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ALLYLSTANNATION

IX *. THE PREPARATION OF 4-CHLORO-2,6-DIALKYL-, 4-BROMO-2,6-DIALKYL-, (*E*/*Z*)-4-CHLORO-2,6-DIALKYL-3-METHYL- AND (*E*/*Z*)-4-BROMO-2,6-DIALKYL-3-METHYL-TETRAHYDROPYRANS BY CONDENSATION OF ALDEHYDES WITH DI- AND TRI-HALIDES OF ALLYLTIN

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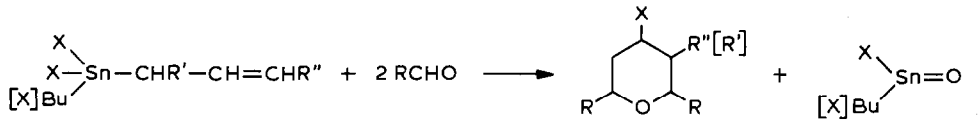
Summary

The reaction recently discovered leading to tetrahydropyrans (THP):



(X = halogen ; R' = R" = H ; R' = H and R" = CH_3 ; R' = CH_3 and R" = H)

has been more extensively investigated by using various allyltin systems, alternate incremental additions of two aldehydes, and scrambling organotin reagents. Unsymmetric halotetrahydropyrans containing various R groups can be readily prepared in this way.

The thermal breakdown of the 1/2-dichloro adducts, namely (*E*/*Z*)-1-alkyl-1-butyldichlorostannoxy, 1-alkyl-3-pentyl ethers and the (*threo*/*erythro*)-1-alkyl-1-butyldichlorostannoxy, 1-alkyl-2-methyl-3-butenyl ethers, is a stereospecific reaction which affords (*E*/*Z*)-halotetrahydropyrans, where the isomerism is at the CHCl–CH(CH_3) bond.

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* For part VIII see ref. 27.

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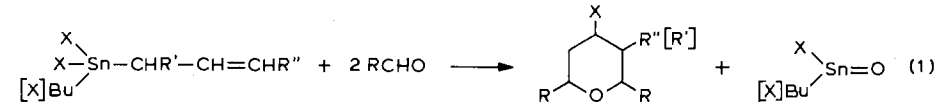
Introduction

Allyltin halides have been shown to be versatile reagents in addition reactions with carbonyl compounds [1], and by their use homoallylic alcohols [2–6], their corresponding esters [7], and 4-halo-2,6-dialkyl- and 4-halo-2,6-dialkyl-3-methyl-tetrahydropyrans can be readily synthetized. In particular, the reaction leading to tetrahydropyrans (eq. 1) takes place only with di- or tri-halides of allyltin [8–10].



(1)

(X = halogen; R′ = R″ = H; R′ = H and R″ = CH_3; R′ = CH_3 and R″ = H)

The 4-halotetrahydropyrans have normally been made in the past by the sulfuric acid-catalyzed reaction of olefins with formaldehyde in water or acetic acid [11] (i.e., the Prins reaction [12] or its modification [13]), the condensation of aldehydes with chloroalkoxyalkanes and formic acid [13–17], the condensation of aldehydes with substituted 3-butanol in hydrochloric acid [18,19], or the chloromethylation of β-ethylenic alcohols [20].

We describe here the preparation of 4-halo-2,6-disubstituted tetrahydropyrans using the following reagent systems:

