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# Hydrated σ-bonded organometallic cations in organic synthesis

# II *. Allylstannation of aldehydes by crotyltin chlorides in acid media **

**Daniele Marton, Giuseppe Tagliavini * and Nicoletta Vanzan**

*Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Universita' di Padova, Via Marzolo, 1, I 35131 Padova (Italy)*

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## Abstract

Allylstannation of three aldehydes RCHO (R = $C_2H_5$, $(CH_3)_2CH$, and $(CH_3)_3C$) with crotyltin chlorides $Bu_{3-n}Cl_nSnCH_2CH{=}CHCH_3$, $n = 1$, 2, and 3, has been carried out in the presence of aqueous 0.1–4.0 *M* $HClO_4$. The stereochemical course of these reactions, to give the *threo/erythro* alcohols $RCH(OH)CH(CH_3)CH{=}CH_2$ and/or the *E/Z* alcohols $RCH(OH)CH_2CH{=}CHCH_3$, depends on the number, *n*, of the chlorine atoms bonded to tin and on the concentration of perchloric acid. In 0.1 *M* $HClO_4$, the *threo/erythro* isomer pair is obtained. With increasing acid concentration, the *threo/erythro* pair is gradually replaced by the *E/Z* isomer pair, which is the sole product in 4 *M* $HClO_4$. However, in most of the examined cases the ratio *anti/syn* = (*threo* + *E*)/(*erythro* + *Z*) remains constant for any given aldehyde and crotyl compound. Stereoselectivity, which is fairly good in some cases, is determined by the nature of the aldehyde: *syn*-convergence occurs with pivalaldehyde, and *anti*-convergence with isobutyraldehyde. No stereoselection is found in the case of propanaldehyde.

## Introduction

Allylstannation of aldehydes with organotin chlorides of the type $Bu_{3-n}Cl_nSnCH_2CH{=}CHCH_3$ ($n = 1$, 2, and 3) has been employed for the formation of C–C and C–O–C bonds [1]. The variety of the recovered products and their

* For Part I, see ref. 8.

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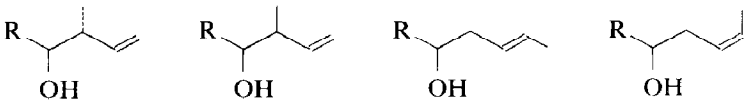
nature depend on the nature of the organoalkoxytin halides $Bu_{3-n}Cl_nSn$-O-CHR-$C_4H_7$ ($C_4H_7$ = *E*-, *Z*-crotyl, or 1-methylallyl group), which show different behaviour [2] depending on the electrophilicity on the tin centre, which increases with the number *n* of halogens bonded to the metal.

After the allylstannation, isolation of homoallylic alcohols requires protonolysis of the organoalkoxytin chlorides, irrespective of whether work-up is made in the absence or in the presence of organic solvents. In many cases, as previously reported (e.g. see ref. 3), a mixture of the following configurational isomers can be obtained:




*threo* *erythro* *E* *Z*

However, the *threo*/*erythro* or the *E*/*Z* pair may predominate, or even be the sole product with one isomer as the major component, depending on the conditions used (see the *Z*-convergence in ref. 4 and 5 and the *erythro*-convergence in ref. 3).

A one-step procedure leading to homoallylic alcohols and using allyl- and allyl-like tin monochlorides in the presence of water has been described previously [6–8]. In extension of our ealier investigations, we present some results of a study of allylstannation of three aldehydes RCHO (R = $C_2H_5$, $(CH_3)_2CH$, and $(CH_3)_3C$) with the crotyltin chlorides in the presence of aqueous $HClO_4$ in the concentration range 0.1–4.0 *M*.

Under these conditions we expected that hydrated cations of the type $Bu_{3-n}(Crot)Sn(OH_2)_m^{n+}$ (Crot = crotyl group) would be favoured [8,9], and the aldehydes would be activated by protonation. Both factors could operate to direct the stereochemical course of allylstannation away from that previously found. An additional objective was to confirm the feasibility of allylstannation under highly acidic conditions.

