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ALLYLSTANNATION

III *. SYNTHESIS OF HOMOALLYLIC ALCOHOLS AND 4-CHLORO-2,6-DIALKYL-3-METHYLTETRAHYDROPYRANS BY REACTIONS BETWEEN (*E*/*Z*)-2-BUTENYLDICHLORO-n-BUTYLTIN AND ALDEHYDES

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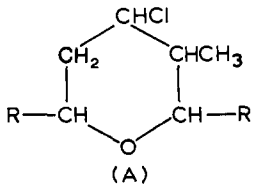
Summary

2-Butenyldichloro-n-butyltin (in various *cis*/*trans* isomer ratios) reacts readily with neat RCHO (R = CH_3, C_2H_5, $(CH_3)_2CH$, and C_6H_5) at 25°C to give (a) linear alcohols, $RCH(OH)CH_2CH{=}CHCH_3$ in the *E* and *Z* forms, (b) branched alcohols, $RCH(OH)CH(CH_3)CH{=}CH_2$ in the *threo* and *erythro* forms, and (c) 2,3,4,6-tetra-substituted tetrahydropyrans (A) as a mixture of *cis*/*trans* isomers arising from the $CH(CH_3)$–CHCl bond. The maximum yields of these tetrahydropyrans were ob-



(A)

(R = CH_3, C_2H_5, $(CH_3)_2CH$)

tained by the use of 3–3.5 molar ratios RCHO/tin compound in the absence of solvents, whereas work-up after reactions in CH_2Cl_2 gave linear alcohols as the main products. The formation of linear alcohols appears to be stereospecific, as the ratio of *E*/*Z* isomers obtained is the same as that in the organotin compound. Tetrahydropyrans are formed preferentially as the *trans* isomers.

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* For Part I, see ref. 20; for Part II, see ref. 21.

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Introduction

Addition of allyltins, such as $R_3SnCH_2CH{=}CH_2$, $R_3SnCH_2CH{=}CHCH_3$ and $(CH_2{=}CHCH_2)_4Sn$, to aldehydes and ketones requires either high temperatures [1–3] or catalysis by strong Lewis acids [4–12]. In contrast allylchloro- and crotylchloro-tins are considerably more reactive [13–22], and addition to a variety of aldehydes and ketones occurs at room temperature in the air in the absence of solvent.

Recent work on the addition to aldehydes of crotyl- and α-methylallyl-chlorotin compounds [18–21], particularly (*E*/*Z*)-2-butenylchlorodi-n-butyltin [20] and α-methylallylchlorodi-n-butyltin [21], has revealed the effectiveness of these substrates in controlling the stereochemistry of non-rigid open-chain reaction products. It has also been shown [17] that the allylstannation reactivity increases in the order $AlkR_3Sn < AlkR_2SnX < AlkRSnX_2 < AlkSnX_3$ (Alk = allyl or crotyl, R = alkyl, X = halogen); that is, the reactivity of these substrates towards a carbonyl compound increases with the acceptor character of the tin centre.

This paper describes reactions of (*E*/*Z*)-2-butenyldichloro-n-butyltin with aldehydes, RCHO (R = CH_3, C_2H_5, $(CH_3)_2CH$, $(CH_3)_3C$, C_6H_5). When R = CH_3, C_2H_5 or $(CH_3)_2CH$, the conditions can be varied so as to produce either homoallylic alcohols or 4-chloro-2,6-dialkyl-3-methyltetrahydropyrans.

Experimental

Details of the IR and NMR equipment and the preparations of most of the starting materials have been described previously [4–9]. Mass spectra were obtained on a VG NM 16F mass spectrometer. GLC analysis were made with a Sigma-3P Perkin–Elmer apparatus operating with a flame-ionization detector.

Preparation of 2-Butenyl-dichloro-n-butyltin

The compound n-$BuSn(C_4H_7)_3$ (C_4H_7 = *E*-, *Z*-crotyl and α-methylallyl group) was first prepared in 60–80% yield by treatment of crotylmagnesium bromide (0.74 mol, from magnesium turnings and commercially available crotyl bromide) with freshly distilled n-$BuSnCl_3$ in a molar ratio of 6/1 in anhydrous diethyl ether; the product was distilled under reduced pressure at 102–105°C/0.04 mmHg and the infrared spectrum in the ν(C=C) range showed three bands, at 1655, 1640 and 1625 cm^{-1}, corresponding respectively to C_4H_7 groups in the forms: *E*- and *Z*-crotyl and α-methylallyl.

