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# ALLYLSTANNATION

## I. STEREOCHEMISTRY OF THE ADDITION OF *trans/cis*-2-BUTENYL-CHLORO-DI-n-BUTYLTIN TO ALDEHYDES

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### Summary

2-Butenyl-chloro-di-n-butyltin, in various *trans/cis* ratios, reacts readily with neat RCHO (R = $CH_3$, $C_2H_5$, $C_2H_5(CH_3)CH$, $(CH_3)_2CH$, $C_6H_5$) at 25°C to give mixtures of *threo/erythro*-α-methylallylcarbinols in high yields. The same mixtures are obtained from the equilibrated mixtures obtained by redistribution between $Bu_3SnC_4H_7$ ($C_4H_7$ = *trans*-, *cis*-crotyl and α-methylallyl group) and $Bu_2SnCl_2$. The reactions are characterized by a high degree of stereoselectivity, especially when bulky R groups are present. The complete allylic rearrangement and the stereoselectivity indicate that an exacyclic transition state is involved. Two stereochemically different transition states lead to two diastereoisomers, *threo*- and *erythro*-α-methylallylcarbinol in the enantioforms *RS*, *SR* and *RR*, *SS*, respectively.

### Introduction

Previous work on allyl- [1—4] and crotylstannation [5,6] has shown that the ability of allyl- and crotyltins to add to the carbonyl C=O double bond falls in the sequences: (i) $BrCl_2SnAll > BuCl_2SnAll > Bu_2ClSnAll > Bu_3SnAll$, (All = allyl group) and (ii) $BuCl_2SnCrot > Bu_2ClSnCrot > Bu_3SnCrot >$ (Crot = crotyl group in the *trans* or *cis* isomeric form). Additions involving allylic systems have mainly been considered so far [3,4], with less attention paid to crotyl systems. The crotyltin systems are worthy of further study in respect of the allylic rear-

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rangements and the stereochemistry of the processes. The present work is concerned with the addition of *trans/cis*-2-butenyl-chloro-di-n-butyltin to aldehydes, RCHO, with R = $CH_3$, $C_2H_5$, $C_2H_5(CH_3)CH$, $(CH_3)_2CH$ and $C_6H_5$.

Two sets of additions were carried out: (i) using 2-butenyl-chloro-di-n-butyltin as *trans* and *cis* isomers at various ratios, (ii) using the equilibrated mixtures obtained from the redistribution of $Bu_3SnC_4H_7$ ($C_4H_7$ = *trans*-, *cis*-crotyl and α-methylallyl group) and $Bu_2SnCl_2$ [7,8]. The use of equilibrated mixtures is a convenient way of obtaining *trans/cis*-$Bu_2ClSnCrot$ starting from whatever isomeric composition of $Bu_3SnC_4H_7$ is obtained by use of a Grignard reagent.

## Experimental

Details of the IR and NMR apparatus and the preparation of starting materials have been reported previously [3—7].

*2-Butenyl-chloro-di-n-butyltin*

This was prepared by three methods: (1) 2-butenyl-chloro-di-n-butyltin (*trans/cis* = 2/1) was synthesized via elimination from 2,3,4-trimethyl-3-chloro-di-n-butylstannoxy-5-heptene [6], (ii) 2-butenyl-chloro-di-n-butyltin (*trans/cis* ≅ 1/1) was prepared by redistribution between $Bu_2Sn(CH_2CH{=}CHCH_3)_2$ and $Bu_2SnCl_2$ in 1/1 molar ratio [8], (iii) 2-butenyl-chloro-di-n-butyltin (*trans/cis* ≅ 1/1) was prepared mixed with $Bu_3SnCl$ and $Bu_2SnCl_2$ in the ratio 1/1.5 [8], (see also ref. 7); the equilibrated mixtures were used for the additions without separation of the components.

The *trans/cis* ratios were determined by analysing neat samples by $^{13}C$ NMR spectroscopy, using the integrated signals from the olefinic carbon atoms [4,7].

*Addition reactions*

Equimolecular amount (25—36 mmol) of the organotin and carbonyl compound was mixed. The solvent-free mixture was stirred at constant temperature (25°C, unless otherwise indicated in Table 2). The progress of the reactions 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. Then aqueous $NH_4Cl$ was added, and the carbinol and the organotins were extracted with ethyl ether and separated by distillation (yield of carbinol 75—98%).

