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# PREPARATION OF α-ALLENIC AND β-ACETYLENIC ALCOHOLS BY TREATMENT OF A MIXTURE OF $Bu_3SnCH{=}C{=}CH_2$ AND RCHO WITH $Bu_2SnCl_2$ AND WATER

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## Summary

Treatment of a mixture of $Bu_3SnCH{=}C{=}CH_2$ and RCHO ($R = CH_3$, $C_2H_5$, $(CH_3)_2CH$, $(CH_3)_3C$) with $Bu_2SnCl_2$ in the presence of water gives isomeric mixtures of α-allenic and β-acetylenic alcohols with the α-allenic isomer predominating (~ 75%). Reactions carried out without water give mixtures in which the isomeric ratio between the allenic and acetylenic alcohol varies between 70/30 and 50/50. In contrast β-acetylenic alcohols predominate when HCHO and α,β-unsaturated aldehydes ($R = CH_2{=}CH$, $CH_2{=}C(CH_3)$, $CH_3CH{=}CH$, $C_3H_7CH{=}CH$) are used. The stereochemical course of the reactions appear to depend upon the addition and isomerization rates of the $Bu_2Sn(CH_2C{\equiv}CH)Cl$ intermediate.

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## Introduction

We previously reported [1] that dibutylallenyltin chloride adds to carbonyl compounds in a one pot reaction in the presence of water to give a mixture of β-acetylenic and α-allenic alcohols:

$$Bu_2(CH_2{=}C{=}CH)SnCl + RCOR' + \tfrac{1}{2}H_2O \rightarrow$$

$$\left\{\begin{array}{c} RC(OH)R'CH_2C{\equiv}CH \\ (90\text{–}95\%) \\ + \\ RC(OH)R'CH{=}C{=}CH_2 \\ (10\text{–}5\%) \end{array}\right\} + \tfrac{1}{2}[Bu_2SnCl]_2O$$

This reaction involving the allenic substrate is characterized by a rearrangement of the unsaturated chain, the propargylic carbinol being the major product isolated.

Since the stereochemical course of the reactions involving β,γ-unsaturated

TABLE 1

PRODUCTS OF THE REACTIONS OF A MIXTURE OF $Bu_3SnCH{=}C{=}CH_2$ AND RCHO IN THE PRESENCE OF $Bu_2SnCl_2$ IN WATER AT 25°C

| Run | R in RCHO | Amount of product (g(% yield)) | Product composition | |
|---|---|---|---|---|
| | | | Allenic isomer (%) | Propargylic isomer (%) |
| 1 | H | 1.4 (100) | $HCH(OH)CH{=}C{=}CH_2$ (10) | $HCH(OH)CH_2C{\equiv}CH$ (90) |
| 2 | $CH_3$ | 1.6 (95) | $CH_3CH(OH)CH{=}C{=}CH_2$ (75) | $CH_3CH(OH)CH_2C{\equiv}CH$ (25) |
| 3 | $C_2H_5$ | 1.9 (97) | $C_2H_5CH(OH)CH{=}C{=}CH_2$ (75) | $C_2H_5CH(OH)CH_2C{\equiv}CH$ (25) |
| 4 | $(CH_3)_2CH$ | 2.2 (97) | $(CH_3)_2CHCH(OH)CH{=}C{=}CH_2$ (76) | $(CH_3)_2CHCH(OH)CH_2C{\equiv}CH$ (24) |
| 5 | $(CH_3)_3C$ | 2.4 (95) | $(CH_3)_3CCH(OH)CH{=}C{=}CH_2$ (60) | $(CH_3)_3CCH(OH)CH_2C{\equiv}CH$ (40) |
| 6 [a] | $C_2H_5$ | 2.4 (98) | $C_2H_5CH(OH)CH{=}C{=}CH_2$ (80) | $C_2H_5CH(OH)CH_2C{\equiv}CH$ (20) |
| 7 | $CH_2{=}CH$ | 1.9 (98) | $CH_2{=}CHCH(OH)CH{=}C{=}CH_2$ (10) | $CH_2{=}CHCH(OH)CH_2C{\equiv}CH$ (90) |
| 8 | $CH_2{=}C(CH_3)$ | 2.0 (90) | $CH_2{=}C(CH_3)CH(OH)CH{=}C{=}CH_2$ (35) | $CH_2{=}C(CH_3)CH(OH)CH_2C{\equiv}CH$ (65) |
| 9 | (*E*)-$CH_3CH{=}CH$ | 2.1 (95) | (*E*)-$CH_3CH{=}CHCH(OH)CH{=}C{=}CH_2$ (5) | (*E*)-$CH_3CH{=}CHCH(OH)CH_2C{\equiv}CN$ (95) |
| 10 | (*E*)-$C_3H_7CH{=}CH$ | 2.5 (90) | (*E*)-$C_3H_7CH{=}CHCH(OH)CH{=}C{=}CH_2$ (10) | (*E*)-$C_3H_7CH{=}CHCH(OH)CH_2C{\equiv}CH$ (90) |