2-Butenyldichloro-n-butyltin was then prepared by redistribution at room temperature between $BuSnCl_3$ and the mixture of isomers of $BuSn(C_4H_7)_3$ (35 mmol) in the molar ratio 2/1. Reaction was complete after 2–3 h, and the products were then distilled under reduced pressure to give *E*/*Z*-n-$BuCl_2SnCH_2CH{=}CHCH_3$ in 90% yield, b.p. 103°C/0.07 mmHg (Lit.[6] 92°C/0.06 mmHg). This procedure gave a product with the crotyl group in only the *E* and *Z* forms; the *E*/*Z* ratios were determined by ^{13}C NMR spectroscopy [5,7], and batches of product were prepared with *E*/*Z* ratios in the range 60/40 to 70/30.

Results

Addition reactions

Three procedures were used, as follows:

(Continued on p. 299)

TABLE 1

RESULTS OF THE REACTIONS OF (*E*/*Z*)-2-BUTENYLDICHLORO-n-BUTYLTIN WITH EQUIMOLECULAR AMOUNTS OF ALDEHYDES IN THE ABSENCE OF SOLVENT

Run no.	RCHO		$BuCl_2SnCH_2$-CH=$CHCH_3$	Time of hydrolysis [a]	amount of products (g)	Composition of the product mixture						
	R	(mmol)	*E*/*Z* ratio		Yield (%) [b]	Alcohols				4-Chlorotetrahydropyran		$CH_3CH(OH)$-CH=CH_2
						Linear $X_1 \times 100$ [c]		Branched $X_2 \times 100$ [c]		$X_3 \times 100$ [c]		$X_4 \times 100$ [c]
						E (%)	*Z* (%)	*Threo* (%)	*Erythro* (%)	*Trans* (%)	*Cis* (%)	
1	C_2H_5	23.5	60/40	8 min	(2.5)		63		12		25	Traces
					80	60	40	48	52	59	41	
2	C_2H_5	21.5	66/34	11 min	(2.2)		62		15		23	Traces
					77	67	33	51	49	58	42	
3	C_2H_5	24.9	69/31	4 days	(2.45)		44		3		50	3
					68	68	32	50	50	52	48	
4	$(CH_3)_2CH$	19.4	62/38	30 min	(2.3)		12		46		40	2
					71	62	38	77	23	72	28	
5	$(CH_3)_2CH$	26.3	63/37	35 min	(2.6)		13		48		39	0
					60	62	38	77	23	73	27	
6	$(CH_3)_2CH$	27.3	70/30	30 min	(3.2)		13		46		41	0
					71	71	29	75	25	75	25	
7	C_6H_5	25.0	66/34	18 h	(2.9)		75		25		0	0
					72	66	34	66	34			
8	C_6H_5	30.0	64/36	18 h	(3.1)		76		24		0	0
					64	64	36	64	36			

[a] This time is the period between the mixing of the reactants and the quenching of the reaction by hydrolysis. The times for disappearance of the C=O stretching frequency of the aldehyde were 8 min, 30 min and 18 h for C_2H_5, $(CH_3)_2CH$ and C_6H_5, respectively. [b] The total yield is based on the quantity of the tin substrate taken (see text). [c] X_1, X_2, X_3, X_4 represent the molar fractions of the components.