α-Methylallylcarbinols were obtained in all cases as mixtures of *threo* and *erythro* * isomers as shown by $^{13}C$ NMR spectroscopy. The IR spectra show the $\nu$(OH), $\nu$(=$CH_2$) and $\nu$(C=C) bands centered at 3450—3370, 3080, 1640—1635 $cm^{-1}$, respectively, in agreement with previous assignments [9].

Assignments of the signals of each carbon in the $^{13}C$ NMR spectra were performed by examining the proton-coupled spectra and in the light of the data for the previously resolved methyl-*iso*-propyl-α-methylallylcarbinol [6].

* The term *erythro* is used for the compound for which the Newman projection leads to the same group sequences around the two chiral carbons as given by the priority rule. The other configuration is termed *threo*. The sequence rules are those of the Cahn-Ingold-Prelog.

## Results and discussion

*Determination of the isomeric composition of the product alcohols by $^{13}C$ NMR spectroscopy.*

Carbon-13 NMR spectroscopy was found to be useful in determining the *threo/erythro* ratios of the mixtures of α-methylallylcarbinols, $RCH(OH)CH(CH_3)CH{=}CH_2$ obtained. The spectra show that the signal of each carbon is split into doublets with intensity ratios which depend on the *threo/erythro* composition. The isomer ratio was similarly determined for the same alcohols prepared from Grignard reagents.

Examination of the olefinic carbon doublets for the various alcohols shows that the chemical shift (cf. Table 1) of one line of each doublet has a range narrower (e.g., $\delta(=CH-) = 141.3 \pm 0.7$ and $\delta(=CH_2) = 114.0 \pm 0.45$ ppm) than that of the other line ($\delta(=CH-) = 142.8 \pm 2.1$ and $\delta(=CH_2) = 113.9 \pm 1.5$ ppm). In these series of alcohols the *threo* form is stabilized in the eclipsed structure by intramolecular interaction between the OH group and the olefinic π-electrons [10], and thus it is likely that the chemical environment around the olefinic carbons in the *threo* isomers does not change very much on varying the R groups, even if they are bulky. In contrast, changes can be expected for the *erythro* isomers. Thus we conclude that the signals which lie in the narrow range can be assigned to the *threo* form.

Four diastereoisomers are possible in the case of the alcohol $C^7H_3{-}C^6H_2{-}(C^{5'}H_3){-}C^5H{-}C^4H(OH){-}C^3H(C^{3'}H_3){-}C^2H{=}C^1H_2$, in which three chiral centers (carbons 3,4 and 5) are present. Examination of the values listed in Table 1 shows that the $^{13}C$ NMR spectrum shows four lines for each carbon atom. In particular, the olefinic methine gives four well resolved signals which can be used to calculate the composition of the four diastereoisomers (cf. Table 2, column 6). As one can see, the calculated barycenters of the two pairs of lines lie at the same values as the *threo* and *erythro* lines of the alcohol having $R = (CH_3)_2CH$ (cf. Table 1). Thus assignments are possible and the calculations based on the barycenter lines, which represent the sum of pairs of diastereoisomers, give the "*threo*" and "*erythro*" ratios, while these may be only approximate, they are useful for comparisons with the other systems considered.

*Stereochemistry of the addition reactions.*

The additions go to completion in 10 to 180 minutes under mild conditions in a solvent-free mixture. The rates are mainly dependent on steric effects and the following reactivity order can be written: $CH_3$, $C_2H_5 > (CH_3)_2CH$, $CH_2H_5{-}(CH_3)CH > C_6H_5 >> (CH_3)_3C$ *.

Table 2 lists the data for additions performed with either the mixed *trans*- and *cis*-2-butenyl-chloro-di-n-butyltins (column 2) or the equilibrated scrambled mixtures (columns 3 and 4) containing the crotyltin compound together with $Bu_3SnCl$ and the excess of $Bu_2SnCl_2$ [7,8]. It can be seen that the *threo/erythro* compositions found are the same for both sets (column 6).

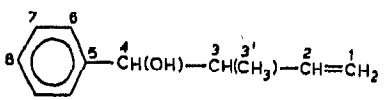
In no case is there evidence for "reversible" processes, such as the elimination

*(Continued on p. 154)*

* In the case of $(CH_3)_3CCHO$ the addition is slow: even after 5 days at 25°C followed by 3 days at 100°C little reaction had occurred, as shown by the infrared spectrum.