[a] This run involved dropwise addition (20 min) of an ether solution of $Bu_2SnCl_2$ (37.5 mmol in 10 ml of ether) to an equimolecular mixture of $Bu_3SnCH{=}C{=}CH_2$ and $C_2H_5CHO$ (25 mmol).

TABLE 2

PRODUCTS OF THE REACTION OF $Bu_3SnCH{=}C{=}CH_2$ WITH RCHO IN THE PRESENCE OF NEAT $Bu_2SnCl_2$ AT 25°C [a]

| Run | R in RCHO | Reaction time [b] (min) | Amount of product g(% yield) | Product composition | |
|---|---|---|---|---|---|
| | | | | Allenic isomer (%) | Propargylic isomer (%) |
| 11 | $CH_3$ | 40 | 1.8 (86) | $CH_3CH(OH)CH{=}C{=}CH_2$ (70) | $CH_3CH(OH)CH_2C{\equiv}CH_3$ (30) |
| 12 | $C_2H_5$ | 40 | 2.2 (88) | $C_2H_5CH(OH)CH{=}C{=}CH_2$ (58) | $C_2H_5CH(OH)CH_2C{\equiv}CH_3$ (42) |
| 13 | $(CH_3)_2CH$ | 50 | 2.2 (78) | $(CH_3)_2CHCH(OH)CH{=}C{=}CH_2$ (51) | $(CH_3)_2CHCH(OH)CH_2C{\equiv}CH_3$ (49) |
| 14 | $(CH_3)_3C$ | 120 | 2.6 (82) | $(CH_3)_3CCH(OH)CH{=}C{=}CH_2$ (50) | $(CH_3)_3CCH(OH)CH_2C{\equiv}CH_3$ (50) |

[a] These runs involved 25 mmol of each component. [b] The time betwen the mixing of the reactants and the quenching of the reaction by hydrolysis.

organotin compounds can be changed by using scrambling reagents [2–5]. we have now studied a mixture of $Bu_3SnCH=C=CH_2$ and RCHO with $Bu_2SnCl_2$ in the presence of water. When the rate of addition of the first-formed mixed chloroorganotin ($Bu_2(CH\equiv CCH_2)SnCl$) is greater than that of its isomerization mixtures of alcohols are formed in which α-allenic carbinols predominate.

## Experimental

Commercial samples of dibutyltin dichloride and carbonyl compounds were purified before use.

The recovered carbinol mixtures were identified by their IR spectra recorded on a Perkin–Elmer Model 599B spectrophotometer. Analyses of the isomeric mixtures were performed by GLC as previously described [1].

### *Preparation of tributylallenyltin*

Following the procedure described by Prevost et al. [6], allenylmagnesium bromide was obtained by dropwise addition (5 h) of a solution of propargyl bromide (1.5 mol, 178 g) in 500 ml of diethyl ether to magnesium turnings (4.5 mol, 110 g) amalgamated with mercury chloride. The solution was decanted from the residue and a solution of tributyltin chloride (0.5 mol, 162 g) in 300 ml of diethyl ether was slowly added (3 h) to it. After hydrolysis with ice the ethereal layer was separated and dried over $Na_2SO_4$. Most of the solvent was distilled off and 100 ml of methanol were added. The solution was refluxed for 15 min to bring about isomerization of the product to the allenic form [1] *. Distillation under reduced pressure gave 124 g (75% yield) of tributylallenyltin, b.p. 90–92°C/0.1 mmHg (Lit. [7], b.p. 80–82°C/0.15 mmHg). The IR spectrum showed the presence of the C=C=C stretching vibration band centered at about 1930 $cm^{-1}$, and no $\nu(C\equiv C)$ band was observed.

### *Addition reactions*

A mixture of tributylallenyltin and the appropriate aldehyde in equimolecular amounts (20 mmol) was added with stirring to solid $Bu_2SnCl_2$ (20 mmol) in the presence of 10 ml of water at 25°C. After an appropriate time (less than 30 min) work-up of the mixture, followed by extraction with diethyl ether and removal of the ether by trap-to-trap distillation in a cold bath (liquid nitrogen) gave a mixture of α-allenic and β-acetylenic alcohols.