(i) $Bu_2ClSnCH_2CH{=}CH_2/C_2H_5CHO/BuSnCl_3/C_2H_5CHO$;
(ii) $Bu_2ClSnCH_2CH{=}CH_2/C_2H_5CHO/BuSnCl_3/(CH_3)_2CHCHO$;
(iii) $CH_2{=}CHCH_2CH(OK)CH_3/BuSnCl_3/C_2H_5CHO$;
(iv) (*E/Z*)-$Bu_2ClSnCH_2CH{=}CHCH_3/(CH_3)_2CHCHO/BuSnCl_3/(CH_3)_2$-CHCHO;
(v) (*E/Z*)-$Bu_3SnCH_2CH{=}CHCH_3 + (CH_3)_2CHCHO/Bu_2SnCl_2/BuSnCl_3/(CH_3)_2CHCHO$;
(vi) (*E/Z*)-$BuCl_2SnCH_2CH{=}CHCH_3/C_2H_5CHO$;
(vii) $Bu_3SnCH_2CH{=}CH_2 + C_2H_5CHO/BuSnCl_3$;
(viii) $Bu_3SnCH_2CH{=}CH_2 + RCHO/SnCl_4$(or $SnBr_4$);
(ix) (*E/Z*)-$Bu_3SnCH_2CH{=}CHCH_3 + RCHO/SnCl_4$ (or $SnBr_4$),

where R = CH_3, C_2H_5, $(CH_3)_2CH$, $C_2H_5(CH_3)CH$, $(CH_3)_3C$, for systems viii and ix.

By using the method of alternate incremental additions and scrambling organotin reagents, (see systems i–v) we have confirmed that the initial 1/2 condensation products between allyltin halides and two molecules of aldehydes, viz.: $Bu_{3-n}X_nSn{-}O{-}CH(R^a){-}O{-}CH(R^b){-}CHR'{-}CH{=}CHR''$ ($n = 2,3$), give the cyclic compounds by intramolecular rearrangement.

Experimental

Details of the IR and NMR equipment and the preparation of the starting materials have been described previously [8–10]. GLC analyses were carried out with a Sigma-3B Perkin–Elmer apparatus equipped with a flame-ionization detector.

System i. $Bu_2ClSnCH_2CH{=}CH_2/C_2H_5CHO/BuSnCl_3/C_2H_5CHO$; preparation of 4-chloro-2,6-diethyltetrahydropyran (1)

In a 100 ml two-necked flask, equimolecular amounts (25 mmol) of Bu_2Cl-

$SnCH_2CH{=}CH_2$ and C_2H_5CHO were mixed at 0°C with stirring. After 20 min the mixture was allowed to reach room temperature and 25 mmol of $BuSnCl_3$ were added. Then after 20 min a further amount of C_2H_5CHO (25 mmol) was added. Hydrolysis was carried out after 30 min with 2*M* aqueous Na_2CO_3 (10 ml). The tetrahydropyran $CH(Cl)CH_2CH(C_2H_5)OCH(C_2H_5)CH_2$ (**1**) was recovered (2.7 g, 61% yield) after extraction with diethyl ether and subsequent distillation.

*System ii. $Bu_2ClSnCH_2CH{=}CH_2 / C_2H_5CHO / BuSnCl_3 / (CH_3)_2CHCHO$; preparation of a mixture of 4-chloro-2,6-diethyl- (**1**), 4-chloro-2-ethyl-6-isopropyl- (**2**) and 4-chloro-2,6-diisopropyl-tetrahydropyran (**3**)*

In a 100 ml two-necked flask equimolecular amounts (25 mmol) of $Bu_2ClSnCH_2CH{=}CH_2$ and C_2H_5CHO were mixed at 0°C with stirring. After 20 min the mixture was allowed to reach room temperature and 25 mmol of $BuSnCl_3$ were added. Then after 20 min 25 mmol of $(CH_3)_2CHCHO$ were added. Hydrolysis of the mixture was performed after 30 min with 10 ml of 2*M* Na_2CO_3. After extraction with diethyl ether a mixture of the tetrahydropyrans **1**, **2** and **3** (2.9 g) was obtained. Analysis by GLC gave the following results: 33% of **1**, 47% of **2** and 20% of **3**.