*TABLE 1*

CARBON-13 NMR CHEMICAL SHIFTS [a] OF THE EXAMINED CARBINOLS (304 K)

| Carbinol | Diastereoisomers | Carbon Atoms | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 3′ | 4 | 5 | 5′ | 6 | 7 | 8 |
| $CH_3-\overset{5}{C}H(OH)-\overset{3}{C}H(\overset{3''}{C}H_3)-\overset{2}{C}H=\overset{1}{C}H_2$ | *erythro* | 114.4 | 141.2 | 45.3 | 15.9 | 70.8 | 19.8 | | | | |
| | *threo* | 114.8 | 141.4 | 45.6 | 15.3 | 71.0 | 20.5 | | | | |
| $\overset{6}{C}H_3-\overset{5}{C}H_2-\overset{4}{C}H(OH)-\overset{3}{C}H(\overset{3'}{C}H_3)-\overset{2}{C}H=\overset{1}{C}H_2$ | *erythro* | 114.1 | 142.1 | 44.3 | 15.6 | 76.6 | 27.6 | | 10.6 | | |
| | *threo* | 114.8 | 141.0 | 44.0 | 16.3 | 76.6 | 27.4 | | 10.6 | | |
| $\overset{6}{C}H_3-\overset{5}{C}H(\overset{5'}{C}H_3)-\overset{4}{C}H(OH)-\overset{3}{C}H(\overset{3'}{C}H_3)-\overset{2}{C}H=\overset{1}{C}H_2$ | *erythro* | 113.9 | 142.5 | 41.8 | 15.4 [b] | 79.7 | 30.9 | 16.7 [b] | 20.1 [b] | | |
| | *threo* | 115.0 | 140.8 | 41.5 | 17.7 [b] | 80.0 | 31.2 | 17.8 [b] | 19.8 [b] | | |
| $\overset{6}{C}H_3-\overset{6}{C}H_2-\overset{5}{C}H(\overset{5'}{C}H_3)-\overset{4}{C}H(OH)-\overset{3}{C}H(\overset{3'}{C}H_3)-\overset{2}{C}H=\overset{1}{C}H_2$ | "*erythro*" [d] *SSS, RRR* | 113.9 | 142.8 | 41.2 | 13.6 [c] | 79.0 | 37.8 [c] | 16.0 [c] | 24.4 [c] | 11.4 | |
| | | (113.9) | (142.5) | (41.9) | | (78.3) | | | | (11.4) | |
| | *RSS, SRR* | 113.9 | 142.2 | 42.7 | 12.7 | 77.6 | 37.5 | 16.8 | 26.8 | 11.4 | |
| | "*threo*" [d] *SRS, RSR* | 115.2 | 141.7 | 41.8 | 13.3 | 77.4 | 37.2 | 17.2 | 26.8 | 11.7 | |
| | | (115.2) | (141.2) | (41.5) | | (78.2) | | | | (11.7) | |
| | *SSR, RRS* | 115.2 | 140.7 | 41.2 | 14.5 [c] | 79.0 | 38.1 [c] | 18.0 [c] | 23.8 [c] | 11.7 | |
| $(\overset{6}{C}H_3)_3\equiv\overset{5}{C}-\overset{4}{C}H(OH)-\overset{3}{C}H(\overset{3'}{C}H_3)-\overset{2}{C}H=\overset{1}{C}H_2$ | *erythro* | 112.5 | 144.9 | 40.5 | 16.1 | 81.6 | 36.1 | | 27.1 | | |
| | *threo* | 114.2 | 141.1 | 40.2 | 21.4 | 82.8 | 36.1 | | 27.1 | | |
|  | *erythro* | 114.6 | 140.6 | 44.7 | 14.8 | 77.5 | 143.2 | | 126.9 | 127.9 | 127.2 |
| | *threo* | 115.4 | 140.6 | 45.2 | 15.9 | 77.7 | 142.9 | | 126.9 | 127.9 | 127.2 |
| | *erythro* [e] | 115.3 | 140.4 | 44.7 | 14.3 | 77.3 | 142.7 | | 126.8 | 128.0 | 127.5 |
| | *threo* [e] | 116.4 | 140.6 | 46.0 | 16.4 | 77.9 | 142.5 | | 126.6 | 128.2 | 127.3 |

[a] ppm from internal TMS of pure liquids. [b] The assignments of these carbons are given only tentatively. [c] These figures may be interchanged inside each column. [d] This formalism is used in order to compare this system with the others. The calculated barycenter values of the resonance lines of couples of diastereoisomers are given between parentheses. [e] Chemical shifts in $CDCl_3$ solution.

