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Comparison of the allylation reactions of aldehydes using allylstannanes with boron trifluoride etherate and boron trichloride

Daniele Marton, Giuseppe Tagliavini *, Michele Zordan,

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

and James L. Wardell

Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB9 2UE (U.K.)

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Abstract

Reactions between allylstannanes, $R^2CH{=}CHCHR^1SnBu_3$ ($R^1 = R^2 = H$ (**4**); $R^1 = H$, $R^2 = Me$ (**5**); $R^1R^2 = (CH_2)_3$ (**6**)) and aldehydes, RCHO (e.g. R = Et) in the presence of $BF_3 \cdot OEt_2$ in CH_2Cl_2 at −78 °C produce stereoselectively *erythro*-$RCH(OH)CHR^2CH{=}CHR^1$ (with one equivalent RCHO) and 4-OH-3-R^1-5-R^2-2,6-R_2-tetrahydropyrans (with an excess of RCHO). In contrast, when BCl_3 is used in place of $BF_3 \cdot OEt_2$ the reactions give mixtures of chlorinated alkenes (both homoallyl chlorides and allyl chlorides) and 4-Cl-3-R^1-5-R^2-2,6-R_2-tetrahydropyurans (**3**; X = Cl). Thus **5**, EtCHO and BCl_3 (all equimolar) provide $EtCHClCH_2CH{=}CHMe$ (51%, (*E*) + (*Z*)), $EtCHClCHMeCH{=}CH_2$ (7%, *erythro* + *threo*), $EtCH_2CH{=}CH$-CHMeCl (30%, (*E*) + (*Z*)) and **3** (12%, X = Cl); with EtCHO (2.2 equivalents), **3** (X = Cl; *cis*/*trans* = 70/30) becomes the sole product. The product, *erythro*-$EtCHClCHCH{=}CH(CH_2)_2CH_2$ (97%) was produced from equimolar EtCHO, BCl_3 and **6**; with excess EtCHO (2.2 equivalents), 9-Cl-2,4-Et_2-*cis*-3-oxabicyclo[3.3.1]nonane (17%; *cis*/*trans* = 45/55) and *erythro*-$EtCHClCHCH{=}CH(CH_2)_2CH_2$ (78%) were obtained.

Introduction

The uses of organotin compounds in organic synthesis has attracted considerable attention [1–3]. Of particular interest have been allylations of aldehydes by allylstannanes [1–17]. The reactions proceed on heating [e.g. 13], under pressure [e.g.

16], or preferably under milder conditions, e.g. at −78°C, in the presence of such Lewis acids as $BF_3 \cdot OEt_2$, $TiCl_4$, and tin(IV) halides [1–15], eq. 1.

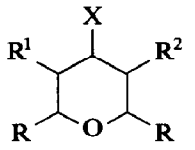
$$R^1CH{=}CHCHR^2SnR^3_3 + RCHO \xrightarrow[(ii)\ H_2O]{(i)\ \Delta,\ P \text{ or Lewis acid}} RCH(OH)CHR^2CH{=}CHR^1 + RCH(OH)CHR^1CH{=}CHR^2 \quad (1)$$

(1) **(2)**

The regio- and stereo-selectivities of the homoallylic alcohol products **1** and/or **2**, can depend on such factors as whether or not a Lewis acid is present, the particular Lewis acid, and even the order of mixing of the reagents [e.g. 13, 17] if this leads to different allylation agents.

A further development of the allylation reactions has been the synthesis of halotetrahydropyrans (**3**; X = Cl or Br), via the incorporation of a second aldehyde molecule [18–22], eq. 2.

$$R^1CH{=}CHCHR^2SnR^3_3 + 2RCHO \xrightarrow[\text{or } TiCl_4]{Bu_nSnX_{4-n}\ (X = Cl \text{ or } Br)} \quad (2)$$



(**3**; X = Br or Cl)

Whereas $BF_3 \cdot OEt_2$/allylstannane/RCHO reactions have been fairly extensively studied previously, those involving BCl_3 as the Lewis acid have not. In this paper, we report findings of a comparative study of BCl_3- and BF_3-mediated allylations of RCHO.

Results and discussion

Three allylstannanes were used in this study; namely **4**, **5** and **6**.