*System iii. $CH_2{=}CHCH_2CH(OK)CH_3 / BuSnCl_3 / C_2H_5CHO$; preparation of a mixture of 4-chloro-2,6-dimethyl- (**4**), 4-chloro-2-methyl-6-ethyl-(**5**), and 4-chloro-2,6-diethyl-tetrahydropyran (**1**)*

In a 100 ml two-necked flask 140 mmol of 1-penten-4-ol were mixed with 25 ml of n-pentane, and 30 mmol of potassium were slowly added with stirring under nitrogen to give the corresponding alkoxide. The alkoxide was added dropwise to a solution of $BuSnCl_3$ (30 mmol) in 25 ml of n-pentane at 0°C. The mixture was refluxed for 20 min then the KCl was filtered off (recovered 2.2 g, calcd. 2.25). After removal of the solvent and the unreacted 1-penten-4-ol, the IR spectrum of the mixture showed the presence of the alkoxide $CH_3CH(OSnBuCl_2)CH_2CH{=}CH_2$. Subsequently 30 mmol of C_2H_5CHO (1.7 g) were added dropwise at room temperature. After 24 h 2*M* aqueous Na_2CO_3 (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 residue was distilled and a mixture of 2.95 g of tetrahydropyrans (THP) was recovered.

Analysis of the THP mixture by GLC gave the following results: 6% of **4**, 72% of **5** and 22% of **1**.

*System iv. (E / Z)-$Bu_2ClSnCH_2CH{=}CHCH_3 / (CH_3)_2CHCHO / BuSnCl_3 / (CH_3)_2$-CHCHO; preparation of (E / Z)-4-chloro-2,6-diisopropyl-3-methyltetrahydropyran (**6**)*

In a 100 ml two-necked flask equimolecular amounts (25 mmol) of (*E*/*Z*)-$Bu_2ClSnCH_2CH{=}CHCH_3$ (*E*/*Z* 60/40) and i-PrCHO were mixed with stirring at 0°C to give the alkoxides $Bu_2ClSnOCH(i\text{-}Pr)CH(CH_3)CH{=}CH_2$ in the ratio *threo*/*erythro* 66/34 [4]. After 2 h the system was scrambled with 25 mmol of $BuSnCl_3$, and after 1 h 25 mmol of i-PrCHO were added and the mixture was stirred (17 h) until disappearance of the IR ν(C=O) stretching vibration band. Hydrolysis with 25 ml of Na_2CO_3 of the mixture gave 2.5 g (47% yield) of tetrahydropyran **6** in the isomer ratio *E*/*Z* 68/32 *.

* The isomerism occurs at the $CH(CH_3)$–CH(Cl) bond.

System v. (E / Z)-$Bu_3SnCH_2CH=CHCH_3$ + $(CH_3)_2CHCHO$ / Bu_2SnCl_2 / $BuSnCl_3$ / $(CH_3)_2CHCHO$, preparation of (E / Z)-4-chloro-2,6-diisopropyl-3-methyltetrahydropyran (6)

A mixture in equimolecular amounts (25 mmol) of (*E/Z*)-$Bu_3SnCH_2CH=CHCH_3$ (*E/Z* 66/34) and $(CH_3)_2CHCHO$ was added to Bu_2SnCl_2 (37.5 mmol) at 0°C with stirring; the reaction gave a 1/1-monochloro adduct with an *E/Z* ratio of about 13/87 [10]. The disappearance on the IR spectrum of the ν(C=O) stretching vibration band was observed after 90 min and $BuSnCl_3$ (25 mmol) was added. After 1.5 h $(CH_3)_2CHCHO$ (25 mmol) was added and hydrolysis was carried out after 18 h with 40 ml of 2*M* Na_2CO_3 aqueous solution.

Work-up as described above gave 4 g (75% yield) of **6** in the isomer ratio *E/Z* 15/85.

System vi. (E / Z)-$BuCl_2SnCH_2CH=CHCH_3$ / C_2H_5CHO; preparation of (E / Z)-4-chloro-2,6-diethyl-3-methyltetrahydropyran (7) by thermal treatment

C_2H_5CHO (75 mmol) was addded to (*E/Z*)-$BuCl_2SnCH_2CH=CHCH_3$ (30 mmol, (*E/Z* 52/48) with stirring at room temperature. After 2 h volatile components were transferred by trap-to-trap distillation using liquid nitrogen cooling.

