

PREPARATION OF α -ALLENIC AND β -ACETYLENIC ALCOHOLS BY TREATMENT OF A MIXTURE OF $\text{Bu}_3\text{SnCH}=\text{C}=\text{CH}_2$ AND RCHO WITH Bu_2SnCl_2 AND WATER

ANDREA BOARETTO, DANIELE MARTON and GIUSEPPE TAGLIAVINI*

Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Università di Padova, Via Marzolo, 1 I-35131 - Padova (Italy)

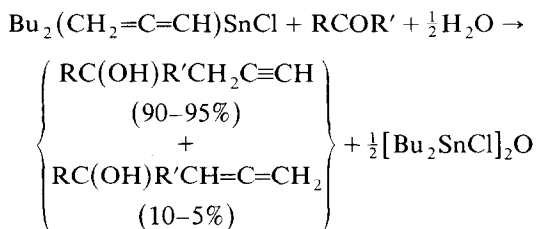
(Received June 21st, 1985)

Summary

Treatment of a mixture of $\text{Bu}_3\text{SnCH}=\text{C}=\text{CH}_2$ and RCHO ($\text{R} = \text{CH}_3$, C_2H_5 , $(\text{CH}_3)_2\text{CH}$, $(\text{CH}_3)_3\text{C}$) 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 ($\sim 75\%$). 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 ($\text{R} = \text{CH}_2=\text{CH}$, $\text{CH}_2=\text{C}(\text{CH}_3)$, $\text{CH}_3\text{CH}=\text{CH}$, $\text{C}_3\text{H}_7\text{CH}=\text{CH}$) are used. The stereochemical course of the reactions appear to depend upon the addition and isomerization rates of the $\text{Bu}_2\text{Sn}(\text{CH}_2\text{C}\equiv\text{CH})\text{Cl}$ intermediate.

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:



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 $\text{Bu}_3\text{SnCH}=\text{C}=\text{CH}_2$ AND RCHO IN THE PRESENCE OF Bu_3SnCl_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)	$\text{HCH(OH)CH}=\text{C}=\text{CH}_2$ (10)	$\text{HCH(OH)CH}_2\text{C}\equiv\text{CH}$ (90)
2	CH_3	1.6 (95)	$\text{CH}_3\text{CH(OH)CH}=\text{C}=\text{CH}_2$ (75)	$\text{CH}_3\text{CH(OH)CH}_2\text{C}\equiv\text{CH}$ (25)
3	C_2H_5	1.9 (97)	$\text{C}_2\text{H}_5\text{CH(OH)CH}=\text{C}=\text{CH}_2$ (75)	$\text{C}_2\text{H}_5\text{CH(OH)CH}_2\text{C}\equiv\text{CH}$ (25)
4	$(\text{CH}_3)_2\text{CH}$	2.2 (97)	$(\text{CH}_3)_2\text{CHCH(OH)CH}=\text{C}=\text{CH}_2$ (76)	$(\text{CH}_3)_2\text{CHCH(OH)CH}_2\text{C}\equiv\text{CH}$ (24)
5	$(\text{CH}_3)_3\text{C}$	2.4 (95)	$(\text{CH}_3)_3\text{CCH(OH)CH}=\text{C}=\text{CH}_2$ (60)	$(\text{CH}_3)_3\text{CCH(OH)CH}_2\text{C}\equiv\text{CH}$ (40)
6 ^a	C_2H_5	2.4 (98)	$\text{C}_2\text{H}_5\text{CH(OH)CH}=\text{C}=\text{CH}_2$ (80)	$\text{C}_2\text{H}_5\text{CH(OH)CH}_2\text{C}\equiv\text{CH}$ (20)
7	$\text{CH}_2=\text{C}(\text{CH}_3)$	1.9 (98)	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH(OH)CH}=\text{C}=\text{CH}_2$ (10)	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH(OH)CH}_2\text{C}\equiv\text{CH}$ (90)
8	$\text{CH}_2=\text{C}(\text{CH}_3)$	2.0 (90)	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH(OH)CH}=\text{C}=\text{CH}_2$ (35)	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH(OH)CH}_2\text{C}\equiv\text{CH}$ (65)
9	$(E)\text{-CH}_3\text{CH}=\text{CH}$	2.1 (95)	$(E)\text{-CH}_3\text{CH}=\text{CHCH(OH)CH}=\text{C}=\text{CH}_2$ (5)	$(E)\text{-CH}_3\text{CH}=\text{CHCH(OH)CH}_2\text{C}\equiv\text{CN}$ (95)
10	$(E)\text{-C}_3\text{H}_5\text{CH}=\text{CH}$	2.5 (90)	$(E)\text{-C}_3\text{H}_5\text{CH}=\text{CHCH(OH)CH}=\text{C}=\text{CH}_2$ (10)	$(E)\text{-C}_3\text{H}_5\text{CH}=\text{CHCH(OH)CH}_2\text{C}\equiv\text{CH}$ (90)