## Experimental

Crotyldibutyltin chloride and crotylbutyltin dichloride were prepared as previously described [1]. Crotyltin trichloride was prepared in situ by redistribution between crotyltributyltin and tin tetrachloride [10,11]. Commercial samples of the organic compounds were distilled before use.

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

The isomeric composition of the recovered mixtures were determined by GLC and checked by $^{13}C$ NMR spectroscopy [3,4,12]. $^{13}C$ NMR spectra were recorded by 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 [13].

*Additions involving crotyldibutyltin chloride (1) and crotylbutyltin dichloride (2)*

Equimolecular amounts (10 mmol) of **1** (or **2**) and the appropriate aldehyde were allowed to react in the presence of water or aqueous $HClO_4$ (20 ml, 0.1–4.0 *M*) with

Table 1

System $(E/Z)$-$Bu_2ClSnCH_2CH{=}CHCH_3/(CH_3)_2CHCHO/H_2O$, $HClO_4$ $x$ $M$ [a] at 20 °C

| Run | $HClO_4$ ($M$) | Total yield g (%) | $(CH_3)_2CHCH(OH)C_4H_7$, isomeric composition (%) | | | |
|---|---|---|---|---|---|---|
| | | | *threo* | *erythro* | *E* | *Z* |
| *Direct slow addition* [b] | | | | | | |
| 1 | 0 | 1.25 (97) | 66 | 34 | – | – |
| 2 | 0.1 | 1.18 (92) | 64 | 35 | – | 1 |
| 3 | 1.0 | 1.25 (97) | 53 | 35 | 8 | 4 |
| 4 | 2.0 | 0.81 (63) | 32 | 28 | 28 | 12 |
| 5 | 3.0 | 0.78 (61) | 24 | 25 | 33 | 18 |
| 6 | 4.0 | 0.75 (58) | 11 | 22 | 42 | 25 |
| *Inverse slow addition* | | | | | | |
| 7 | 0 | 1.26 (98) | 65 | 35 | – | – |
| 8 | 0.1 | 1.27 (99) | 62 | 37 | – | 1 |
| 9 | 1.0 | 1.24 (97) | 57 | 38 | 3 | 2 |
| 10 | 2.0 | 0.96 (75) | 47 | 38 | 8 | 7 |
| 11 | 3.0 | 0.94 (73) | 21 | 30 | 33 | 16 |
| 12 | 4.0 | 0.72 (59) | 10 | 20 | 43 | 29 |

[a] $(E/Z) = 55/45$, equimolecular amounts of organotin and aldehyde, 10 mmol. [b] The organotin was added to a stirred mixture of aldehyde and aqueous $HClO_4$ (20 ml) in about 3 h. [c] The aldehyde was added to a stirred mixture of organotin and aqueous $HClO_4$ (20 ml) in about 2 h.

stirring at room temperature. Two procedures which differ in the mode of mixing were used: (a) direct addition in which compound **1** or **2** is added to the aqueous aldehyde, and (b) inverse addition in which aqueous aldehyde is added to compound **1** or **2**; in both cases the addition was normally rapid, but slow addition (90–120 min) was used for the system $Bu_2ClSnCH_2CH{=}CHCH_3/(CH_3)_2CHCHO$, (see Table 1).

The mixture was worked-up after 1 h by extraction with diethyl ether, followed by removal of the ether solution by trap-to-trap distillation with cooling in liquid nitrogen. Mixtures of homoallylic alcohols were separated from the ether and their composition determined by use of the physical-chemical data previously reported [1,12].

