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SELECTIVITY IN REACTIONS INVOLVING α-ALKOXYALLYLTRIBUTYLTINS

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SUMMARY

The behaviour of α-alkoxyallyltributyltins has been studied in terms of chemo-, regio- and stereoselectivity. Chemoselectivity is readily controlled by the experimental conditions, as exemplified by the reaction of p-bromobenzaldehyde with α-ethoxycrotyltributyltin. Cross-coupling products are the sole products when the reaction is catalyzed by $Pd(PPh_3)_4$ while the use of Lewis acids, or even simple heating of the reagents, cause addition to the aldehyde group.

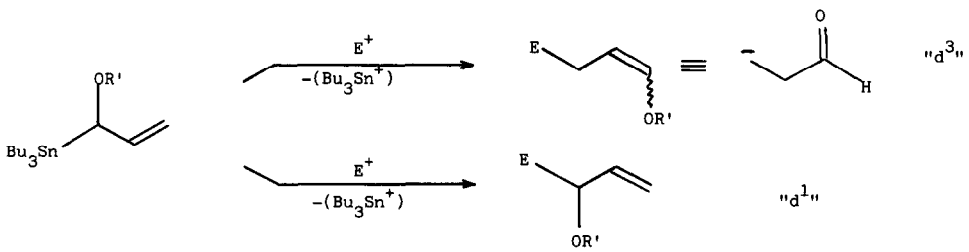
The regio and stereochemistries of the addition reactions can also be controlled in some circumstances. For instance, the $BF_3.Et_2O$ promoted reactions (CH_2Cl_2, - 78°C) lead regio- and stereoselectively to the α-glycol monoether 16E (93 % syn E).[2] On the other hand, the (E)-α-ethoxycrotyltributyltin has been shown to be much more reactive than the (Z)- isomer. It allows highly regio and stereoselective reaction affording 19Z (anti Z) on heating (100°C, 6 h).

These results are discussed and an interpretation of the stereochemical trends is given on the basis of the interactions occurring in usually accepted transition states.

I - INTRODUCTION

Modern organic synthesis requires new selective reagents efficient in terms of chemo-, regio- and stereoselectivity (1). In this area, allyltin derivatives have been shown to be promising tools because of the weakness of the allylic tin-carbon bond which allows numerous cross-coupling or addition reactions whose mechanisms and subsequent selectivities can be controlled by the experimental conditions (2-9).

When the allyl unit contains an α-alkoxy group, the α-alkoxyallyl triorganotins constitute "umpolung reagents" useful for the introduction of carbonyl or hydroxyl groups. Depending on whether an allylic rearrangement occurs or not, they can act as d^3 or d^1 "umpolung reagents" (10, 11) :



Our goal has been to guide these reagents to react at a single site when different functionalities are present in the substrate (chemoselectivity) and to control the regiochemistry (occurrence of an allylic rearrangement or not) and the stereoselectivity of the reaction, especially when γ-substituted α-alkoxyallyltriorganotins are used (for early reports see references 11 and 12).

Taking account of the ability of allyltins to react with aryl or acyl halides in the presence of palladium catalysts (5-7) or with carbonyl compounds under various experimental conditions (2, 8, 9), we have focussed our attention on the reactivity of α-ethoxyallyltributyltin derivatives towards appropriate substrates. These organotin reagents are readily obtained from diethoxymethyltributyltin according to the following scheme (13, 14) :

$$Bu_3Sn\ CH(OEt)_2 \xrightarrow[2)\ RMgX]{1)\ AcCl} Bu_3Sn\text{-}CHR\text{-}OEt$$

1 - 4

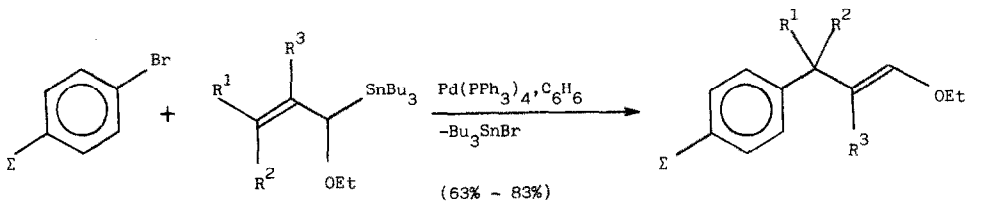
1, R = $-CH=CH_2$ (72 %) ; **2**, R = $-CMe=CH_2$ (71 %)
3 (E+Z), R = $-CH=CHMe$ (70 %) ; **4**, R = $-CH=CMe_2$ (58 %)

It should be noted that **1** and **2** must be used as crude products in order to avoid their isomerization to γ-ethoxyallyltin derivatives (13) ; and that **4** is now more conveniently obtained by the reaction of isobutenylaluminium bromides with diethoxymethyltributyltin (15).