$CH_2{=}CHCH_2SnBu_3$ $MeCH{=}CHCH_2SnBu_3$ $\overline{CH_2(CH_2)_2CH{=}CHCH}SnBu_3$

(4) **(5**: *E*/*Z* 40/60**)** **(6)**

Differences between $BF_3 \cdot OEt_2$ and BCl_3 as co-reagents

The products of allylation of EtCHO with **4**, **5** or **6** in the presence of BCl_3 or $BF_3 \cdot OE_2$, generally at −78°C in CH_2Cl_2 solution, are given in Table 1; reactions involving (i) an equimolar amount and (ii) an excess of EtCHO (relative to the allylstannane) were studied. The product yields were not optimized. As can be seen from Table 1, there are major differences in the types of products obtained from the two boron halides. These include: (i) formations of mixtures of isomeric homoallyl and allyl chlorides and 4-chlorotetrahydropyrans (**3**; X = Cl) in the BCl_3 reactions, in contrast to those of homoallyl alcohols (with a high *erythro*-stereoselectivity) when one equivalent of RCHO is used and of 4-hydroxytetrahydropyrans (**3**: X = OH) when an excess of RCHO is used in the $BF_3 \cdot OEt_2$ reactions, and (ii) the readier formation of tetrahydropyran derivatives from **4** and **5** in the BCl_3 reactions (e.g. as shown by the formation of **3** (X = Cl), even when only one equivalent of EtCHO is used).

We and others have shown from spectroscopic data that BCl_3 (and BBr_3), but no $BF_3 \cdot OEt_2$, undergoes transmetallations with allylstannanes * at low temperatures (e.g. ca. $-80\,^\circ C$) [10,23,24], eq. 3. As a consequence, the effects of BCl_3 and $BF_3 \cdot OEt_2$ on the initial allylation of the aldehyde at $-78\,^\circ C$ must be accounted for

$$BCl_3 + R^1CH{=}CHCHR^2Sn^3{}_3 \rightarrow [R^1CH{=}CHCHR^2]BCl_2 + R^3{}_3SnCl \qquad (3)$$

differently; namely in BCl_3 reactions, transmetallations (eq. 3) provide more active allylboron species, whereas in $BF_3 \cdot OEt_2$ reactions, activation arises via complexation of RCHO by BF_3 [25]. 1/1 complexes of BF_3 and RCHO have been isolated and their structures investigated [11]. An additional effect of BCl_3 is its ability to act as a chloride ion donor. Schemes 1 and 2 represent the pathways for the BCl_3- and $BF_3 \cdot OEt_2$-mediated reactions. The various products obtained from the BCl_3 reactions, in particular the isomeric chloroalkenes, makes a comparison of the stereoselectivities obtained in the BCl_3 and $BF_3 \cdot OEt_2$ reactions difficult and of little value.

Further comments on the $BF_3 \cdot OEt_2$ mediated reactions

With $BF_3 \cdot OEt_2$ as the co-reagent, crotylstannanes, $MeCH{=}CHCH_2SnR_3$ (**7**) and RCHO invariably produce the *erythro*-homoallylic alcohol $RCH(OH)CHMeCH{=}CH_2$ (**8**), as the major product with a very high selectivity, irrespective of whether (*E*)-**7** or (*Z*)-**7** is used [16]. The *erythro*-homoallylic alcohol **8** ($R = Pr^i$) is indeed the major product from reaction of Pr^iCHO, $BF_3 \cdot OEt_2$ and **5**, of differing (*E*)/(*Z*) ratios (eq. 4) (Table 2). However, the amounts and stereochemical composition of minor products, e.g. $Pr^iCH(OH)CH_2CH{=}CHMe$, are affected by the order of mixing reagents, as shown by the results from this and earlier studies [13]. These reaction mixtures were maintained initially at $-78\,^\circ C$

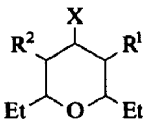
$$\mathbf{5} + Pr^iCHO \xrightarrow[\text{(ii) } H_2O]{\text{(i) } BF_3 \cdot OEt_2,\ -78\,^\circ C,\ \text{room temp.}} Pr^iCH(OH)CHMeCH{=}CH_2 \quad (\mathbf{8},\ R = Pr^i,\ \textit{erythro} \text{ and } \textit{threo}) + Pr^iCH(OH)CH_2CH{=}CHMe \quad ((E) \text{ and } (Z)) \qquad (4)$$

then raised to ambient temperature. One explanation for these changes is that the allylation of the hindered Pr^iCHO is not complete at $-78\,^\circ C$, at which any reaction would simply involve **5** and $BF_3 \cdot Pr^iCHO$. At the higher temperatures required to bring the reaction to completion, other active allylating agents, with differing selectivities, are now present. No explanation can be found for the exclusive formation of **8** ($R = Pr^i$) as observed by Yamamoto et al. for the same reaction