*Additions involving crotyltin trichloride (3)*

Crotyltin trichloride (**3**) was prepared in situ by the redistribution method [10,11]:

$$Bu_3SnCH_2CH{=}CHCH_3 + SnCl_4 \longrightarrow CH_3CH{=}CHCH_2SnCl_3 + Bu_3SnCl$$

Equimolecular amounts (10 mmol) of crotyltributyltin and tin tetrachloride were stirred at −25 °C for few minutes under dry nitrogen, and the mixture was then allowed to warm to room temperature and stirred for 25–30 min. A solution of 10 mmol of aldehyde in 20 ml of aqueous $HClO_4$ was then added with stirring. Work-up, after 1 h, was as above described.

## Results and discussion

*$Bu_2(CH_3CH{=}CHCH_2)SnCl/(CH_3)_2CHCHO$ system*

Reactions were carried out with the system $(E/Z)$-$Bu_2(CH_3CH{=}CHCH_2)SnCl/(CH_3)_2CHCHO/H_2O$, $HClO_4$ $x$ $M$ $(E/Z) = 55/45$, $x = 0$, 1, 2, 3, and 4) by direct

Table 2

Systems $(E/Z)$-$Bu_{3-n}Cl_nSnCH_2CH{=}CHCH_3/(CH_3)_2CHCHO$ [a] at 20 °C

| Run [b] | $n$ | Medium | $(CH_3)_2CH$-CH(OH)-$C_4H_7$, isomeric composition % | | | | Ratio *anti*/*syn* [c] |
|---|---|---|---|---|---|---|---|
| | | | *threo* | *erythro* | *E* | *Z* | |
| 13 | 1 | neat | 66 | 34 | – | – | 66/34 |
| 14 | | water/py | 65 | 35 | – | – | 65/35 |
| 15 | | DMSO | 66 | 34 | – | – | 66/34 |
| 16 | | NaOH, 0.1 *M* | 62 | 38 | – | – | 62/38 |
| 17 | | water | 66 | 34 | – | – | 66/34 |
| 18 | | HCl, 0.1 *M* | 64 | 36 | – | – | 63/37 |
| 19 | | $HClO_4$, 0.1 *M* | 63 | 37 | – | – | |
| 20 | 1 | $HClO_4$, 1 *M* | 57 | 38 | 3 | 2 | 60/40 |
| 21 | | $HClO_4$, 2 *M* | 54 | 37 | 6 | 3 | 60/40 |
| 22 | | $HClO_4$, 3 *M* | 34 | 28 | 26 | 12 | 60/40 |
| 23 | | $HClO_4$, 4 *M* | 2 | 1 | 57 | 40 | 59/41 |
| 24 | 1 | HCl, 4 *M* | 20 | 28 | 40 | 12 | 60/40 |
| 25 | 2 | water | 75 | 25 | 1 | 1 | 76/24 |
| 26 | | $HClO_4$, 0.1 *M* | 77 | 21 | 1 | 1 | 78/22 |
| 27 | | $HClO_4$, 2 *M* | 56 | 17 | 22 | 5 | 78/22 |
| 28 | | $HClO_4$, 4 *M* | 3 | 2 | 72 | 23 | 75/25 |
| 29 | 3 | water | 68 | 23 | 6 | 3 | 74/26 |
| 30 | | $HClO_4$, 0.1 *M* | 64 | 23 | 9 | 4 | 73/27 |
| 31 | | $HClO_4$, 4 *M* | 2 | 4 | 78 | 26 | 80/20 |

[a] $E/Z = 50/50$ for $n = 1$; 64/36 for $n = 2$; 66/34 for $n = 3$. [b] Runs involved rapid inverse addition. [c] *Anti*/*syn* = (*threo* + *E*)/(*erythro* + *Z*).

and inverse slow addition of the components. The results (see, Table 1) appear to be independent of the mode of mixing. The lower yields in $HClO_4$ 2–4 *M* may be ascribed to loss of organotin compound by protonolysis of the tin–crotyl bond during the long reaction time. It is noteworthy that allylstannation performed with allyltin monochlorides in the presence of water is quantitative [7,8].