Distillation of the residue (6.7 g) gave 5.1 g (90% yield) of the pure compound **7** in the isomer ratio *E/Z* 62/38.

System vii. $Bu_3SnCH_2CH=CH_2$ + C_2H_5CHO / $BuSnCl_3$ (ratio 1 / 3 / 1); preparation of tetrahydropyran 1

A mixture of $Bu_3SnCH_2CH=CH_2$ and C_2H_5CHO in 1/3 ratio was added to $BuSnCl_3$ in an amount equimolecular with the allyltin substrate. The solvent-free mixture was stirred for 1 h, then hydrolyzed with a 2*M* Na_2CO_3 solution. Tetrahydropyran **1** (b.p. 70–71°C/6 mmHg) was recovered as described above.

Table 1 shows the data for three runs in which increased amounts of the reactants were used in order to show the synthetic value of the reaction.

System viii. $Bu_3SnCH_2CH=CH_2$ + RCHO / $SnCl_4$ (or $SnBr_4$) (ratio 1 / 2.2 / 1, R = CH_3, $(CH_3)_2CH$, $C_2H_5(CH_3)CH$, $(CH_3)_3C$); preparation of 4-chloro- and 4-bromo-2,6-dialkyltetrahydropyrans

A mixture of $Bu_3SnCH_2CH=CH_2$ and RCHO in the ratio 1/2.2 was added with stirring at −15°C to $SnCl_4$ or $SnBr_4$ in an amount equimolecular with the allyltin substrate. Work-up as above gave the corresponding tetrahydropyrans (cf. Table 2).

TABLE 1

PREPARATION OF 4-CHLORO-2,6-DIETHYLTETRAHYDROPYRAN (**1**) FROM THE SYSTEM $Bu_3SnAll/C_2H_5CHO/BuSnCl_3$ (All = $CH_2CH=CH_2$) IN 1/3/1 RATIO AT 0°C

C_2H_5CHO (mmol)	Bu_3SnAll=$BuSnCl_3$ (mmol)	Tetrahydropyran yield (g (%))
90	30	4.3 (81)
180	60	9.0 (85)
270	90	14.5 (91)

System ix. (E/Z)-$Bu_3SnCH_2CH{=}CHCH_3$ + RCHO/$SnCl_4$ (or $SnBr_4$) (ratio 1/2.2/1, R = CH_3, C_2H_5, $(CH_3)_2CH$, $C_2H_5(CH_3)CH$, $(CH_3)_3C$); preparation of 4-chloro- and 4-bromo-2,6-dialkyl-3-methyltetrahydropyrans

A mixture of (*E*/*Z*)-$Bu_3SnCH_2CH{=}CHCH_3$ and the appropriate RCHO in the ratio 1/2.2 was added with stirring at −15°C to $SnCl_4$ or $SnBr_4$ in equimolecular amount with the crotyl substrate. Work-up as above gave the corresponding tetrahydropyrans. Data of the runs are given in Table 3.

Characterization and analysis of products

All the isolated compounds were identified by carbon-13 NMR spectroscopy as previously reported [8–10]. For example, Table 4 lists the carbon-13 NMR data for the tetrahydropyrans **1**, **2** and **3** obtained from system ii.