* Although transmetallation reactions do not occur between $BF_3 \cdot OEt_2$ and allylstannanes at $-78\,^\circ C$, other reactions can. These include (i) redistribution of the allylstannane, e.g. $Me_3SnCH_2CH{=}CH_2$ or $Me_nSn(CH_2CH{=}CH_2)_{4-n}$ ($n = 0$–4), (ii) geometric isomerisations, e.g. (*E*)/(*Z*)-$Bu_3SnCH_2CH{=}CHMe$ [10] and (iii) allylic transpositions, e.g. $Bu_3SnCH(OEt)CH{=}CHMe/Bu_3SnCHMeCH{=}CHOEt$ [7]. Neither redistribution nor geometric isomerisation would effect the stereoselectivities of the allylation reactions

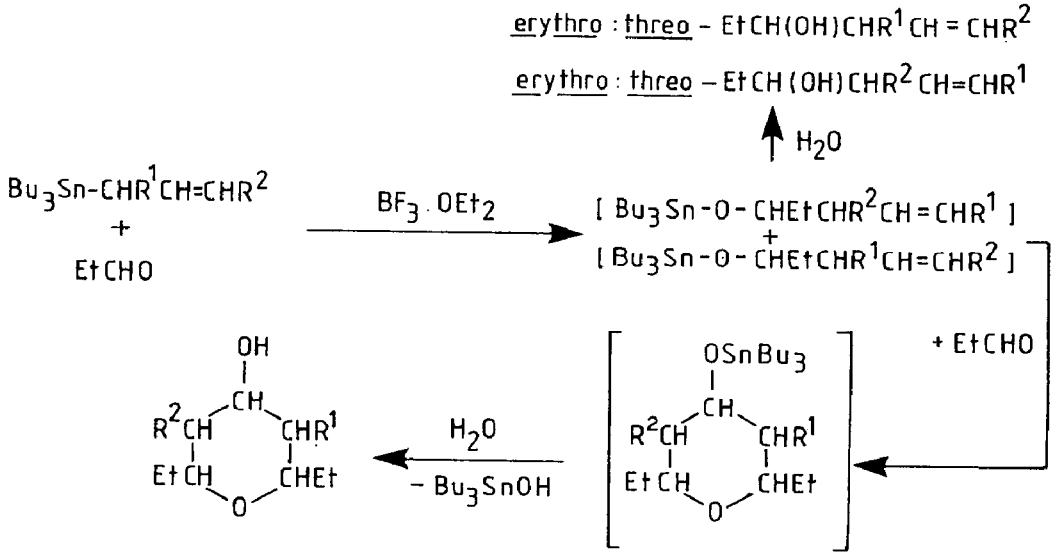
Table 1

Reactions of allylstannanes, EtCHO and $BF_3 \cdot OEt_2$ or BCl_3 in CH_2Cl_2 solutions at $-78°C$ [a]

Allylstannanes	Boron halide Lewis acid (LA)	Mixing sequence	Products (yield (%))	
			Alkenes	
$Bu_3SnCH_2CH{=}CH_2$ (4)	$BF_3 \cdot OEt_2$ (2 equiv.)	4 → [LA + EtCHO (1 equiv.)]	$EtCH(OH)CH_2CH{=}CH_2$ (90)	
	$BF_3 \cdot OEt_2$ (1 equiv.)	4 → [LA + EtCHO (1 equiv.)]	$EtCH(OH)CH_2CH{=}CH_2$ (95)	
	$BF_3 \cdot OEt_2$ (1 equiv.)	(LA) → [4 + EtCHO (2.5 equiv.)] [b]	–	($R^1 = R^2 = H$; X = OH) (75) one isomer
	BCl_3 (1 equiv.)	4 → [EtCHO (1 equiv.) + LA]	$EtCHClCH_2CH{=}CH_2$ (40) $EtCH_2CH_2CH{=}CHCH_2Cl$ (25) ((*E*)/(*Z*) 72/28)	($R^1 = R^2 = H$; X = Cl) (13) (one isomer)
	BCl_3 (1 equiv.)	4 → [EtCHO (2.2 equiv.) + LA]	–	($R^1 = R^2 = H$; X = Cl) (68) one isomer
$Bu_3SnCH_2CH{=}CHMe$ (5: (*E*)/(*Z*) 40/60)	BCl_3 (1 equiv.)	5 → [EtCHO (1 equiv.) + LA]	$EtCHClCH_2CH{=}CHMe$ (51) [c] ((*E*)/(*Z*) 76/24) + $EtCH_2CH_2CH{=}CHCHMeCl$ (30) [c] (*E*) + (*Z*) $EtCHClCHMeCH{=}CH_2$ (7) [c] (*erythro* + *threo*)	($R^1 = H$, $R^2 = Me$; X = Cl) (12)