Two further observations are significant. (i) in water, as well as in 0.1 *M* $HClO_4$, only the diastereoisomeric pair *threo*/*erythro* is formed. With increasing the $HClO_4$ concentration, the diastereoisomeric pair $E/Z$ is increasingly formed, and, in 4.0 *M* $HClO_4$, this is the predominant pair (compare run 1 with 6 and run 7 with 12). (ii) The composition of the mixture of isomeric homoallylic alcohols changes with increasing the $HClO_4$ concentration: the *threo*-isomer being progressively replaced by the *E*-isomer, and the *erythro*-isomer by the *Z*-isomer (cf. Table 1).

*$(E/Z)$-$Bu_{3-n}Cl_nSnCH_2CH{=}CHCH_3/(CH_3)_2CHCHO$ systems*

The results listed in Table 2 refer to the runs performed in various media with the systems $(E/Z)$-$Bu_{3-n}Cl_nSnCH_2CH{=}CHCH_3/(CH_3)_2CHCHO/H_2O$, $HClO_4$ *x M* ($E/Z = 50/50$ for $n = 1$, 64/36 for $n = 2$, and 66/34 for $n = 3$ [8,9]). Table 2 lists results for runs performed in neat, water/pyridine mixture, or in DMSO, aqueous 0.1 *M* HCl, 0.1 *M* NaOH or 4 *M* HCl (runs 13–18, and 24). In all cases, inverse rapid mixing of the reactants was used.

Table 3

Systems $(E/Z)$-$Bu_{3-n}Cl_nSnCH_2CH{=}CHCH_3/(CH_3)_3CCHO$ [a] at 20 °C

| Run [b] | $n$ | Medium | $(CH_3)_3CCH(OH)C_4H_7$, isomeric composition (%) | | | | Ratio *anti/syn* [c] |
|---|---|---|---|---|---|---|---|
| | | | *threo* | *erythro* | *E* | *Z* | |
| 32 | 1 | water | 46 | 54 | – | – | 46/54 |
| 33 | | $HClO_4$, 0.1 *M* | 39 | 61 | – | – | 39/61 |
| 34 | | $HClO_4$, 4 *M* | – | – | 20 | 80 | 20/80 |
| 35 | 2 | water | 31 | 39 | – | 30 | 31/69 |
| 36 | | $HClO_4$, 0.1 *M* | 31 | 45 | – | 24 | 31/69 |
| 37 | | $HClO_4$, 4 *M* | – | – | 30 | 70 | 30/70 |
| 38 | 3 | water | 16 | 56 | 9 | 19 | 25/75 |
| 39 | | $HClO_4$, 0.1 *M* | 17 | 54 | 10 | 19 | 27/73 |
| 40 | | $HClO_4$, 4 *M* | – | – | 24 | 76 | 24/76 |

[a] $E/Z = 50/50$ for $n = 1$; 64/36 for $n = 2$; 66/34 for $n = 3$. [b] Runs involved rapid inverse addition. [c] *Anti/syn = (threo + E)/(erythro + Z)*.

It can be seen that the stereochemical outcome in such systems depends on the crotyl compound used and on the acid concentration. When $n = 1$, a *threo/erythro* mixture having a constant isomer ratio of 66/34 is recovered both in the absence and in the presence of solvents, and in 0.1 *M* in base or acid media. As the concentration of $HClO_4$ is increased from 1 to 4 *M*, the $E/Z$ diastereoisomeric pair is progressively formed, and it predominates (ratio 59/41) in the 4 *M*-acid. The effect of the chloride anion on the isomeric composition of the alcohols is evident from run 24 (compare run 24 with run 23 performed in $HClO_4$ 4 *M*). Nevertheless, since the *threo*-isomer is replaced by the *E*-isomer and the *erythro*-isomer is replaced by the *Z*-isomer, the *anti/syn* ratio ((*threo* + *E*)/(*erythro* + *Z*)) remains constant at 60/40.