^a This run involved dropwise addition (20 min) of an ether solution of Bu_3SnCl_2 (37.5 mmol in 10 ml of ether) to an equimolecular mixture of $\text{Bu}_3\text{SnCH}=\text{C}=\text{CH}_2$ and $\text{C}_3\text{H}_5\text{CHO}$ (25 mmol).

TABLE 2

PRODUCTS OF THE REACTION OF $\text{Bu}_3\text{SnCH}=\text{C}=\text{CH}_2$ WITH RCHO IN THE PRESENCE OF NEAT Bu_3SnCl_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)	$\text{CH}_3\text{CH(OH)CH}=\text{C}=\text{CH}_2$ (70)	$\text{CH}_3\text{CH(OH)CH}_2\text{C}\equiv\text{CH}$ (30)
12	C_2H_5	40	2.2 (88)	$\text{C}_2\text{H}_5\text{CH(OH)CH}=\text{C}=\text{CH}_2$ (58)	$\text{C}_2\text{H}_5\text{CH(OH)CH}_2\text{C}\equiv\text{CH}$ (42)
13	$(\text{CH}_3)_2\text{CH}$	50	2.2 (78)	$(\text{CH}_3)_2\text{CHCH(OH)CH}=\text{C}=\text{CH}_2$ (51)	$(\text{CH}_3)_2\text{CHCH(OH)CH}_2\text{C}\equiv\text{CH}$ (49)
14	$(\text{CH}_3)_3\text{C}$	120	2.6 (82)	$(\text{CH}_3)_3\text{CCH(OH)CH}=\text{C}=\text{CH}_2$ (50)	$(\text{CH}_3)_3\text{CCH(OH)CH}_2\text{C}\equiv\text{CH}$ (50)

^a These runs involved 2.5 mmol of each component. ^b The time between 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 $\text{Bu}_3\text{SnCH}=\text{C}=\text{CH}_2$ and RCHO with Bu_2SnCl_2 in the presence of water. When the rate of addition of the first-formed mixed chloro-organotin ($\text{Bu}_2(\text{CH}\equiv\text{CCH}_2)\text{SnCl}$) 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. $90\text{--}92^\circ\text{C}/0.1\text{ mmHg}$ (Lit. [7], b.p. $80\text{--}82^\circ\text{C}/0.15\text{ mmHg}$). The IR spectrum showed the presence of the $\text{C}=\text{C}=\text{C}$ stretching vibration band centered at about 1930 cm^{-1} , and no $\nu(\text{C}\equiv\text{C})$ band was observed.

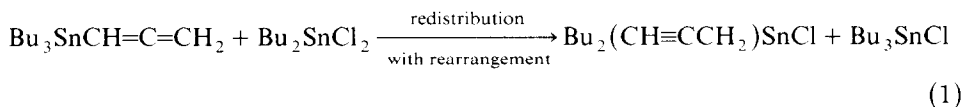
Addition reactions

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.