	BCl_3 (1 equiv.)	**5** → [EtCHO (2.2 equiv.) + LA]		(R^1 = H, R^2 = Me; X = Cl) (50) [d] *cis/trans* 70/30
$Bu_3Sn\overline{CHCH=CH(CH_2)}_3$ **(6)**	$BF_3 \cdot OEt_2$ (2 equiv.)	**6** → [(LA + EtCHO (1 equiv.)]	$EtCH(OH)\overline{CHCH=CH(CH_2)_2}CH_2$ (71) *erythro/threo* 80/20	
	$BF_3 \cdot OEt_2$ (2 equiv.)	EtCHO (1 equiv.) → [(LA) + (**6**)]	$EtCH(OH)\overline{CHCH=CH_2(CH_2)_2}CH_2$ (78) *erytrho/threo* 77/23	
	$BF_3 \cdot OEt_2$ (1 equiv.)	**6** → [LA + EtCHO (2.2 equiv.)]		($R^1 = R^2 = (CH_2)_3$; X = OH)) 88/12 isomeric mixture
	BCl_3 (1 equiv.)	**6** → [LA + EtCHO (1 equiv.)]	$EtCHCl\overline{CHCH=CH(CH_2)_2}CH_2$ (95) *erythro*	
	BCl_3 (1 equiv.)	EtCHO (1 equiv.) → [LA + **6**]	$EtCHCl\overline{CHCH=CH(CH_2)_2}CH_2$ (97) *erythro*	
	BCl_3 (1 equiv.)	**6** → [LA + EtCHO (2.2 equiv.)]	$EtCHCl\overline{CHCH=CH(CH_2)_2}CH_2$ (78) *erythro*	($R^1 = R^2 = (CH_2)_3$; X = Cl) (12) *cis/trans* 45/55

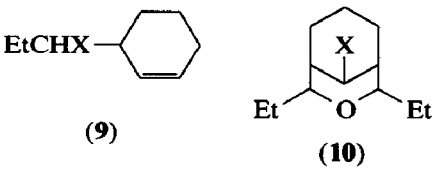
[a] Reactions initially at −78° C; slowly allowed to warm to room temperature. [b] At −15° C, no solvent. [c] Relative yields. [d] Additional products: EtCH=CMeCHO and cyclohex-2-enol.



Scheme 1

(Table 2; entry No. 4); it may be significant that different amounts of reagents were used and that a different method of analysis (GC rather than NMR) was adopted.

The high *erythro* selectivity for homoallyl alcohols in the $BF_3 \cdot OEt_2$ mediated reaction was maintained in the reaction of EtCHO with **6**; the ratio *erythro/threo*-**9** (X = OH) 79/21 was independent of the order of mixing the reagents.



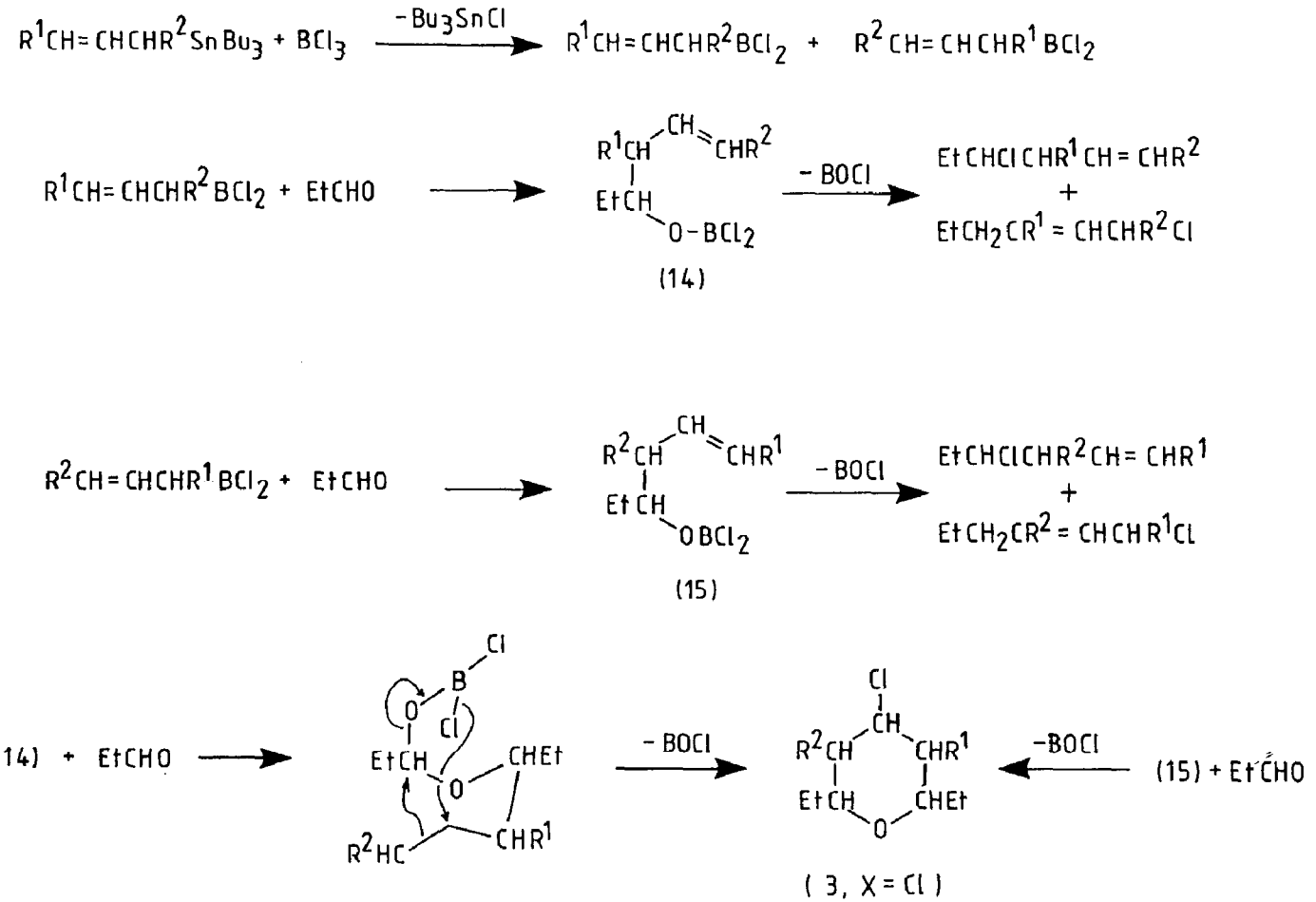
(**9**) (**10**) (5)