A similar procedure was carried out in some cases in the absence of water using 25 mmol of each component.

## Results and discussion

The results (cf. Table 1) can be accounted for in terms of equations 1–4.

$$Bu_3SnCH=C=CH_2 + Bu_2SnCl_2 \xrightarrow[\text{with rearrangement}]{\text{redistribution}} Bu_2(CH\equiv CCH_2)SnCl + Bu_3SnCl \quad (1)$$

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* A mixture of $Bu_3Sn(C_3H_3)$ ($C_3H_3$ = allenyl or propargyl group) which has not been treated with methanol isomerizes completely to $Bu_3SnCH=C=CH_2$ when stored for more than three months.

$$\mathrm{Bu_2(CH{\equiv}CCH_2)SnCl} \xrightarrow[\text{isomerization}]{\mathrm{Bu_2SnCl_2}} \mathrm{Bu_2(CH_2{=}C{=}CH)SnCl} \qquad (2)$$

$$\mathrm{Bu_2(CH{\equiv}CCH_2)SnCl + RCHO + \tfrac{1}{2}H_2O} \xrightarrow[\text{rearrangement}]{\text{addition with}}$$

$$\mathrm{RCH(OH)CH{=}C{=}CH_2 + \tfrac{1}{2}[Bu_2SnCl]_2O} \qquad (3)$$

(α-allenic alcohol)

$$\mathrm{Bu_2(CH_2{=}C{=}CH)SnCl + RCHO + \tfrac{1}{2}H_2O} \xrightarrow[\text{rearrangement}]{\text{addition with}}$$

$$\mathrm{RCH(OH)CH_2C{\equiv}CH + [\tfrac{1}{2}Bu_2SnCl]_2O} \qquad (4)$$

(β-acetylenic alcohol)

When the mixture of $Bu_3SnCH{=}C{=}CH_2$ and RCHO is added to the scrambling reagent $Bu_2SnCl_2$, the mixed $Bu_2(CH{\equiv}CCH_2)SnCl$ is rapidly formed (eq. 1). This can add to the aldehyde (eq. 3), and if the rate of this addition is greater than that of the isomerization (eq. 2) the α-allenic alcohol is formed in major amount, otherwise the β-acetylenic alcohol is produced via reaction 4.

The results in Table 1 show that for the aldehyde RCHO with R = $CH_3$, $C_2H_5$, $(CH_3)_2CH$ or $(CH_3)_3C$, the addition rate (10–30 min) of the propargyltin chloride is greater than that of the isomerization and the α-allenic alcohol was produced in major amount (60–76%). Similar reasoning can be applied to the result of run 6, in which dropwise addition of an ether solution of $Bu_2SnCl_2$ to the binary system gave rise to 80% yield of the α-allenic alcohol.

In contrast, when formic and α,β-unsaturated aldehydes are used (runs 1, 7–10 of Table 1) the β-acetylenic alcohols are formed predominantly. In these cases we have noticed that the additions are slower, and take roughly 1 to 2 hours, this behavior is similar to that previously found for the systems $Bu_2(CH_2{=}C{=}CH)SnCl/RCHO/H_2O$ (see Table 3 of ref. 1).

It is interesting to compare the data in Table 1 with those in Table 2, which refer to runs 11–14, carried out by mixing the three components neat. Non aqueous work-up gives overall yields (78–88%) lower than those obtained in the presence of water (90–100%). Furthermore the allenic-convergence is lower when neat reagents are used, the ratio between the allenic and the propargylic isomer being between 70/30 and 50/50, compared with the 75/25 produced in the aqueous medium. Such results are not surprising since the addition rates in the aqueous medium are greater than those in the neat system.

The results of reactions performed with α,β-unsaturated aldehydes without water are not specifically reported because they were the same as those obtained from reactions in water.

We conclude that β,γ-unsaturated organotin halides provide convenient reagents for synthesis, and that use of other organotin reagents to induce scrambling enables the stereochemical course of the reactions to be changed [2–5]. The results can be compared with those previously obtained with organo-zinc [8], -chromium [9], -magnesium, and -aluminum compounds [10] and in reactions involving use of metallic aluminum and tin [11].

Unfortunately complete α-allenic stereoconvergence, such as was found on treatment of propargyltrimethylsilane and carbonyl substrates in the presence of tetrabutylammonium fluoride [12], was not observed in the present study.

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