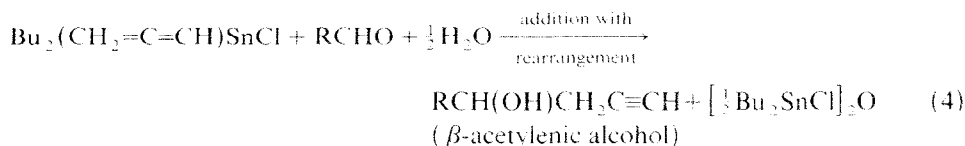
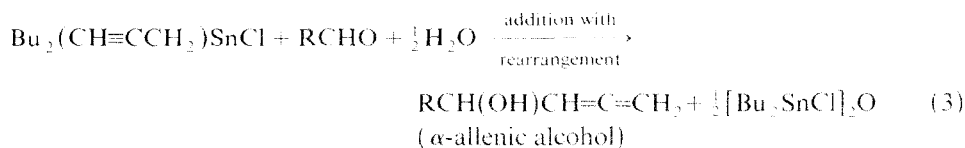
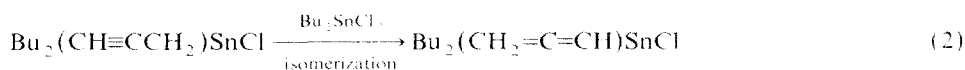
A similar procedure was carried out in some cases in the absence of water using 25 mmol of each component.

Results and discussion

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



* A mixture of $\text{Bu}_3\text{Sn}(\text{C}_3\text{H}_3)$ (C_3H_3 = allenyl or propargyl group) which has not been treated with methanol isomerizes completely to $\text{Bu}_3\text{SnCH}=\text{C}=\text{CH}_2$ when stored for more than three months.



When the mixture of $\text{Bu}_3\text{SnCH}=\text{C}=\text{CH}_2$ and RCHO is added to the scrambling reagent Bu_2SnCl_2 , the mixed $\text{Bu}_2(\text{CH}\equiv\text{CCH}_2)\text{SnCl}$ 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 $\text{R} = \text{CH}_3$, C_2H_5 , $(\text{CH}_3)_2\text{CH}$ or $(\text{CH}_3)_3\text{C}$, 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 $\text{Bu}_2(\text{CH}_2=\text{C}=\text{CH})\text{SnCl}/\text{RCHO}/\text{H}_2\text{O}$ (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.

Acknowledgements

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

References

- 1 A. Boaretto, D. Marton, G. Tagliavini and A. Gambaro, *J. Organomet. Chem.*, 286 (1985) 9.
- 2 A. Gambaro, P. Ganis, D. Marton, V. Peruzzo and G. Tagliavini, *J. Organomet. Chem.*, 231 (1982) 307.
- 3 A. Boaretto, D. Marton, G. Tagliavini and A. Gambaro, *Inorg. Chim. Acta*, 77 (1983) L196.
- 4 A. Gambaro, A. Boaretto, D. Marton and G. Tagliavini, *J. Organomet. Chem.*, 260 (1984) 255.
- 5 G. Tagliavini, *Rev. SiGeSnPb*, in press.
- 6 C. Prevost, M. Gaudemar and J. Honigberg, *C.R. Acad. Sci. (Paris)*, 230 (1950) 1186.
- 7 Y. Ueno and M. Okawara, *J. Am. Chem. Soc.*, 101 (1979) 1893.
- 8 J.L. Moreau and M. Gaudemar, *Bull. Soc. Chim. France*, (1970) 2175.
- 9 P. Place, C. Vernière and J. Goré, *Tetrahedron*, 37 (1981) 1359.
- 10 M. Huché, *Bull. Soc. Chim. France*, (1975) 2369.
- 11 J. Nokami, T. Tamaoka, T. Koguchi and R. Okawara, *Chem. Lett.*, (1984) 1939.
- 12 J. Pornet, *Tetrahedron Lett.*, 22 (1981) 455.