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ALLYLSTANNATION

VI *. ALLYLATION AND ALLENYLATION OF ALDEHYDES AND KETONES BY ALLYL- AND ALLENYL-TIN CHLORIDES IN THE PRESENCE OF WATER

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Summary

Allyl- and propargyl-carbinols can be readily prepared in one pot reaction, in the presence of water, by addition of allyl- or allenyl-tin chlorides to carbonyl compounds. The reactions of $Bu_{3-n}(CH_2{=}CHCH_2)SnCl_n$, $Bu_{3-n}(CH_3CH{=}CH{-}CH_2)SnCl_n$ ($n = 1$, 2) and $Bu_2(CH_2{=}C{=}CH)SnCl$ and the carbonyl compounds RCHO (R = H, C_2H_5, $(CH_3)_2CH$, $(CH_3)_3C$, (*E*)-$CH_3CH{=}CH$, C_6H_5) and RCOR′ (R = R′ = CH_3 and R = CH_3 and R′ = $(CH_3)_2CH$) have been examined. The monochloroorganotin derivatives undergo the following quantitative reactions:

$$Bu_2(CH_2{=}CHCH_2)SnCl + RCOR' + \tfrac{1}{2}H_2O \rightarrow R(HO)C(R')CH_2CH{=}CH_2 + \tfrac{1}{2}[Bu_2SnCl]_2O\downarrow \quad (1)$$

$$Bu_2(CH_2{=}C{=}CH)SnCl + RCOR' + \tfrac{1}{2}H_2O \rightarrow R(HO)C(R')CH_2C{\equiv}CH + \tfrac{1}{2}[Bu_2SnCl]_2O\downarrow \quad (2)$$

Reaction (2), which involves the allenic substrate, is characterized by a rearrangement of the unsaturated chain, the propargylic carbinol being isolated as the major product (~ 90%).

Introduction

Allylchlorotins, $R_{3-n}AllSnCl_n$ and $R_{3-n}CrotSnCl_n$ (R = alkyl, All = $CH_2{=}CHCH_2$, Crot = *E*/*Z*-$CH_3CH{=}CHCH_2$, $n = 1$, 2, 3), are much more reactive

* For Part V, see ref. 10.

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than the corresponding R_3AllSn and $R_3CrotSn$ as allylating agents, and readily add to aldehydes and ketones [1–10]. These reactions take place under mild conditions in the absence of solvent and catalysts, and can be carried out without any special precautions [11]. During our studies we have ascertained that the tin–allyl bond in such substrates is so inert that it undergoes no decomposition in the presence of water over a long period at room temperature. Thus we have studied addition reactions of these compounds to carbonyl compounds in water under heterogeneous conditions. We have also extended this study to new organotin species containing an allenic group, such as $Bu_2(CH_2{=}C{=}CH)SnCl$.

Several examples of addition reactions of these substrates with aldehydes and ketones in the presence of water are reported below.

Experimental

Allyl-di-n-butyltin chloride, allyl-n-butyltin dichloride, crotyl-di-n-butyltin chloride and crotyl-n-butyltin dichloride were prepared as previously described [1,2,5,7]. Commercial samples of the carbonyl compounds were distilled before use.

The recovered products were characterized by their IR and carbon-13 NMR spectra, respectively recorded on a Perkin–Elmer Model 599B spectrophotometer and on a Bruker WH 90 spectrometer operating in the FT mode.