TABLE 2

RESULTS OF THE REACTIONS OF (*E*/*Z*)-2-BUTENYLDICHLORO-n-BUTYLTIN WITH EQUIMOLECULAR AMOUNTS OF ALDEHYDES IN CH_2Cl_2

Run no.	RCHO		$BuCl_2SnCH_2$-$CH{=}CHCH_3$	Time of hydrolysis [a]	Amount of products (g)	Composition of the product mixture						
	R	(mmol)	*E*/*Z* ratio		Yield (%) [b]	Alcohols				4-Chloro-tetrahydropyran		$CH_3CH(OH)$-$CH{=}CH_2$
						Linear $X_1 \times 100$ [c]		Branched $X_2 \times 100$ [c]		$X_3 \times 100$ [c]		$X_4 \times 100$ [c]
						E (%)	*Z* (%)	*Threo* (%)	*Erythro* (%)	*Trans* (%)	*Cis* (%)	
9	C_2H_5	35.6	62/38	18 min	(3.3)	69		28		0		3
					82	62	38	54	46			
10	C_2H_5	24.9	69/31	45 min	(2.35)	67		33		0		0
					82	68	32	55	45			
11	C_2H_5	30.5	64/36	3 h	(3.2)	66		25		7		2
					88	65	35	46	54	55	45	
12	C_2H_5	28.4	68/32	2 days	(3.0)	63		9		26		0
					79	68	32	45	55	44	56	
13	C_2H_5	24.8	64/36	4 days	(2.6)	63		6		26		5
					79	63	37	43	57	45	55	
14	$(CH_3)_2CH$	24.5	70/30	6 h	(2.8)	34		31		31		4
					74	69	31	66	34	71	29	
15	$(CH_3)_2CH$	25.0	68/32	5 h	(2.9)	31		36		33		0
					73	68	32	70	30	75	25	

a,*b* and [c] As in Table 1.

TABLE 3
RESULTS OF THE REACTIONS OF (*E*/*Z*)-2-BUTENYL-DICHLORO-n-BUTYLTIN WITH ALDEHYDES IN VARIOUS MOLAR RATIOS

Run no.	RCHO R	$BuCl_2SnCH_2CH{=}CHCH_3$ *E*/*Z* ratio	(mmol)	RCHO/ $BuCl_2$-SnCrot. Molar ratio	Amount of products (g) Yield (%) [b]	Composition of the product mixture								Trimeric aldehyde $(RCHO)_3$ $X_4 \times 100$ [c]
						Alcohols						4-chloro-tetrahydropyran		
						Linear $X_1 \times 100$ [c]		Branched $X_2 \times 100$ [c]		$X_3 \times 100$ [c]				
						E (%)	*Z* (%)	*Threo* (%)	*Erythro* (%)	*Trans* (%)	*Cis* (%)			
16	CH_3	67/33	30	3.5	(4.3)		6		0		64			30
					67					55	45			
17	CH_3	67/33	30	6	(4.0)		4		0		32			64
					34					56	44			
18	C_2H_5	66/34	24.5	1	(2.5)		63		13		24			0
					77	66	34	54	46	58	42			
19	C_2H_5	62/38	43.7	1.5	(4.5)		60		5		35			0
					73	62	38	48	52	57	43			
20	C_2H_5	64/36	29.8	2	(4.3)		37		0		63			traces
					88	62	38			56	44			
21	C_2H_5	70/30	24.9	3	(4.5)		12		0		84			4
					95	70	30			62	38			
22	C_2H_5	70/30	23.2	5	(4.3)		13		0		53			34
					70	70	30			61	39			
23	C_2H_5	68/32	24.9	5	(4.7)		15		0		42			41
					64	67	33			63	37			
24	$(CH_3)_2CH$	69/31	21.9	5	(3.5)		7		7		56			28
					56	69	31	79	21	76	24			

[a] For all runs the hydrolysis time was 1 h. [b and c] As in Table 1.

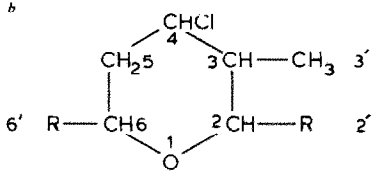
TABLE 4

CARBON-13 NMR CHEMICAL SHIFTS [a] AND ν(C–Cl) IR FREQUENCIES (cm^{-1}) OF THE PREPARED 4-CHLOROTETRAHYDROPYRANS [b]