TABLE 2

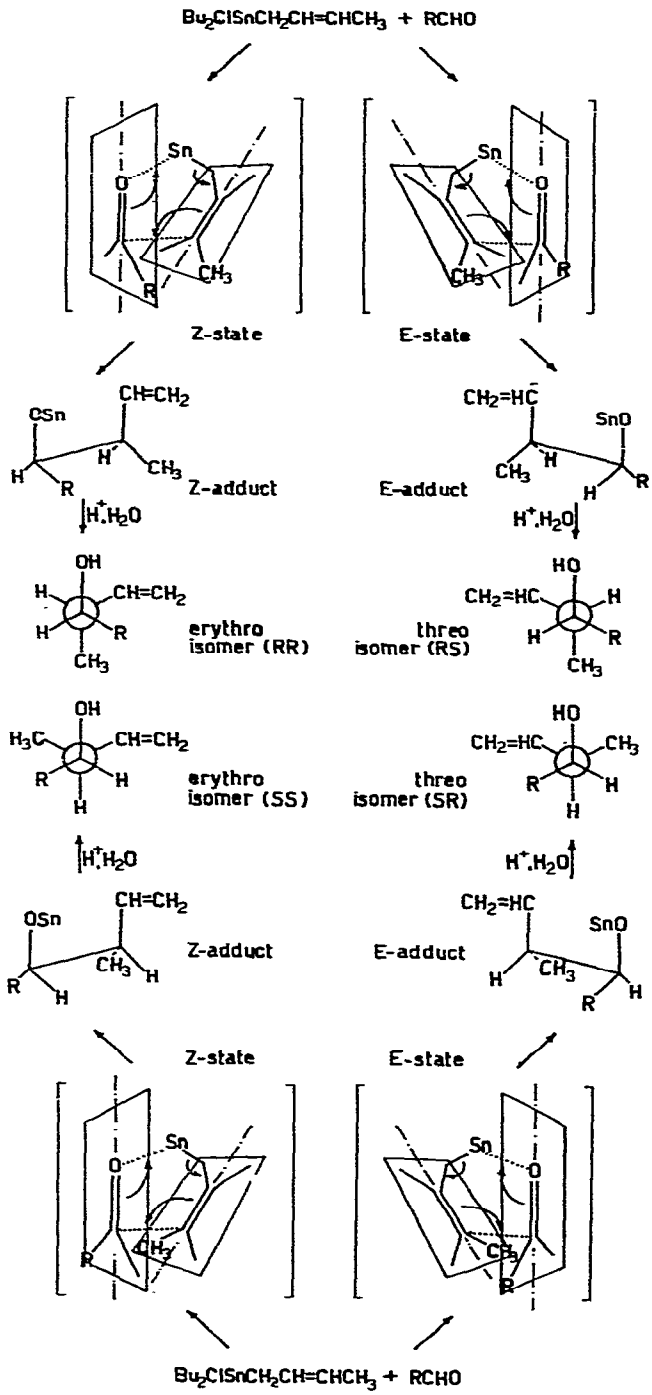
RESULTS FOR THE ADDITION REACTIONS OF 2-BUTENYL-CHLORO-DI-N-BUTYLTIN AND ALDEHYDES IN EQUIMOLECULAR AMOUNTS AT 25°C