Preparation of diallenyldibutyltin

Following the procedure described by Prevost et al. [12], allenylmagnesium bromide was obtained by dropwise addition (4 h) of an ether solution of propargyl bromide (1.38 mol, 165 g, 400 ml of diethyl ether) to magnesium turnings (2.86 mol, 70 g) amalgamated with mercury chloride. The Grignard reagent solution was separated and a solution of dibutyltin dichloride (0.23 mol, 70 g) in 250 ml of diethyl ether was added to it during 2 h. 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 10 min in order to isomerize the product to the allenic form, the isomerization being monitored by observing the disappearance of the band centered at 2100 cm^{-1} which is related to the C≡C stretching vibration of the propargylic group bonded to the tin atom [13]. Distillation of the residue under reduced pressure gave 61 g (85%) of diallenyldibutyltin, b.p. 88–90°C/0.1 mmHg. The product was characterized by IR spectroscopy: the band associated with the C=C=C stretching vibration centered at 1932 cm^{-1}, was present, whereas that at 2100 cm^{-1} (ν(C≡C)) was completely absent.

Preparation of allenyl-di-n-butyltin chloride

This compound was prepared by the following redistribution process:

$$(CH_2{=}C{=}CH)_2SnBu_2 + Bu_2SnCl_2 \xrightarrow[\text{r.t.}]{2h} 2Bu_2(CH{=}C{=}CH)SnCl$$

Equimolecular amounts (30 mmol) of dibutyldiallenyltin and dibutyltin dichloride were stirred together at room temperature for 2 h. After this time the IR spectrum showed the strong band at 1932 cm^{-1} associated with the C=C=C stretching vibration [13]. Several batches of this compound were prepared and used in the addition reactions without further treatment. Two batches were distilled under

reduced pressure, and had b.p.'s of 90–91°C/0.05 mmHg and 83–83.5°C/0.04 mmHg, respectively.

Addition reactions

Equimolecular amounts (30–35 mmol) of the allyltin or allenyltin compound and the carbonyl compound were allowed to react in the presence of 5 ml of water with stirring at room temperature. A white precipitate of tetrabutyl-1,3-dichlorodistannoxane separated in the reactions of the monochloro derivatives. Reactions involving the dichloro derivatives were characterized by the initial formation of a suspension which disappeared later. The point of appearance of the precipitate in the former case and that of the disappearance of the suspension in latter case were used in determining the reaction time (cf. Tables 1–3).

Work-up of the mixture followed by extraction with diethyl ether then removal of the ether solution by trap-to trap distillation in a cold bath (liquid nitrogen) gave pure homoallylic alcohols in the case of the allylic substrates, and a mixture of propargylic and allenic carbinols in the case of the allenyltin compounds.

Characterization and analysis of products

Analytical data for the homoallylic alcohols isolated were in agreement with those previously given [2]. The carbon-13 chemical shifts for the propargylic and allenic carbinols are listed in Table 4.

TABLE 1

ALLYLATION OF ALDEHYDES AND KETONES BY $Bu_2(CH_2{=}CHCH_2)SnCl$ AND $Bu_2(CH_3CH{=}CHCH_2)SnCl$ SUBSTRATES IN WATER AT 25°C

Organotin compound (mmol)	Carbonyl compound (mmol)	Reaction time [a] (min)	Prepared homoallylic alcohol (g (%yield))
$Bu_2(CH_2{=}$ $CHCH_2)SnCl$ (30)	HCHO (60)	5	$CH_2(OH)CH_2CH{=}CH_2$ 2.1(97)
	C_2H_5CHO (30)	10	$C_2H_5CH(OH)CH_2CH{=}CH_2$ 3.0 (~ 100)
	$(CH_3)_2CHCHO$ (30)	20	$(CH_3)_2CHCH(OH)CH_2CH{=}CH_2$ 3.4(99)
	$(CH_3)_3CCHO$ (30)	30	$(CH_3)_3CCH(OH)CH_2CH{=}CH_2$ 3.7(96)
	(*E*)-$CH_3CH{=}CHCHO$ (30)	10	(*E*)-$CH_3CH{=}CHCH(OH)CH_2CH{=}CH_2$ 3.3 (98)
	C_6H_5CHO (30)	10	$C_6H_5CH(OH)CH_2CH{=}CH_2$ 4.4(99)
	CH_3COCH_3 (35)	60	$CH_3(CH_3)C(OH)CH_2CH{=}CH_2$ 2.7(90)
	$CH_3COCH(CH_3)_2$ (30)	60	$CH_3[(CH_3)_2CH]C(OH)CH_2CH{=}CH_2$ 3.8(99)
$Bu(CH_3CH{=}$ $CHCH_2)SnCl$ [b] (30)	C_2H_5CHO (30)	20	$C_2H_5CH(OH)CH(CH_3)CH{=}CH_2$ [c] 3.0(87)