Chloro THP R		Isomer	Carbon atoms										ν(C–Cl) (cm^{-1})	
			2	2′	2″	3	3′	4	5	6	6′	6″	Equatorial	Axial
CH_3		*Trans*	78.0	20.0		46.5	14.7	63.7	45.1	72.2	21.5		755	565
(2′,6′)		*Cis*	75.1	19.1		40.1	5.8	61.5	38.6	73.1	21.5		785	645
$CH_3—CH_2$		*Trans*	82.9	26.4	10.5	44.6	14.5	64.3	43.3	77.7	29.0	10.0	750	580
(2″,6″)	(2′,6′)	*Cis*	81.4	26.4	9.7	39.2	6.1	62.0	37.1	78.7	29.1	9.9	780	665
$(CH_3)_2—CH$		*Trans*	85.4	33.2	c	42.3	14.3	65.0	40.6	81.3	29.2	c	740	585
(2″,6″)	(2′,6′)	*Cis*	85.8	33.2	c	37.1	5.9	62.5	35.0	82.4	30.2	c	765	670

[a] ppm from internal TMS of pure liquids.

[b]



[c] Chemical shifts of the CH_3 groups in the i-C_3H_7 moiety have been found at: 13.9, 18.2, 18.7, 20.8 for the *trans* form and at: 17.0, 18.4, 18.7, 20.4 for the *cis* form.

(i) Equimolecular amounts (20–30 mmol) of (E/Z)-$BuCl_2SnCH_2CH{=}CHCH_3$ and carbonyl compound were mixed at 0°C. The solvent-free mixture was stirred and allowed to reach a constant temperature of 25°C. The progress of the reaction was monitored by infrared spectroscopy using liquid cells (0.1 or 0.2 mm path, KBr optics). When the complete disappearance of the C=O stretching band in the range 1700–1750 cm^{-1} showed that reaction was complete, 2 *M* aqueous Na_2CO_3 (10–15 ml) was added and the products were extracted with diethyl ether. Volatile compounds were distilled off under vacuum into a cold trap (liquid nitrogen); the solvent was then distilled off and the residue analyzed. The results are summarized in Table 1 and show that three main products were obtained: (a) linear alcohols, $RCH(OH)CH_2CH{=}CHCH_3$, in the *E* and *Z* isomeric ratio, (b) branched alcohols, $RCH(OH)CH(CH_3)CH{=}CH_2$, in the *threo* and *erythro* forms, and (c) 4-chloro-2,6-dialkyl-3-methyltetrahydropyrans with $R = CH_3$, C_2H_5 and $(CH_3)_2CH$. In some experiments a small amount of 1-buten-3-ol was obtained.

(ii) Equimolecular amounts (25–35 mmol) of the organotin and carbonyl compounds were mixed in 40 ml CH_2Cl_2 and the subsequent procedure was then as in (i). The main products obtained, summarized in Table 2, are the same as those obtained by procedure (i). The composition of the mixtures depend upon the time of hydrolysis.

(iii) Organotin compound (25–40 mmol) was mixed with carbonyl compound in various molar ratios from 1 to 6. The products were recovered as above after hydrolysis with 2 *M* aqueous Na_2CO_3; the results are summarized in Table 3 and show that trimeric aldehyde is recovered when the ratio $RCHO/BuCl_2SnCH_2CH{=}CHCH_3$ is > 3.

Characterization and analysis of products

All the compounds isolated were identified by ^{13}C NMR spectroscopy. The ^{13}C NMR spectra of the *Z*-linear and branched alcohols have been previously reported [20,21]. The ^{13}C chemical shifts for the tetrahydropyrans and *E*-carbinols are given in Table 4 and 5. The NMR spectra and the IR patterns show that the tetrahydropyrans are obtained as mixtures with *cis / trans* isomerism about the $CH(CH_3)$–CHCl bond. As an example Fig. 1 shows the NMR spectrum of the 4-chloro-2,3,6-trimethyltetrahydropyran. Chemical shifts for trimeric aldehydes are as follow: $(CH_3CHO)_3$,

TABLE 5

CARBON-13 NMR CHEMICAL SHIFTS [a] OF THE PREPARED *E*-CARBINOLS [b]