It is of interest that only one equivalent of $BF_3 \cdot OEt_2$, relative to the allylstannane, need be used; in many of previously repeated studies, two equivalents of $BF_3 \cdot OEt_2$ were employed. In this study, yields of $EtCH(OH)CH_2CH{=}CH_2$ were found to be > 90% when either one or two equivalents of $BF_3 \cdot OEt_2$ were used with **4** and EtCHO.

The formation of substituted 4-hydroxytetrahydropyrans **3** (X = OH) from an excess of EtCHO (at least two equivalents) further adds to the value of these allylation reactions. Boron trifluoride-etherate reactions stand alone among those involving Lewis acids ($TiCl_4$, Bu_nSnX_{4-n}, and BCl_3) [19–22] in giving hydroxy- rather than halo-tetrahydropyrans. From the simple allylstannane, **4**, only 1 stereoisomer of **3** ($R^1 = R^2 = H$, R = Et or Pr^i, X = OH) was produced from an excess of RCHO (Et or Pr^i); from **6** and EtCHO two stereoisomers of 9-OH-2,4-Et_2-*cis*-3-oxabicyclo[3.3.1]nonane (**10**; X = OH) in a ratio of 88/12, were isolated, as well as some EtCH=CMeCHO, the aldol product from EtCHO.

BCl_3-mediated reactions

From reactions of **4** or **5** with an equimolar amount of EtCHO both homoallylic and allyl chlorides **11** and **12** are obtained, as well as **3** (X = Cl). The formation of



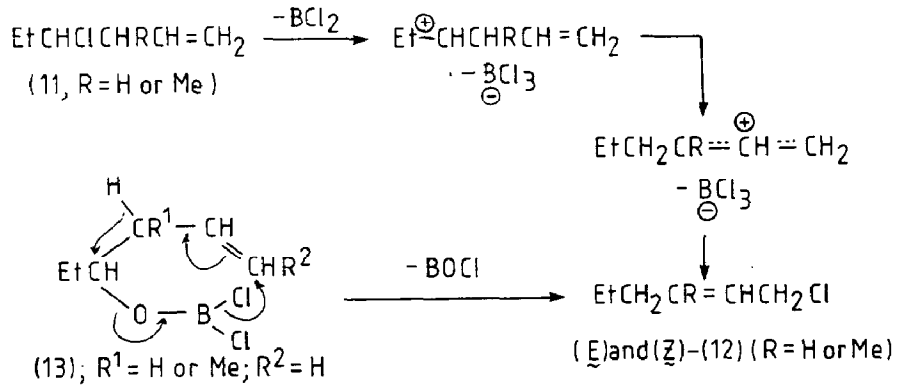
Scheme 2

Table 2

Products of reactions of 5, $BF_3 \cdot Et_2O$ and Pr^iCHO in CH_2Cl_2, initially at $-78°C$