[a] This is the time between the mixing of the reactants and the appearance of the distannoxane precipitate. [b] A mixture of isomers *E*/*Z* 50/50. [c] A mixture of isomers *erythro*/*threo* 40/60.

TABLE 2

ALLYLATION OF ALDEHYDES AND KETONES BY $Bu(CH_2{=}CHCH_2)SnCl_2$ AND $Bu(CH_3CH{=}CHCH_2)SnCl_2$ SUBSTRATES IN WATER AT 25°C

Organotin compound (mmol)	Carbonyl compound (mmol)	Reaction time [a] (h)	Prepared homoallylic alcohol (g (%yield))
$Bu(CH_2{=}CHCH_2)SnCl_2$ (30)	C_2H_5CHO (35)	1	$C_2H_5CH(OH)CH_2CH{=}CH_2$ 2.5(83)
	$(CH_3)_2CHCHO$ (30)	1	$(CH_3)_2CHCH(OH)CH_2CH{=}CH_2$ 2.8(82)
	$(CH_3)_3CCHO$ (30)	24	$(CH_3)_3CCH(OH)CH_2CH{=}CH_2$ 2.8(73)
	(*E*)-$CH_3CH{=}CHCHO$ (30)	1	(*E*)-$CH_3CH{=}CHCH(OH)CH_2CH{=}CH_2$ 2.7(80)
	C_6H_5CHO (30)	2	$C_6H_5CH(OH)CH_2CH{=}CH_2$ 4.3(96)
	CH_3COCH_3 (35)	4	$CH_3(CH_3)C(OH)CH_2CH{=}CH_2$ 2.1(70)
	$CH_3COCH(CH_3)_2$ (30)	24	$(CH_3)_2CH(CH_3)C(OH)CH_2CH{=}CH_2$ 3.1(81)
$Bu(CH_3CH{=}CHCH_2)SnCl_2$ [b] (30)	C_2H_5CHO (30)	1	$C_2H_5CH(OH)CH(CH)_3)CH{=}CH_2$ [c] 2.9(85)

[a] This is the time between the mixing of the reactants and the disappearance of the suspension initially present. [b] A mixture of isomers *E*/*Z* 62/38. [c] A mixture of isomers *erythro*/*threo* = 50/50.

The IR and NMR spectra show that the carbinols are obtained as mixtures of two isomers in which the propargylic carbinols are the major products (90–95%). Analysis of these isomer mixtures was based on the integrated intensities of the appropriate carbon-13 NMR signals. Quantitative determinations of the carbon-13 NMR spectra were made by using sufficiently long pulse intervals in order to avoid saturation of the nuclear spins (at least 25 s) and the nuclear Overhauser effect (NOE) was suppressed by the gated decoupling method [14]. This analysis was supplemented by GLC analysis (2 m column, 1/8 inch i.d. filled with SE30, T_i 250°C, T_d 270°C and T_c 105°C, gas rate 20 ml/m) which shows two well resolved peaks the former corresponding to the propargylic and the latter to the allenic isomer. For example, retention times are 3 min 18 s and 4 min 27 s for R = $(CH_3)_2CH$ and 4 min 22 s and 5 min 48 s for R = $(CH_3)_3C$, respectively. The area ratios were the same as the ratios obtained from the integrated carbon-13 NMR signals.