Carbinols	Carbon atoms							
	1	2	3	4	5	6	6′	7
$^{1}CH_3{}^{2}CH{=}{}^{3}CH{}^{4}CH_2{}^{5}CH(OH){}^{6}CH_2{}^{7}CH_3$	18.1	127.1	128.3	40.7	73.0	29.6		10.1
$^{1}CH_3{}^{2}CH{=}{}^{3}CH{}^{4}CH_2{}^{5}CH(OH){}^{6}CH({}^{6'}CH_3){}^{7}CH_3$	17.4	126.8	128.6	37.9	76.0	33.1	17.9 [c]	18.6 [c]
$^{1}CH_3{}^{2}CH{=}{}^{3}CH{}^{4}CH_2{}^{5}CH(OH){}^{6}C_6H_5$	20.0	[d]	[d]	42.6	73.7	144.2		

[a] ppm from internal TMS of pure liquids. [b] For ^{13}C NMR data of *Z*-carbinols see ref. 21. [c] These assignments between 7 and 6′ should possibly be inversed. [d] Carbon 2 and 3 and the phenylic carbons resonate in the same range, 126–128 ppm.

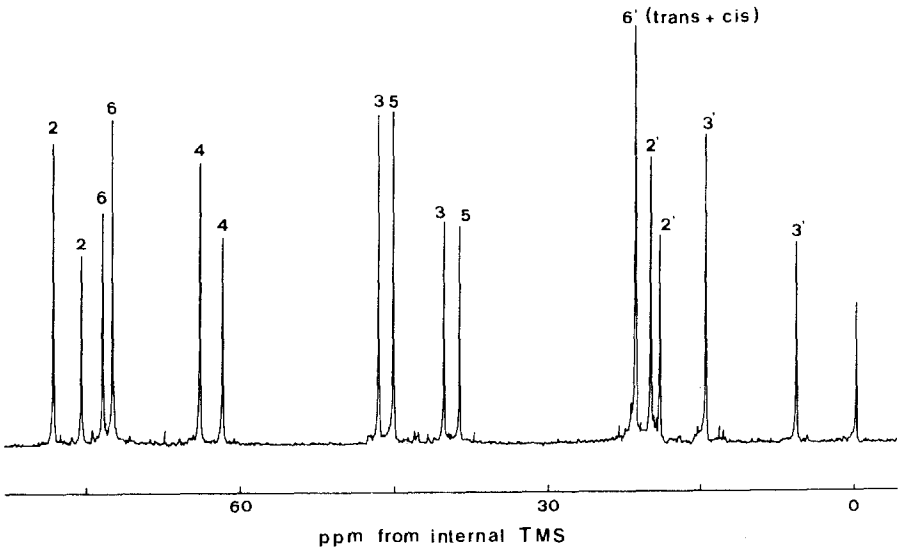


Fig. 1. ^{13}C NMR spectrum of the 4-chloro-2,3,6-trimethyltetrahydropyran. The higher intensity lines are due to the *trans*-isomer. (For figures of the carbon atoms, see Table 4, footnote b).

20.7 and 98.1; $(CH_3CH_2CHO)_3$, 7.8, 27.8 and 102.0; $((CH_3)_2CHCHO)_3$, 16.7, 32.6 and 104.8 ppm. The tetrahydropyrans were further characterized by mass spectrometry of separated, purified samples. Mass spectra were measured at 20 eV; samples were introduced directly into the ion source (150°C) and no pyrolysis was apparent. The spectra are consistent with the assumed structures, showing parent ion peaks with $m/e = 162$ ($R = CH_3$), 190 ($R = C_2H_5$) and 218 ($R = (CH_3)_2CH$) for ions containing ^{35}Cl, and with $m/e = 164$, 192 and 220 for ions containing ^{37}Cl with relative intensities of 3/1. Ion fragments formed by loss of R are observed with $m/e = 147$ and 149, 161 and 163, 175 and 177 with correct intensity ratios.

Analysis of the mixtures was based on integrated intensities of the appropriate ^{13}C NMR signals, in some cases 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 150°C, gas rate 20 ml/min) which showed two well resolved peaks, corresponding to *trans*- and *cis*-isomers. Retention times were 3'0" and 3'24" ($R = CH_3$), 6'50" and 7'50" ($R = C_2H_5$), 11'45" and 13'50" ($R = (CH_3)_2CH$); these times are in agreement with those reported for 3-chloro-2-n-butyltetrahydro-pyrans and related compounds [23]. The area ratios are consistent with those of the integrated ^{13}C signals if the lower retention times are those of the *trans* forms. This is also in line with the IR spectra of this family of compounds [24], for which the C–Cl stretching absorption consists of four bands arising from the equatorial and axial positions of the Cl (cf. Table 4).