Order of mixing reagents	(*E*)/(*Z*)-5	$Pr^iCH(OH)CHMeCH{=}CH_2$		$Pr^iCH(OH)CH_2CH{=}CHMe$		Ref.
		erythro	*threo*	(*Z*)	(*E*)	
5 to [$Pr^iCHO + BF_3$]	70/30	55	9	36	–	13 [a]
Pr^iCHO to [5 + BF_3]	52/48	54	11	5	30	13 [a]
[5 + Pr^iCHO] to BF_3	40/60	80	18	2	–	[a,b]
5 to [$Pr^iCHO + BF_3$]	100/0	91	9	–	–	25 [c]

[a] 5 20 mmol; Pr^iCHO 20 mmol; BF_3 40 mmol in CH_2Cl_2 (40 ml). [b] This study. [c] 5 2 mmol; Pr^iCHO 2 mmol; BF_3 4 mmol.



Scheme 3

the allyl chloride **12** arises from a rearrangement, either of the homoallyl chloride **11** or of the initial boron alkoxide **13** (see Scheme 3). No allyl chlorides are formed from reactions of **6**; only the *erythro*-homoallylic chloride (**9**, X = Cl) is produced from equimolar **6** and EtCHO. Even from 2.2 equivalents of EtCHO, **9** (X = Cl) is obtained (78% yield) along with only a small amount of **10** (X = Cl) with a *cis/trans* ratio of 45/55; this ratio compares with a 25/75 ratio for **10** (X = Cl) obtained from **6**, EtCHO (excess) and $BuSnCl_3$ [18]. From either **4** or **5** and an excess of EtCHO (2.2 equivalents), **3** (X = Cl) is obtained as the sole product. A single stereoisomer of **3** ($R^1 = R^2 = H$, R = Et; X = Cl) was obtained from **4**, whereas from **5**, two stereoisomers of **3** ($R^1 = H$, $R^2 = Me$, R = Et, X = Cl) (*cis/trans* 70/30) were produced.

Boron trichloride has been found to chlorinate EtCHO to form bis(α-chloroethyl) ether [26]; however the products in Scheme 2 suggest that this does not occur in the allylation reactions.

Experimental

Allylstannanes, **4** and **6** were obtained by standard methods [13,18,22]. Boron trichloride (a 1 *M* solution in CH_2Cl_2) and boron trifluoride etherate were the best commercial grades available and were used as received. Aldehydes were redistilled prior to use.

General reaction procedure

The reagents were mixed in a particular sequence at −78 °C in CH_2Cl_2 solution (unless otherwise indicated) under N_2, the usual scale being 20 mmol based on the allylstannane in ca. 40 ml solutions. The reaction mixtures were usually held at −78 °C for set times before the temperature was allowed to rise to room temperature during a specified period. After treatment with saturated aqueous NH_4Cl, the organic material was extracted with CH_2Cl_2, the extracts dried, and the organic products separated by fractional distillation. Products were identified by GLC and ^{13}C NMR and IR spectroscopy and by comparison with authentic samples; mainly available from earlier studies.

Specific reactions

Reactions of EtCHO and 4

(i) With $BF_3 \cdot OEt_2$. (a) Compound **4** (20 mmol) was added to EtCHO (20 mmol) and $BF_3 \cdot OEt_2$ (40 mmol) in CH_2Cl_2 at $-78\,^\circ C$. Product: $EtCH(OH)CH_2CH{=}CH_2$ (90% yield): identical to an authentic sample [27].

(b) Reaction was repeated with $BF_3 \cdot OEt_2$ (20 mmol). Product: $EtCH(OH)CH_2CH{=}CH_2$ (95% yield).

(c) $BF_3 \cdot OEt_2$ (30 mmol) was added to EtCHO (105 mmol) and **4** at $-15\,^\circ C$ under N_2. The mixture was allowed to warm to room temperature. Product: 4-hydroxy-2,6-diethyltetrahydropyran **3** (X = OH, R = Et, R^1, R^2 = H) (3.55 g, 75% yield). IR 3430(s)(OH), 1060 (s)(C–O–C), 890(s), 615(m) cm^{-1}. ^{13}C NMR $\delta(^{13}C)$ 10.2(CH_3), 29.3(CH_2), 41.1(C-3, C-5), 67.9(C-4) and 77.0(C-2, C-6) [28].