Results and discussion

Tables 1 and 2 show the results obtained for the allylation of carbonyl compounds employing $Bu_2(CH_2{=}CHCH_2)SnCl$ and $Bu(CH_2{=}CHCH_2)SnCl_2$ substrates, respectively: two examples with crotyl derivatives are also given. Table 3 shows the corresponding results for the allenic substrate.

It should be emphasized that these reactions can be carried out in one pot reaction in the presence of water under heterogeneous conditions. The times of reaction in the case of monochloro derivatives (cf. Tables 1 and 3) are short, the

longest for aldehydes being about 45 min. Furthermore reactions 3 and 4 are effectively quantitative.

$$Bu_2(CH_2{=}CHCH_2)SnCl + RCHO + \tfrac{1}{2}H_2O \rightarrow$$
$$RCH(OH)CH_2CH{=}CH_2 + \tfrac{1}{2}Bu_2Sn(Cl)OSn(Cl)Bu_2 \downarrow \quad (3)$$

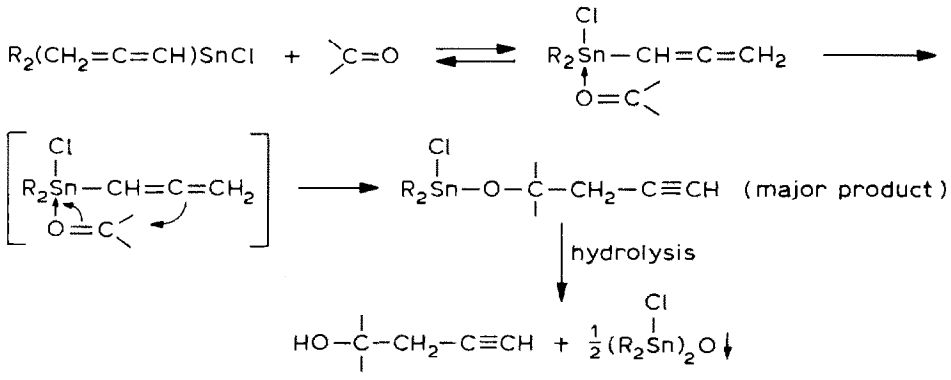
$$Bu_2(CH_2{=}C{=}CH)SnCl + RCHO + \tfrac{1}{2}H_2O \rightarrow$$
$$RCH(OH)CH_2C{\equiv}CH + RCH(OH)CH{=}C{=}CH_2 + \tfrac{1}{2}Bu_2Sn(Cl)OSn(Cl)Bu_2 \downarrow \quad (4)$$
(90–95% yield) (10–5% yield)

The carbinols recovered (cf. Tables 1, 2) using crotyl substrates are mixtures of *erythro* and *threo* isomers: their ratio is the same as that previously found under different conditions [1,2,4,5]. This shows that the stereochemical course is not changed.

In connection with the addition reactions involving the allenyltin compound, it is noteworthy that allenic tin substrates have not previously been used for synthetic purposes involving additions to carbonyl compounds. The only work involving the substrate $Ph_3SnCH{=}C{=}CH_2$ concerned the kinetics of its reaction with chloral [15]. The reaction rate in this case was not very high compared to those found for the allenyltin chloride substrate.

Organotin chlorides containing allyl– or allenic–tin bonds, are activated reagents, the carbonyl species being able to coordinate to the tin centre [1] in a process which facilitates the overall reaction as depicted in Scheme 1.

SCHEME 1



Since the reaction involves an allenic rearrangement, the major product being the propargylic carbinol, we agree with a previous report of a cyclic mechanism (S_Ei') [15].

This new route to known propargylic carbinols is simple and convenient and the use of this organotin substrate greatly improves this method, which has advantages over the previous methods [16].