Discussion

There is an important difference between the product of the reactions of aldehydes with the substrate $BuCl_2SnCH_2CH{=}CHCH_3$, now reported, and those previously reported with the substrates $Bu_3SnCH_2CH{=}CHCH_3$ [2], $Bu_2ClSnCH_2CH{=}CHCH_3$ [20] and $Bu_2ClSnCH(CH_3)CH{=}CH_2$ [21]. In these systems

complete allylic rearrangements are observed, and homoallylic alcohols are the sole products; furthermore these reactions have a common pattern independent of R in RCHO.

In the reactions now reported allylic rearrangement is not complete, since not only linear alcohols but also heterocyclic compounds such as tetrahydropyrans are isolated. The nature and proportion of products obtained are also strongly dependent on the aldehyde used (cf. Tables 1–3). In particular, PhCHO (cf. Table 1) does not yield tetrahydropyrans and $(CH_3)_3CCHO$ does not react at all, even at higher temperatures (50–80°C).

The results in Table 2 show that careful work-up after reaction in a solvent (CH_2Cl_2) with short hydrolysis time can restrict the products exclusively to homoallylic alcohols, (see runs 9 and 10). An increased hydrolysis time leads to an increased yield of tetrahydropyrans at the expence of branched alcohols. Figure 2 depicts this behaviour in the case of C_2H_5CHO.

The formation of tetrahydropyrans is associated with increased $RCHO/BuCl_2SnCH_2CH{=}CHCH_3$ ratio up to a molar ratio of about 3/1, after which the yield of pyran is lower because of the competing formation of trimeric aldehyde (see Fig. 3).

The stereochemistry of the products is little affected by variation of the conditions. Reactions leading to linear alcohols appear to be stereospecific since the *E/Z* ratios in the products are the same as in the organotin substrates. The tetrahydropyrans are also formed preferentially as *trans*-isomers, and this effect increases as R in RCHO changes: $CH_3 < C_2H_5 < (CH_3)_2CH$; a prolonged hydrolysis time (Table 1 runs 1, 2, 3; Table 2 runs 11, 12, 13), however, leads to more nearly equal amounts of *cis*- and *trans*-isomers.

In the light of the observed stereochemistry we can tentatively discuss possible mechanisms for the main reactions. The linear alcohols are not produced via an exocyclic transition state formed from the carbonyl compound and rearranged substrate $\equiv SnCH(CH_3)CH{=}CH_2$ [25,26], since (a) no reaction is observed with the aldehyde $(CH_3)_3CCHO$, and (b) there is no *cis*-preference such as has been observed with other systems involving an α-methylallyl moiety [21]. Moreover, the reduced yields of linear alcohols from $(CH_3)_2CHCHO$ (Table 1 runs 4–6, Table 2 runs 14

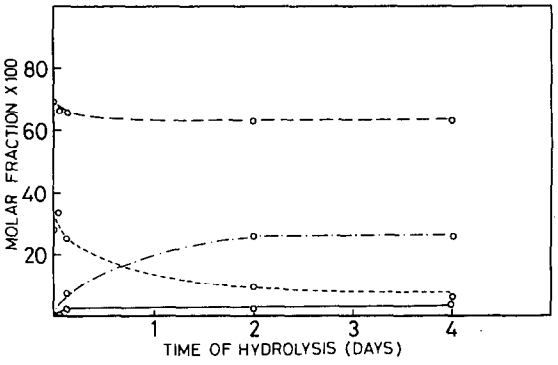


Fig. 2. Dependence of the product composition on the hydrolysis time for the system $BuCl_2SnCrot/C_2H_5CHO$ in CH_2Cl_2, runs 9–13 of Table 2. — — — Linear alcohols; - - - - - - branched alcohols; – · – · – 4-chloro-2,6-diethyl-3-methyltetrahydropyran; ——— 1-buten-3-ol.