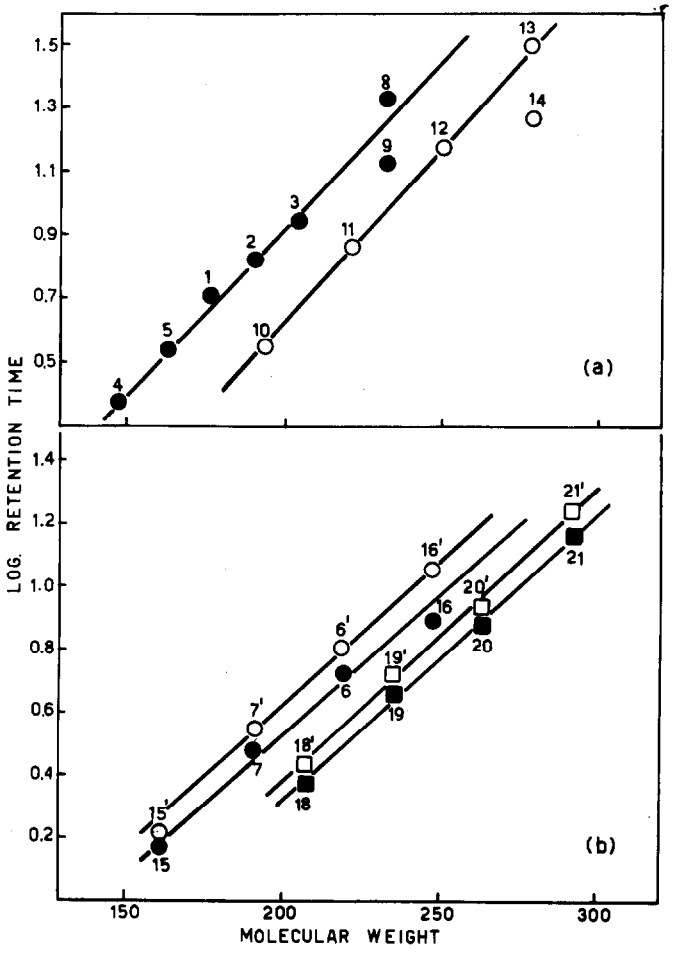


Fig. 1. Plot of the log t_r against the molecular weight of THP. (a) ● 4-chloro-2,6-dialkyltetrahydropyrans, ○ 4-bromo-2,6-dialkyltetrahydropyrans; (b) ● (*E*)-4-chloro-2,6-dialkyl-3-methyltetrahydropyrans, ○ (*Z*)-4-chloro-2,6-dialkyl-3-methyltetrahydropyrans, ■ (*E*)-4-bromo-2,6-dialkyl-3-methyltetrahydropyrans, □ (*Z*)-4-bromo-2,6-dialkyl-3-methyltetrahydropyrans.

GLC analysis (2 m column, 1/8 inch i.d., filled with SE30 20% chromosorb, T_i 250°C, T_d 270°C and T_c 150°C, gas rate 20 ml/min) was performed over all samples, in order to determine the composition of the mixtures obtained. A plot of the log t_r against the molecular weight is given in Fig. 1 for all the prepared compounds.

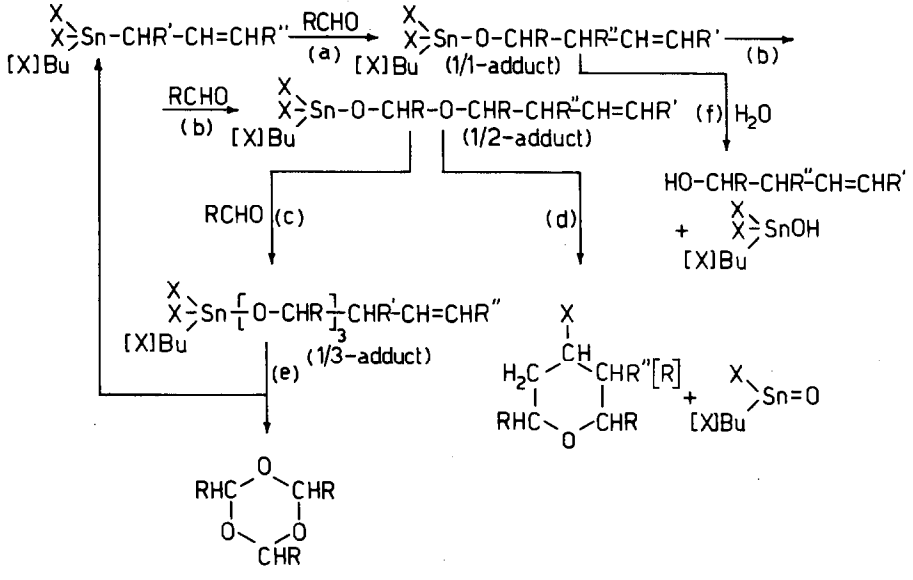
Results and discussion

Additions of aldehydes to allyltin halides having at least two halogens bonded to the tin atom can give three adducts [8,10], as shown in Scheme 1.