(ii) With BCl_3. (a) Compound **4** (20 mmol) was added to a mixture of EtCHO (20 mmol) in CH_2Cl_2 (20 ml) and BCl_3 (20 ml of 1*M* solution in CH_2Cl_2) at $-78\,^\circ C$ under N_2. The mixture was allowed to warm to room temperature and left for 4 h. Total product, 1.8 g. Products: $CH_3CH_2CHClCH_2CH{=}CH_2$ (40%). ^{13}C NMR $\delta(^{13}C)$ 10.9(C-6), 32.3(C-5), 42.8(C-3), 63.9(C-4), 117.6(C-1) and 134.3(C-2) [29]. (*E*)-$CH_3CH_2CH_2CH{=}CHCH_2Cl$ (18%). ^{13}C NMR $\delta(^{13}C)$ 13.8(C-6), 25.9(C-5), 36.4(C-4), 44.2(C-1), 124.7(C-2) and 135.4(C-3). (*Z*)-$CH_3CH_2CH_2CH{=}CHCH_2Cl$ (7%). ^{13}C NMR $\delta(^{13}C)$ 13.8(C-6), 22.7(C-5), 34.4(C-4), 45.5(C-1), 126.8(C-2) and 135.5(C-3). 4-Chloro-2,6-diethyltetrahydropyran (**3**: X = Cl, R = Et, $R^1 = R^2$ = H) (13%). ^{13}C NMR δ (^{13}C) 9.9(CH_3), 29.2(CH_2), 42.8(C-3 and C-5), 56.1(C-4), and 78.0(C-2 and C-6) [30].

(b) Compound **4** (10 mmol) was added to a mixture of EtCHO (22 mmol) in CH_2Cl_2 (20 ml) and BCl_3 (10 ml of 1 *M* solution in CH_2Cl_2) at $-78\,^\circ C$ under N_2. Product: 4-chloro-2,6-diethyltetrahydropyran, 1.2 g (68%) (**3**, X = Cl, R = Et, $R^1 = R^2$ = H) identical with above product [30].

Reaction of Pr^iCHO and 4

$BF_3 \cdot OEt_2$ (30 mmol) was added to **4** (30 mmol) and Pr^iCHO (105 mmol) at $-15\,^\circ C$ under N_2. Product: 4-hydroxy-2,6-di-isopropyltetrahydropyran (**3**: X = OH, R = Pr^i, $R^1 = R^2$ = H) (3.5 g, 63% yield). IR 3380(m)(OH), 1075(s)(C–O–C), 885(s) and 605(m) cm^{-1} [19,20].

Reaction of Pr^iCHO and 5

A mixture of Pr^iCHO and **5** (both 20 mmol) was added to $BF_3 \cdot OEt_2$ (40 mmol) in CH_2Cl_2 at $-78\,^\circ C$ under N_2. The mixture was allowed to warm to 25 °C. Total product 2.5 g. Products: *erythro*-$Pr^iCH(OH)CHMeCH{=}CH_2$ (80%); *threo*-$Pr^iCH(OH)CHMeCH{=}CH_2$ (18%); (*Z*)-$Pr^iCH(OH)CH_2CH{=}CHMe$ (2%), all identical with samples obtained in earlier studies [31,32].

Reaction of EtCHO and 5

(a) Compound **5** (20 mmol) was added to a solution of EtCHO (20 mmol) and BCl_3 (20 mmol; 20 ml of 1 *M* CH_2Cl_2 solution) at $-78\,^\circ C$ under N_2. The mixture was allowed to warm to room temperature during $1\frac{1}{2}$ h. Total product: 2.0 g. Products: (*E*)-$CH_3CH_2CHClCH_2CH{=}CHCH_3$ (38%). ^{13}C NMR $\delta(^{13}C)$ 10.9(C-7), 17.9(C-1), 31.0(C-6), 43.8(C-4), 64.5(C-5), 127.9(C-2) and 128(C-3) [20,32,33]. (*Z*)-

$CH_3CH_2CHClCH_2CH{=}CHCH_3$ (13%). ^{13}C NMR $\delta(^{13}C)$ 10.11(C-7), 13.0(C-1), 31.9(C-6), 41.7(C-4), 64.5(C-5), 124.5(C-2), and 135.7(C-3) [20,32,33]. (*E*)-$CH_3CH_2CH_2CH{=}CHCHMeCl$. ^{13}C NMR $\delta(^{13}C)$ 13.8(C-6), 24.7(CH_3), 25.6(C-5), 38.2(C-4), 57.5(C-1), 124.5(C-2) and 134.5(C-3). (*Z*)-$CH_3CH_2CH_2CH{=}CHCHMeCl$. ^{13}C NMR $\delta(^{13}C)$ 13.8(C-6), 24.7(CH_3), 25.9(C-5), 35.9(C-4), 57.5(C-1), 126.3(C-2) and 126.5(C-3). Combined yield of (*E*)- and (*Z*)-$CH_3CH_2CH_2CH{=}CHCHMeCl$ (30%). 4-Chloro-2,6-diethyl-3-methyltetrahydropyran (**3**: X = Cl, R = Et, R^1 = H, R^2 = Me) (12%) (identical with sample obtained in earlier studies [19,20]), and *erythro*- and *threo*-$CH_3CH_2CHClCHMeCH{=}CH_2$ (7%).