II - RESULTS

A - Reaction of α-ethoxyallyltins with organic halides

In benzene as solvent and using tetrakistriphenylphosphine palladium as catalyst, α-ethoxyallyltins react with aryl bromides as d^3 propionaldehyde-type equivalents to give the corresponding vinylethers with a high tolerance towards other functionalities (cf. Table I).



1-4 **5-14**

The vinylic ethers were obtained as mixtures of geometric isomers ; treatment with acid (H_2SO_4 30 %) led when attempted to the expected aldehydes in 87-95 % isolated yields (compounds **5**, **6**, **8**, **9**, **12**).

In these experimental conditions (C_6H_6, $Pd(PPh_3)_4$) it is of interest to underline the complete absence of addition to the carbonyl group when the aryl bromide also contains a ketone or an aldehyde function.

The extensions of these cross-coupling reactions to acyl halides in the presence of $PhCH_2PdCl(PPh_3)_2$ appear much more limited. The expected reaction occurs with a reasonable yield in the case of α-ethoxycrotyltributyltin :

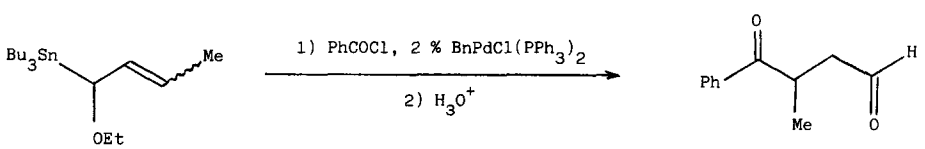
TABLE I - Reaction of α-ethoxyallyltins with aryl bromides[(a)].

Σ-C6H4-Br	Allyltin reagent	Vinylic ether	N°	Z/E[b]	Yields[c]
Σ = H	1	$C_6H_5-CH_2-CH=CH-OEt$	5	5/95	83
	2	$C_6H_5-CH_2-CMe=CH-OEt$	6	n.d.	69
	4	$C_6H_5-CMe_2-CH=CH-OEt$	7	15/85	72
Σ = F	1	$pF-C_6H_4-CH_2-CH=CH-OEt$	8	40/60	78
Σ = Cl	1	$pCl-C_6H_4-CH_2-CH=CH-OEt$	9	35/65	76
Σ = OMe	1	$pMeO-C_6H_4-CH_2-CH=CH-OEt$	10	50/50	63
Σ = Me	1	$pMe-C_6H_4-CH_2-CH=CH-OEt$	11	25/75	71
	3(E+Z)	$pMe-C_6H_4-CHMe-CH=CH-OEt$	12	20/80	74
Σ = COMe	3(E+Z)	$pMe-C(=O)-C_6H_4-CHMe-CH=CH-OEt$	13	37/63	55
Σ = CHO	3(E+Z)	$pH-C(=O)-C_6H_4-CHMe-CH=CHOEt$	14	25/75	80

a) Experimental conditions : solvent = C_6H_6, catalyst = 1 % $Pd(PPh_3)_4$, temp. 110°C, time c.a. 15 h.

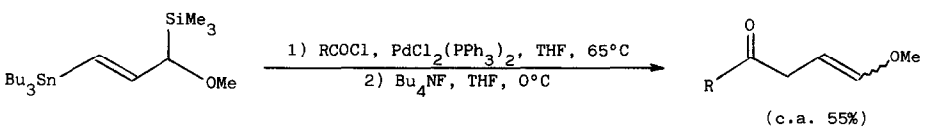
b) Due to hexane/acetonitrile partition and further purification, the reported values for the Z/E ratio can be significantly altered.

c) Non optimized yields after isolation of the products.



3 (Z+E) (77%) 15

However, when a Y-unsubstituted α-ethoxyallyltin is used the reagent undergoes isomerization to the Y-ethoxyallyltins in the presence of the acyl halide ; thus the access to 1,4-keto-aldehydes is not possible using this route. To circumvent this problem it is possible to use a silylated organotin homoenolate equivalent (16) :



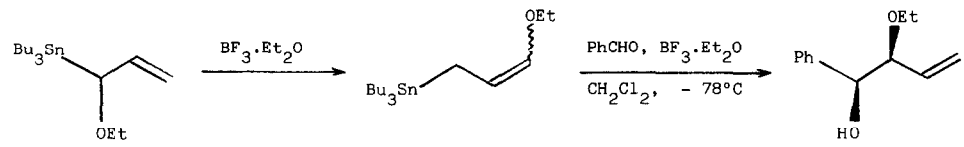
(c.a. 55%)