Step a is an addition reaction characterized by complete allylic rearrangement, and the 1/1-adducts give rise, by hydrolysis (step f), to homoallylic alcohols [1]; step b affords 1/2-adducts, which readily break down (step d) to 4-halo-disubstituted-tetrahydropyrans [8–10] or go on (by step c) to give 1/3-adducts, and hence trimeric aldehydes and the initial organotin substrates (step e).

The basic reaction involved is the formation of a 1/1-adduct, itself a tin alkoxide, which is expected to be able to add to a further carbonyl donor to give a 1/2-adduct, then an oligomer [23]. This growth reaction is similar to that observed in the polymerization of chloral by tributyltin methoxide [24], in the reaction of the tin–oxygen bond with isocyanates [25], and in the polymerization of aldehydes by aluminum alkoxides [26].

The ability to undergo repeated additions seems to be confined to the tin alkoxides having two or three halogen atoms bonded to the metal centre, and consequently only these adducts give tetrahydropyrans or trimeric aldehydes.



SCHEME 1

TABLE 2

PREPARATION OF 4-CHLORO- AND 4-BROMO-2,6-DIALKYLTETRAHYDROPYRANS FROM THE SYSTEMS $Bu_3SnAll + 2RCHO/SnCl_4$ (or $SnBr_4$) (All = $CH_2CH{=}CH_2$) IN 1/2.2/1 RATIO [a] AT −15°C

RCHO R	Time [b]	Tetrahydropyran recovered			Yield (g (%))
		Compound	$XCHCH_2CH(R)OCH(R)CH_2$		
			X	R	
CH_3	30 min	**4**	Cl	CH_3 [c]	3.3 (73)
$(CH_3)_2CH$	45 min	**3**	Cl	$(CH_3)_2CH$	4.7 (76)
$C_2H_5(CH_3)CH$	45 min	**8**	Cl	$C_2H_5(CH_3)CH$	4.4 (63)
$(CH_3)_3C$	6 h	**9**	Cl	$(CH_3)_3C$	4.9 (70)
CH_3	30 min	**10**	Br	CH_3	5.2 (90)
$(CH_3)_2CH$	30 min	**12**	Br	$(CH_3)_2CH$	6.3 (84)
$C_2H_5(CH_3)CH$	45 min	**13**	Br	$C_2H_5(CH_3)CH$	6.8 (81)
$(CH_3)_3C$	6 h	**14**	Br	$(CH_3)_3C$	7.2 (86)

[a] All runs were performed in the absence of solvent with the same quantities of reagents: Bu_3SnAll = $SnCl_4$ (or $SnBr_4$) 30 mmol; RCHO 66 mmol. [b] The period between the mixing of the reactants and the hydrolysis. [c] Of those listed this is the only previously known compound: b.p. found: 56°C/19 mmHg; Lit. [21]: 64°C/22 mmHg; Lit. [22]: 50°C/15 mmHg.