The same type of stereochemical outcome is observed for compounds having $n = 2$ and 3. Significant facts are: the *threo*-convergence (75–77%) is observed both in water and $HClO_4$ 0.1 *M* for $n = 2$ (cf. runs 25 and 26), and *E*-convergence is observed in $HClO_4$ 4 *M*: 72% for $n = 2$ (cf. run 28) and 78% for $n = 3$ (cf. run 31). Also in these cases the *anti/syn* ratios remain constant in the range 75/25–80/20 (runs 25–31).

*$(E/Z)$-$Bu_{3-n}Cl_nSnCH_2CH{=}CHCH_3/(CH_3)_3CCHO$ systems*

Table 3 shows the results for reactions involving the $(E/Z)$-$Bu_{3-n}Cl_nSnCH_2$-$CH{=}CHCH_3/(CH_3)_3CCHO$ systems.

In these cases a different stereochemical outcome is found on varying the organotin compound and the acid concentration. Identical results are obtained in water and 0.1 *M* $HClO_4$; in such media the diastereoisomeric pair *threo/erythro* still dominates, with the *erythro*-form as the major component. This pair is completely absent in 4 *M* $HClO_4$ and the $E/Z$ pair predominates, with the *Z*-isomer as the major component.

In contrast to the results for isobutyraldehyde, a *syn*-convergence is observed, as evidenced by the *anti/syn* ratios values listed in Table 3. For organotins having $n = 2$ and 3, the *anti/syn* values remain constant at 30/70 and 25/75, with a *Z*-convergence of 70 and 76%, respectively (cf. run 37 and 40).

Table 4

Systems ($E/Z$)-$Bu_{3-n}Cl_nSnCH_2CH{=}CHCH_3/C_2H_5CHO$ [a] at 20 °C

| Run [b] | $n$ | Medium | $C_2H_5$-CH(OH)-$C_4H_7$, isomeric composition (%) | | | | Ratio *anti/syn* [c] |
|---|---|---|---|---|---|---|---|
| | | | *threo* | *erythro* | *E* | *Z* | |
| 41 | 1 | water | 52 | 48 | – | – | 52/48 |
| 42 | | $HClO_4$, 0.1 *M* | 47 | 52 | 0.5 | 0.5 | 47.5/52.5 |
| 43 | | $HClO_4$, 4 *M* | – | 8 | 48 | 44 | 48/52 |
| 44 | 2 | water | 48 | 51 | – | 1 | 48/52 |
| 45 | | $HClO_4$, 0.1 *M* | 42 | 50 | 6 | 2 | 48/52 |
| 46 | | $HClO_4$, 4 *M* | – | 11 | 48 | 41 | 48/52 |
| 47 | 3 | water | 42 | 54 | 2 | 2 | 44/56 |
| 48 | | $HClO_4$, 0.1 *M* | 42 | 55 | 1.5 | 1.5 | 43.5/56.5 |
| 49 | | $HClO_4$, 4 *M* | – | 13 | 41 | 46 | 41/59 |

[a] $E/Z = 50/50$ for $n = 1$; 64/36 for $n = 2$; 66/34 for $n = 3$. [b] Runs involved rapid inverse addition. [c] *Anti/syn = (threo + E)/(erythro + Z)*.

*$Bu_{3-n}Cl_nSnCH_2CH{=}CHCH_3/C_2H_5CHO$ systems*

The data in Table 4 refer to the systems $Bu_{3-n}Cl_nSnCH_2CH{=}CHCH_3/C_2H_5CHO$. The stereochemical course of these reactions does not change as the value of $n$ is changed. The isomeric compositions of the *threo/erythro* mixtures obtained in water and 0.1 *M* $HClO_4$ are nearly identical. Furthermore, in 4 *M* $HClO_4$ the $E/Z$ pair predominates, so that these systems behave like these considered earlier. However, propanal gives rise to a very poor stereoselection, with a weak *syn*-convergence, as indicated by the fact that the *anti/syn* values are all in the range 50/50–44/56.