| 1 | | 2 [a] | | 3 [a] | | | 4 [a] | | 5 | 6 [a] | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| RCHO | | $Bu_2ClSnCrot$ | | $Bu_3Sn(C_4H_7)$ | | | $Bu_2ClSnCrot$ [b, c] | | Obtained alcohols | Diastereoisomers composition | |
| R | (mmol) | *trans* (%) | *cis* (%) | *trans* (%) | *cis* (%) | α (%) [d] | *trans* (%) | *cis* (%) | $RCH(OH)CH(CH_3)CH=CH_2$ (Yield %) | *Erythro* (%) | *threo* (%) |
| $CH_3$ | (36.0) | | | 31.5 | 38.5 | 30 | 52 | 48 | 98 | 53 | 47 |
| $C_2H_5$ | (30.8) | 48 | 52 | | | | | | 97 | 45 | 55 |
| $(CH_3)_2CH$ | (27.7) | 66.6 | 33.3 | | | | | | 79 | 33.3 | 66.6 |
| | (33.8) | 50 | 50 | | | | | | 80 | 33.3 | 66.6 |
| | (30.2) | 45 | 55 | | | | | | 88 | 35 | 65 |
| | (27.1) [e] | 45 | 55 | | | | | | 89 | 33.3 | 66.6 |
| | (26.1) | | | 31.5 | 38.5 | 30 | 50 | 50 | 98 | 33.3 | 66.6 |
| | (30.8) | | | 22 | 22 | 56 | 52 | 48 | 97 | 33.3 | 66.6 |
| | (29.4) | | | 33.3 | 66.6 | 0 | 42 | 58 | 76 | 39 | 61 |
| | (29.1) | | | 31.5 | 38.5 | 30 | 50 | 50 | 98 | 35 | 65 |
| $(C_2H_5)(CH_3)CH$ | (30.8) | 66.6 | 33.3 | | | | | | 75 | [21; 10(31) | 45; 24(69)] [f] |
| | (31.1) | 52 | 48 | | | | | | 86 | [23; 12(35) | 42; 23(65)] [f] |
| | (31.3) | | | 31.5 | 38.5 | 30 | 50 | 50 | 97 | [21; 11(32) | 46; 22(68)] [f] |
| | (28.4) | | | 22 | 22 | 56 | 52 | 48 | 79 | [21; 11(32) | 46; 22(68)] [f] |
| $C_6H_5$ | (36.0) [g] | 66.6 | 33.3 | | | | | | 75 | 44 | 56 |
| | (25.3) | 45 | 55 | | | | | | 75 | 54 | 46 |
| | (27.1) [e] | 45 | 55 | | | | | | 82 | 54 | 46 |
| | (25.0) | 52 | 48 | | | | | | 76 | 49 | 51 |
| | (34.1) | | | 22 | 22 | 56 | 50 | 50 | 75 | 48 | 52 |

[a] Compositions were determined from the relative integrations of the $^{13}C$ NMR resonances. [b] The total amount of $Bu_2ClSnCrot$ is assumed to be equal to the amount of the scrambled $Bu_3SnC_4H_7$ = RCHO. [c] Composition of the $Bu_2ClSnCrot$ in the scrambled mixtures which were equilibrated for 15—20 days at 25°C from the components indicated in column 3 and $Bu_2SnCl_2$, in the ratio $Bu_3SnC_4H_7/Bu_2SnCl_2$ = 1.5 [7,8]. [d] α = α-methylallyl group. [e] Temp. 0°C. [f] The four figures represent the percentages of the four diastereoisomers. In parentheses are shown the formal "*erythro*"/"*threo*" compositions to allow comparison with the other systems. [g] Temp. 60°C.

reaction which takes place in the case of the adducts formed from ketones and crotyltin substrates [6]. When bulky R groups are present the reactions appear

SCHEME 1



to be stereoselective, as in the analogous reactions involving magnesium-, zinc- and cadmium-crotyl derivatives [11].

In discussing the possible mechanism of the reactions, we consider the reaction with i-PrCHO. A pericyclic transition state, such as previously proposed [6], is highly probable, because of the complete allylic rearrangement and the evident stereoselectivity in this system. The *threo/erythro* ratio of 2/1 obtained, which is independent of the *trans/cis*-crotyltin ratio, shows that the *threo*-isomer formation rate is twice that of the *erythro*-isomer.

As can be seen from Scheme 1, there are four possible ways of forming the two transition states, depending upon the orientation of the carbonyl compound and upon whether the *trans*- or *cis*-isomer is involved. The *E*-configuration transition state leads to the *threo*-isomer (*RS* and *SR* enantiomers) whereas the *Z*-one leads to the *erythro*-isomer (*RR* and *SS* enantiomers). The *E*-state is energetically more favourable than the *Z*-state which is influenced by the steric hindrance arising from the two opposed R and $CH_3$ groups. Thus, the pathways dealing with the two states must be characterized by different rates especially when bulky R groups are present. Thus it can be concluded that the stereoselectivity is greater when bulky R groups are present; when steric effects are less important or absent, e.g., for R = $CH_3$, $C_2H_5$, $C_6H_5$, the stereoselectivity is very weak.

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