The results obtained in systems vii–ix (cf. Tables 1–3) and systems i–vi show that the condensation of aldehydes and allyltin halides provides a general route to 4-halo-disubstituted-tetrahydropyrans. The data listed in Tables 2 and 3 were obtained by adding the binary systems $Bu_3SnCH_2CH{=}CH_2$ (or $Bu_3SnCH_2CH{=}CHCH_3$), RCHO to $SnCl_4$ (or $SnBr_4$), the $SnCl_4$ and $SnBr_4$ acting as scrambling reagents to form the effective allyltin reactants. When $SnCl_4$ is used, the *E*/*Z* ratio of the recovered Cl-THP is about 50/50 for RCHO compounds having R = CH_3, C_2H_5, $(CH_3)_2CH$ and $C_2H_5(CH_3)CH$, and 70/30 for that with the bulky $(CH_3)_3C$ group (cf. Table 3). In system v, where $BuSnCl_3$ is the scrambling reagent, the resulting *E*/*Z* ratio of the Cl-THP mixture is 15/85, in accord with our previous observation of a high *Z*-convergence (*E*/*Z* ratio in the range 18/82–10/90) [10]. In the present case the *Z*-convergence is lower because of the high Lewis acidity of $SnCl_4$ which leads, through rapid isomerization processes, mainly to *E*- and *threo*-1/2 adducts (see Scheme 2 in ref. 10). On the other hand, when $SnBr_4$ is employed, a major amount of the *Z*-isomer is obtained (cf. Table 3). On going from $SnCl_4$ to $SnBr_4$ then to $BuSnCl_3$, the amount of *Z*-isomer increases in accord with the decreasing scrambling power of the reagent, that is with decrease in its acidity.

The other results involve systems i–v in which we used alternate incremental additions. The nature of the products suggest that the role played by $BuSnCl_3$ is in the formation of the 1/1 dichloro adducts, which undergo insertion of a second aldehyde molecule to form 1/2 adducts; these, by intramolecular collapse, afford THP (see for example system i). Such behaviour indicates that the 1/1 monochloro-adducts are scrambled by $BuSnCl_3$ (or by SnX_4) to form 1/2 dichloro adducts (or 1/2 trihalo adducts) without change in the configuration of the allyl framework.

Use of two different molecules of aldehydes (systems ii and iii, cf. Table 5) produces three THP molecules in various ratio: two of them are symmetric, the third

(Continued on p. 166)

TABLE 3

PREPARATION OF 4-CHLORO- AND 4-BROMO-2,6-DIALKYL-3-METHYLTETRAHYDROPYRANS FROM THE SYSTEMS (E/Z)-$Bu_3SnCrot$ + 2 $RCHO/SnCl_4(SnBr_4)$ (Crot = $CH_2CH{=}CHCH_3$) IN 1/2.2/1 RATIO [a] AT −15°C

RCHO R	$Bu_3SnCrot$ E/Z ratio [b]	Time [c] (h)	Tetrahydropyran recovered				Yield (g (%))
			Compound	$XCHCH(CH_3)CH(R)OCH(R)CH_2$		E/Z ratio [d]	
				X	R		
CH_3	64/36	2	**15**	Cl	CH_3	48/52	3.8 (93)
C_2H_5	66/33	2	**7**	Cl	C_2H_5	53/47	4.2 (88)
$(CH_3)_2CH$	33/66	2	**6**	Cl	$(CH_3)_2CH$	49/51	4.3 (79)
$C_2H_5(CH_3)CH$	64/36	2	**16**	Cl	$C_2H_5(CH_3)CH$	53/47	4.5 (73)
$(CH_3)_3C$	60/40	23	**17**	Cl	$(CH_3)_3C$	70/30	4.6 (74)
CH_3	64/36	2	**18**	Br	CH_3	40/60	5.1 (98)
C_2H_5	36/64	2	**19**	Br	C_2H_5	36/64	5.2 (88)
$(CH_3)_2CH$	36/64	2	**20**	Br	$(CH_3)_2CH$	36/64	6.1 (93)
$C_2H_5(CH_3)CH$	36/64	2	**21**	Br	$C_2H_5(CH_3)CH$	39/61	5.4 (71)
$(CH_3)_3C$	36/64	2	**22**	Br	$(CH_3)_3C$	20/80	5.6 (73)

[a] All runs have been performed in the absence of solvent with the same amount of reagents: $Bu_3SnCrot = SnCl_4$ (or $SnBr_4$) = 25 mmol.; RCHO = 55 mmol. [b] E/Z isomer ratio of $Bu_3SnCrot$. [c] The period between mixing of the reactants and hydrolysis. [d] The E/Z isomerism refers to the $CH(CH_3)$–$CH(Cl)$ bond.