*General comments*

The results reported here provide the first direct evidence for formation of C–C bonds in aqueous acid media for reactions between allylmetals and carbonyl compounds.

Notable is the change in the stereoselection of the reactions on going from water solution to more acidic solutions. In water, the diastereoisomeric pair *threo/erythro* predominates, whereas in 4 *M* $HClO_4$ only the diastereoisomeric pair $E/Z$ is obtained. With $HClO_4$ concentrations in the range 1–3 *M*, mixtures containing all four isomers are formed. In each system, reduction in the amount of *threo*-form is accompanied by increase in that of the *E*-form, and similarly the *erythro*-form is replaced by the *Z*-form. Thus, the data can be rationalized in term of the *anti/syn* ratio values, since these are independent of the isomeric composition of the organotin used.

In most of the examined cases, the *anti/syn* values remain constant for any given aldehyde and crotyl compound, and these values can be used to estimate the stereochemical outcome. In Table 5, figures in italics indicate the cases in which there is fairly good stereoselection, with the major isomer present to the extent of range 66–80%.

Complete explanation of these findings presents a considerable problem because of the complexity of the systems, but we discuss below some of the more important features.

Table 5

Synopsis of the results obtained in water and in $HClO_4$ 4 *M* medium

| RCHO R = | *n* = 1 | | *n* = 2 | | *n* = 3 | |
|---|---|---|---|---|---|---|
| | Water *t/e* [a] | $HClO_4$, 4 *M* *E/Z* | Water *t/e* [a] | $HClO_4$, 4 *M* *E/Z* | Water *t/e* [a] | $HClO_4$, 4 *M* *E/Z* |
| $C_2H_5$ | 52/48 | 52/48 | 49/51 | 54/46 | 44/56 | 47/53 |
| $(CH_3)_2CH$ | *66/34* [b] | 59/41 | *76/24* [b] | *76/24* [c] | *75/25* [b] | *83/17* [c] |
| $(CH_3)C$ | 46/54 | *18/82* [d] | 45/55 | *33/67* [d] | *22/78* [e] | *24/76* [d] |

[a] *t/e* = *threo/erythro*. [b] *Threo*-convergence. [c] *E*-convergence. [d] *Z*-convergence. [e] *Erythro*-convergence.

As previously suggested [8], aqueous organometallic cations $Bu_{3-n}RSn^{n+}_{(aq)}$ (R = $C_4H_7$) must be involved in the allylstannations. Their activity increases with the proton concentration, and decreases with the chloride ion concentration (cf. Table 2, run 24 with run 23). This can be understood in term of the following solvolytic and acid–base equilibria involving the organotin chlorides [9,14]:

$$Bu_{3-n}RSnCl_n \overset{H_2O}{\rightleftharpoons} Bu_{3-n}RSn^{n+}_{(aq)} + n\ Cl^-_{(aq)}$$

$$Bu_{3-n}RSn^{n+}_{(aq)} + H_2O \rightleftharpoons Bu_{3-n}RSn(OH)^{(n-1)}_{(aq)} + H_3O^+ \ldots \text{etc.}$$

It is reasonable to assume that the change in the stereoselection depends on the presence of the hydrated species. Furthermore, activation of the aldehydes by protonation in the acidic medium, can significantly affect the outcome.

It is also noteworthy that the change in the electrophilicity of the tin centre on varying the value of *n* influences the course of the reactions. As we have previously shown [15], the crotyl group can undergo attack at the α-carbon or γ-carbon with respect to tin. Thus, allylstannation produces α-adducts and/or γ-adducts, which upon hydrolysis give rise respectively to "linear alcohols" in the *E* or *Z* configuration or "branched alcohols" in the *threo* or *erythro* configuration.

It thus appears that the ease of electrophilic attack at the α-carbon must be increased on increasing either the number *n* of the chloride atoms or the acid concentration, giving rise to a stereoselection in which the *E/Z* pair is favoured.

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