs 8—10): R' = n-Bu < Me < Ph, which is in agreement with the sequence of acidity for organotin compounds [15].

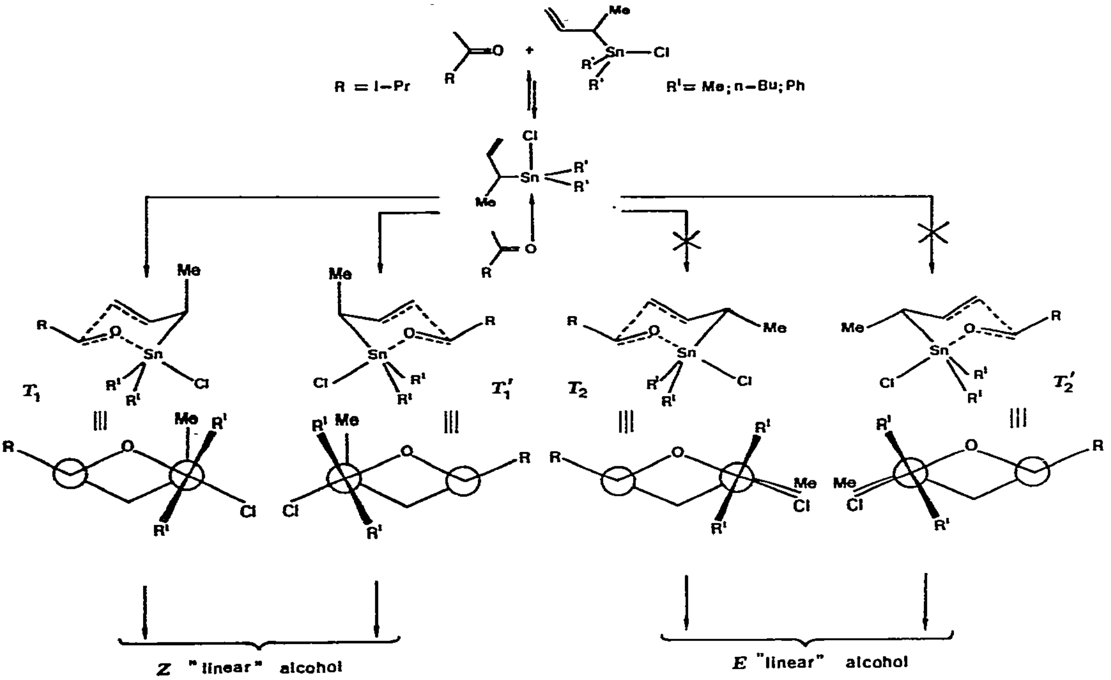
The following reaction sequences account for our results:



SCHEME 1

So far we know this is the first example of additions of Grignard-like reagents to carbonyl compounds which show total "*cis*-preference". *cis*-Preference has been observed in related reactions involving Zn [4], Mg [3] and B [2] substrates and has been reasonably explained in terms of stereochemical factors involving a six-membered-ring activated complex in the chair conformation [16]. Although this hypothesis has been criticized [3], since an unfavoured axial position of the CH_3 group must be assumed to give a *Z*-configuration in the final product, it is still the best way of accounting for the results. The stereochemical arguments also account for the variation of the *Z*/*E* ratio on varying the organic groups bonded to the metal atom [2].

We tentatively adopt the same explanation. We assume that upon forming a six-membered ring in the most stable chair conformation, the tin atom in the activated complex is in the bipyramidal trigonal five-coordinate state, with the most electronegative atoms, Cl and O, in the apical positions [17—19]. As shown in Scheme 2, this would lead to a *Z*-configuration for the final alcohol.



SCHEME 2

It is instructive to compare the conformations T_1 and T'_1 of the two enatiomorphic activated complexes arising from the racemic mixture of the starting organotin compound (the CH_3 group is in the axial position), with the conformations T_2 and T'_2 having the CH_3 group in the radial position. The clear preference for the former conformations T_1 and T'_1 simply in terms of stereochemical considerations is obvious: in T_1 and T'_1 the CH_3 group is in a *gauche* conformation with respect to one R' group and to one oxygen atom, whereas in T_2 and T'_2 the CH_3 group is in an *eclipsed* conformation with respect to the chlorine atom. The difference of internal energy between the two conformers is probably high enough to prevent any detectable production of final alcohol in the *E*-configuration. The conformations T_1 and T'_1 are so much favoured that even increasing the bulk of the R' groups does not change the *Z*/*E* ratio (cf. Table 2). It is interesting to note that in the case of similar reactions involving boron derivatives the *Z*/*E* ratio was found to depend on the steric requirements of the R' groups bonded to the metal [2].

Acknowledgement

We thank Dr. Peter J. Smith of the International Tin Research Institute, Greenford, Middlesex (England) for a gift of organotin compounds, and the C.N.R. (Rome) for financial support.

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