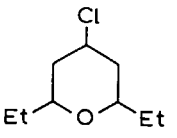
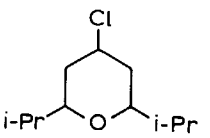
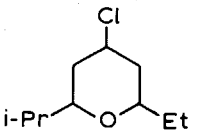
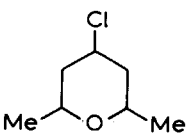
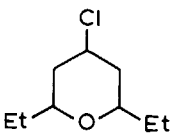
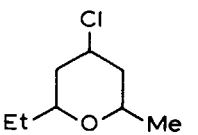
TABLE 4

CARBON-13 NMR SHIFTS (ppm from int. TMS) FOR COMPOUNDS **1**, **2** AND **3**

Compound	C(2)	C(2′)	C(2″)	C(3)	C(4)	C(5)	C(6)	C(6′)	C(6″)
$\overset{2}{O}CH(\overset{2'}{C}H_2\overset{2''}{C}H_3)\overset{3}{C}H_2\overset{4}{C}H(Cl)\overset{5}{C}H_2\overset{6}{C}H(\overset{6'}{C}H_2\overset{6''}{C}H_3)$ (**1**)	77.8	29.0	9.9	42.7	56.0	42.7	77.8	29.0	9.9
$\overset{2}{O}CH(\overset{2'}{C}H_2\overset{2''}{C}H_3)\overset{3}{C}H_2\overset{4}{C}H(Cl)\overset{5}{C}H_2\overset{6}{C}H[\overset{6'}{C}H(\overset{6''}{C}H_3)_2]$ (**2**)	77.8	29.0	9.9	42.7	56.9	40.0	81.5	33.2	18.6 (18.4)
$\overset{2}{O}CH[\overset{2'}{C}H(\overset{2''}{C}H_3)_2]\overset{3}{C}H_2\overset{4}{C}H(Cl)\overset{5}{C}H_2\overset{6}{C}H[\overset{6'}{C}H(\overset{6''}{C}H_3)_2]$ (**3**)	81.5	33.1	18.6 (18.4)	39.9	56.4	39.9	81.5	33.1	18.6 (18.4)

TABLE 5

SUMMARY OF RESULTS OBTAINED BY OF THE METHOD OF ALTERNATE INCREMENTAL ADDITION OF TWO DIFFERENT ALDEHYDES

System	1st Aldehyde	2nd Aldehyde	Recovered tetrahydropyrans with relevant proportion (%)		
			symmetric	asymmetric	
ii	EtCHO	i-PrCHO	 (1, 33)	 (3,20)	 (2,47)
iii	MeCHO [a]	EtCHO	 (4, 6)	 (1, 22)	 (5, 72)

[a] In this system the starting alcohol was $CH_3CH(OH)CH_2CH{=}CH_2$, the product of the condensation of CH_3CHO with an allyl tin substrate.

unsymmetric. The expected unsymmetric molecule is recovered in major amount (47% in system ii and 72% in system iii); the formation of the two symmetric THP molecules is probably due to kinetically competitive exchange processes of the organotin alkoxides, since processes which could be activated by scrambling reagents (for example Bu_2SnCl_2 in system ii) must be ruled out in the light of the result for system iii.

The results with systems iv and v confirm the role of $BuSnCl_3$ described above. Use of (E/Z)-$BuCl_2SnCH_2CH{=}CHCH_3$ and $BuCl_2SnCH(CH_3)CH{=}CH_2$ together (made by the scrambled system $Bu_3SnCH_2CH{=}CHCH_3/BuSnCl_3$) resulted in two different stereochemical reaction paths characterized by an E-convergence in the former case (E/Z 70/30) and a Z-convergence in the latter (E/Z 15/85), in very good agreement with our previous findings [8,10].

Systems i–v clearly show that the THP are the products of the breakdown of the 1/2 dichloro adducts, and our previous hypothesis about their formation receives further support. Hydrolysis, which was always used to assist separation, is not responsible for the intramolecular rearrangement, since, as shown by system vi, the organotin alkoxide itself spontaneously gives the expected heterocyclic compound.

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