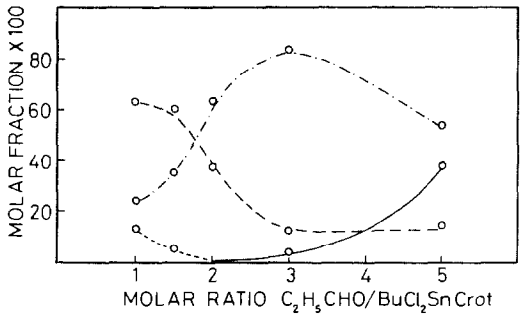
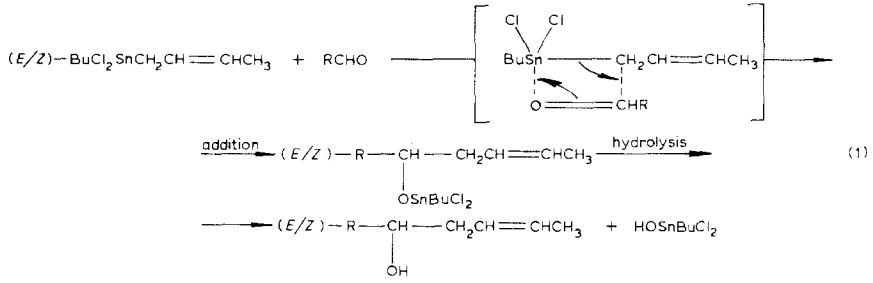
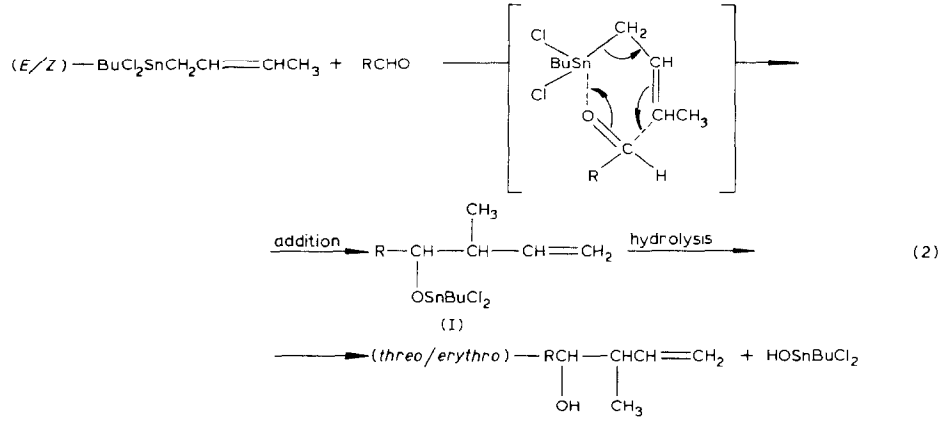


Fig. 3. Dependence of the product composition on the $C_2H_5CHO/BuCl_2SnCH_2CH{=}CHCH_3$ molar ratio in absence of solvent: runs 18–23 of Tables 3. -·-·- 4-Chloro-2,6-diethyl-3-methyltetrahydropyran; — — — linear alcohols; - - - - - - branched alcohols; ——— trimeric aldehyde $(C_2H_5CHO)_3$.

and 15, and Table 3 run 24) suggest the operation of steric effects. Only a four-centre transition state can account for both the steric effects and stereospecificity of the reaction 1.



The branched alcohols, however, may be formed via an exocyclic transition state, as proposed [20,21] for other organotin substrates (eq. 2).