(Continued on p. 16)

TABLE 3

ADDITION REACTIONS OF $Bu_2(CH_2{=}C{=}CH)SnCl$ TO CARBONYL COMPOUNDS IN WATER AT 25°C

Organotin compound (mmol)	Carbonyl compound (mmol)	Reaction time [a] (min)	Amount of product g(%yield)	Composition of the product mixture	
				Propargylic isomer (%)	Allenic isomer (%)
$Bu_2(CH_2{=}C{=}CH)SnCl$ (25)	C_2H_5CHO (25)	30	2.9(~ 100)	$C_2H_5CH(OH)CH_2C{\equiv}CH$ (90)	$C_2H_5CH(OH)CH{=}C{=}CH_2$ (10)
	$(CH_3)_2CHCHO$ (25)	45	2.8(~ 100)	$(CH_3)_2CHCH(OH)CH_2C{\equiv}CH$ (95)	$(CH_3)_2CHCH(OH)CH{=}C{=}CH_2$ (5)
	$(CH_3)_3CCHO$ (25)	55	3.1(98)	$(CH_3)_3CCH(OH)CH_2C{\equiv}CH$ (95)	$(CH_3)_3CCH(OH)CH{=}C{=}CH_2$ (5)
	(*E*)-$CH_3CH{=}CHCHO$ (25)	40	2.7(98)	(*E*)-$CH_3CH{=}CHCH(OH)CH_2C{\equiv}CH$ (90)	(*E*)-$CH_3CH{=}CHCH(OH)CH{=}C{=}CH_2$ (10)
	CH_3COCH_3 (30)	1200	1.3(53)	$CH_3(CH_3)C(OH)CH_2C{\equiv}CH$ (90)	$CH_3(CH_3)C(OH)CH{=}C{=}CH_2$ (10)

[a] This is the period between the mixing of the reactants and the appearance of the distannoxane precipitate.

TABLE 4

CARBON-13 NMR CHEMICAL SHIFTS [a] OF THE PREPARED PROPARGYLIC AND ALLENIC ALCOHOLS

Alcohols	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)
$^{1}CH\equiv{}^{2}C-{}^{3}CH_2-{}^{4}CH(OH)-{}^{5}CH_2-{}^{6}CH_3$	70.79	81.85	27.05	71.46	29.14	9.97	–
$^{1}CH\equiv{}^{2}C-{}^{3}CH_2-{}^{4}CH(OH)-{}^{5}CH(CH_3)-{}^{6}CH_3$	70.70	81.88	24.99	74.76	32.68	19.17 (17.27) [b]	–
$^{1}CH\equiv{}^{2}C-{}^{3}CH_2-{}^{4}CH(OH)-{}^{5}C(CH_3)(CH_3)-{}^{6}CH_3$	70.61	83.06	22.78	77.55	34.83	25.84	–
$^{1}CH\equiv{}^{2}C-{}^{3}CH_2-{}^{4}CH(OH)-{}^{5}CH=CH-{}^{7}CH_3$ -(E)	70.73	81.30	27.69	70.91	132.95	126.83	17.57
$^{1}CH_2={}^{2}C={}^{3}CH-{}^{4}CH(OH)-{}^{5}CH_2-{}^{6}CH_3$	76.27	207.92	94.72	71.46	30.59	9.97	–
$^{1}CH_2={}^{2}C={}^{3}CH-{}^{4}CH(OH)-{}^{5}CH(CH_3)-{}^{6}CH_3$	75.40	208.26	93.09	75.91	34.56	18.33 (18.27) [b]	–
$^{1}CH_2={}^{2}C={}^{3}CH-{}^{4}CH(OH)-{}^{5}C(CH_3)(CH_3)-{}^{6}CH_3$	75.79	208.30	92.03	77.88	35.62	25.84	–
$^{1}CH_2={}^{2}C={}^{3}CH-{}^{4}CH(OH)-{}^{5}CH=CH-{}^{7}CH_3$-(E)	76.30	211.98	93.00	67.91	136.19	124.20	23.32

[a] ppm from internal TMS in pure liquids. [b] The values for C(6) and C(6').

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