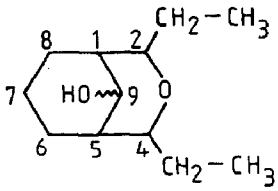
(b) The procedure was repeated with **5** (10 mmol), BCl_3 (10 ml of 1 *M* CH_2Cl_2 solution) and EtCHO (22 mmol) in CH_2Cl_2 (10 ml). Product: 4-chloro-2,6-diethyl-3-methyltetrahydropyran (**3**: X = Cl, R = Et, R^1 = H, R^2 = Me) (1.0 g): *cis/trans* 70/30, identical with sample obtained in earlier studies [19,20].

Reaction of EtCHO and **6**

(i) With $BF_3 \cdot OEt_2$. (a) Compound **6** (10 mmol) was added to EtCHO (10 mmol) and $BF_3 \cdot OEt_2$ (20 mmol) in CH_2Cl_2 (20 ml) at −78 °C under N_2. The mixture was kept at −78 °C for 20 min then allowed to warm up to room temperature. Product: $CH_3CH_2CH(OH)\overline{CHCH{=}CHCH_2CH_2CH_2}$ (**9**: X = OH) (1.0 g, 71%) [34,35], *erythro/threo* 80/20.

(b) EtCHO (10 mmol) was added to **6** (10 mmol) and $BF_3 \cdot OEt_2$ (20 mmol) in CH_2Cl_2 (20 ml) at −78 °C under N_2. Product: $CH_3CH_2CH(OH)\overline{CHCH{=}CHCH_2CH_2CH_2}$ (**9**; X = OH) (1.1 g, 78%), *erythro/threo* 77/23 [34,35].

(c) Compound **6** (10 mmol) was added to EtCHO (22 mmol) and $BF_3 \cdot OEt_2$ (10 mmol) in CH_2Cl_2 (20 ml) at −78 °C under N_2. Products 0.9 g of isomers of 9-hydroxy-2,4-diethyl-*cis*-3-oxabicyclo[3.3.1]nonane [36]. ^{13}C NMR: major isomer



(88%): $\delta(^{13}C)$ 10.6(CH_3), 20.5(CH_2), 18.8(C-7), 26.2(C-6 and C-8), 38.3(C-1 and C-5), 73.4(C-9) and 81.4(C-2 and C-4); minor isomer (12%): $\delta(^{13}C)$ 10.6(CH_3), 17.8(CH_2), 18.8(C-7), 27.0(C-6 and C-8), 37.7(C-1 and C-5), 74.5(C-9) and 82.7(C-2 and C-4), and a mixture of 0.5 g of EtCH=CMeCHO and cyclohex-2-enol, confirmed by GC, from retention times of authentic samples.

(ii) With BCl_3. (a) Compound **6** (10 mmol) was added to EtCHO (22 mmol) in CH_2Cl_2 (20 ml) and BCl_3 (10 ml of 1 *M* solution in CH_2Cl_2) at −78 °C under N_2. The mixture was allowed to warm to room temperature. Product: *erythro*-$CH_3CH_2CHCl\overline{CHCH{=}CHCH_2CH_2CH_2}$ (**9**: X = OH) (1.25 g, 95% yield). ^{13}C NMR $\delta(^{13}C)$ 11.6(CH_3), 21.6(C-5), 25.1(C-6), 25.9(C-4), 28.6(CH_2), 42.2(C-1), 69.4(CHCl), 128.3(C-2) and 129.3(C-3).

(b) EtCHO (10 mmol) was added to a solution of **6** (10 mmol) in CH_2Cl_2 (10 ml) and BCl_3 (10 ml of 1*M* solution in CH_2Cl_2 at −78 °C under N_2. Product: *erythro*-$CH_3CH_2CHCl\overline{CHCH{=}CHCH_2CH_2CH_2}$ (**9**: X = Cl) (1.27 g, 97% yield), identical with the above sample.

(c) Compound **6** (10 mmol) was added to BCl_3 (10 ml of 1 *M* solution in CH_2Cl_2) and EtCHO (22 mmol) in CH_2Cl_2 (30 ml) at $-78°C$ under N_2. Total products: 1.42 g. Products: *erythro*-$CH_3CH_2CHClCHCH{=}CHCH_2CH_2CH_2$ (**9**: X = Cl) (78%) and *cis/trans*-9-chloro-2,4-diethyl-*cis*-3-oxabicyclo[3.3.1]nonane (**10**: X = Cl) (45/55) (17%), identical with authentic samples from a previous study [18].

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