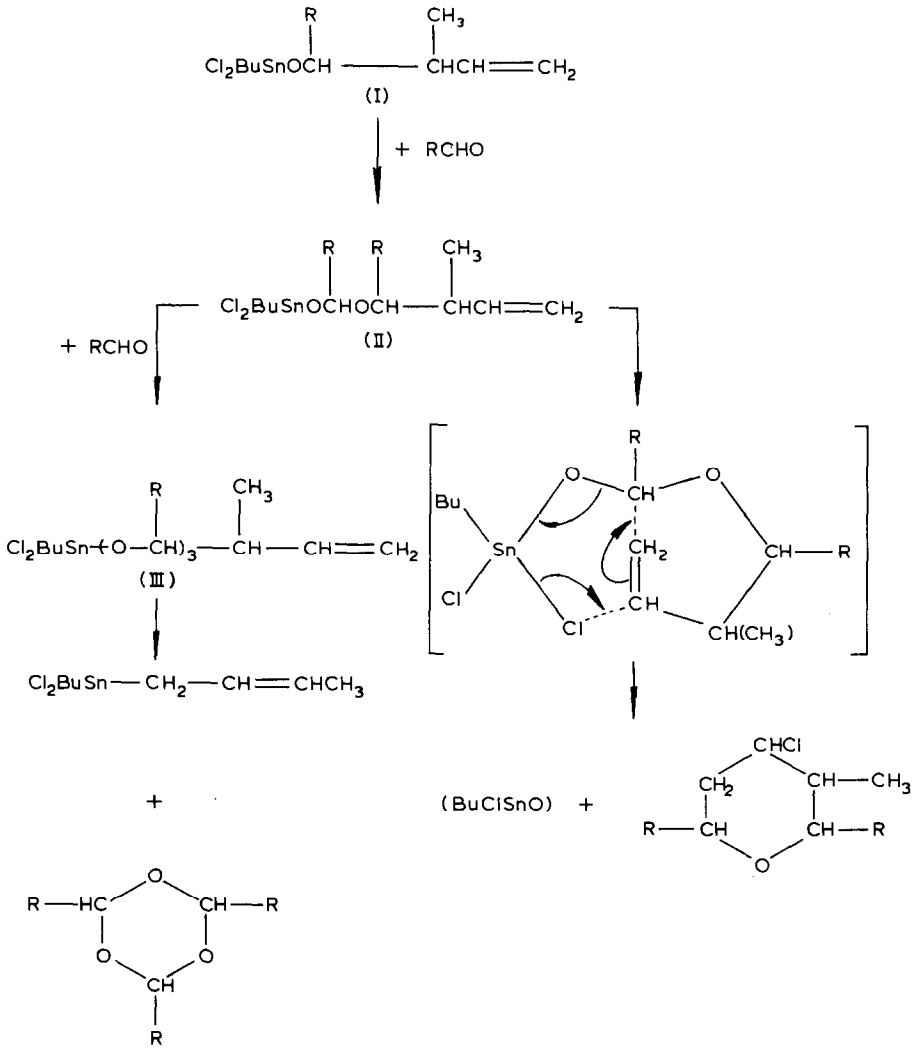


The path by which tetrahydropyrans are formed remains to be considered. This reaction may be similar to the condensation of 1-olefins with formaldehyde [27] (the Prins reaction) or a modification in which 1-olefins condense with aldehydes and hydrogen halides to give 4-halo-3-alkyltetrahydropyrans [28–33]. In the present case

formation of tetrahydropyrans occurs at the expense of branched alcohols (see Fig. 2), which are hydrolysis products of 1-olefin adducts I (see eq. 2). Branched alcohol formation is also reduced by use of excess aldehyde, confirming the relationship between tetrahydropyrans and 1-olefin adducts. Moreover, when RCHO/$BuCl_2SnCH_2CH{=}CHCH_3 > 2$ allylic rearrangement through reaction 2 seems to be favoured over the reaction involving the four-centre transition state (eq. 1, see also Fig. 3). Another feature is the formation of the trimeric aldehyde in competition with that of the tetrahydropyran. Both these products may be formed by repeated insertion of aldehyde into the Sn–O bond of 1-olefin adducts I. This hypothesis is in accord with the existence of many additions of the Sn–O bond to activated unsaturated organic molecules [34–37]; in the present case the activated centre is the tin atom, which is a very good electrophilic site.

We tentatively propose the reaction scheme 1. In this scheme two competitive

SCHEME 1



processes operate: the adduct III can give rise to trimeric aldehyde whereas adduct II can collapse, through an intramolecular rearrangement, to the tetrahydropyran. A large excess of aldehyde favours the formation of III and, under these conditions, trimeric aldehyde is obtained in high yields, and furthermore these yields are related to the ability of the aldehyde to trimerize [38,39], that is: $CH_3CHO > C_2H_5CHO > (CH_3)_2CHCHO$. When this ability is very low, as for C_6H_5CHO, the initial insertion to I appears to be inhibited.

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