B - Reaction of α-ethoxyallyltins with aldehydes

1 - General features

The addition of allyltins to aldehydes, a process widely documented, may occur using simple heating, high pressure or Lewis acid activation (2 and references therein). In the case of

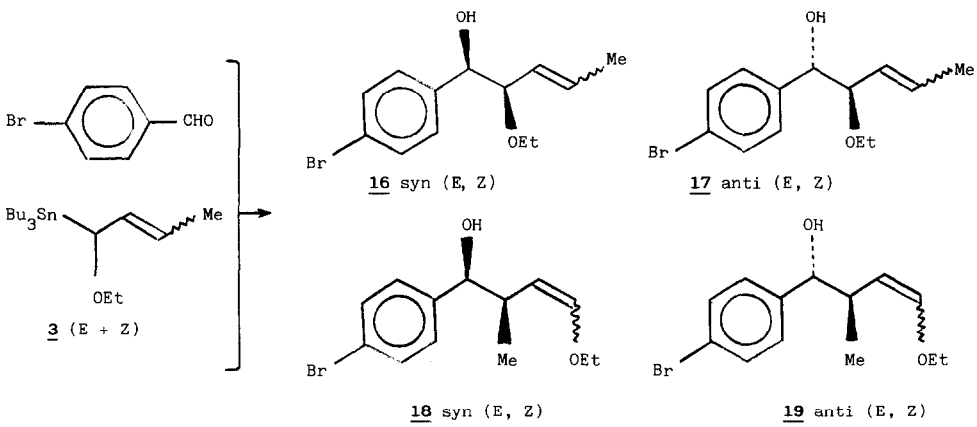
α-alkoxy- (or γ-alkoxy) allyltins, Lewis acid-promoted reactions (9,11,13,17-20) and simple heating (21,22) have been performed ; they lead to adducts with different regio- and stereochemistries. Under the influence of Lewis acids,α-alkoxyallyltins are isomerized into γ-alkoxyallyltins allowing a regioreversed addition compare to the addition observed on simple heating (13) :



1 Z/E = 85/15 93% syn

However, this trend cannot be considered as fully general because a case without initial isomerization has been described when the carbonyl group forms a part of the organotin molecule (intramolecular addition) (20). In this context it was of interest to examine the influence of experimental factors on the regiochemistry and the stereochemistry of the reaction. For this purpose, we decided to examine in detail the reaction of p-bromobenzaldehyde with α-ethoxycrotyltributyltin which has been shown to occur exclusively at bromine in the presence of $Pd(PPh_3)_4$.

Without palladium catalyst under heating, under high pressure or in the presence of boron trifluoride etherate (2 equivalents), the reactions occur exclusively at the carbonyl centre and yield a total of up to eight isomers :



2 - Identification of isomers 16 - 19 (E and Z)

In order to identify the eight possible isomers, we have used rather drastic experimental conditions (150°C, 24 h, neat compounds) to obtain the expected products with a poor selectivity. After partition of the reaction mixture between hexane and acetonitrile, liquid chromatography of the products contained in the acetonitrile phase (silica gel, eluent = pentane/diethyl ether) afforded a series of fractions which were analyzed by proton NMR (200 MHz). Using selective proton decoupling, the eight isomers have been identified unambiguously and complete sets of NMR parameters have been obtained for 7 isomers. It is simple to distinguish between α-glycol monoethers (16, 17) and vinylic ethers (18, 19) as well as between E and Z isomers on the basis of the vinylic patterns. Furthermore the consideration of steric interactions in the staggered conformations associated with the possibility of intramolecular chelation allows us to predict a lower vicinal coupling constant for the benzylic proton in 17 (anti) compared to 16 (syn) and for 18 (syn) compared to 19 (anti). (^1H NMR spectra for 16-19 are given in the experimental section).

For subsequent regio and stereochemical studies, the analyses of the reaction mixtures were performed using high performance gas-chromatography. The retention time of each isomer was clearly assigned on the basis of the previous ^{1}H NMR study.

3 - Experimental results

The influence of the experimental conditions (Lewis acids promoted reactions, thermic reactions or high pressure induced reactions) has been examined in connection with the stoichiometry of the reagents and with the geometry of α-ethoxycrotyltributyltin (3Z/3E). The results summarized in Table II imply the following conclusions :

. The reaction of 3 with a mixture of p-bromobenzaldehyde and boron trifluoride etherate (2 eq) in methylene chloride at -78°C affords exclusively the α-glycol monoethers 16 and 17 with an E configuration. Furthermore a high syn selectivity (c.a. 93 %) is observed irrespective of the geometry of 3 (entries a, b).

. Under gentle heating (100°C, 6 h) 3E appears to be much more reactive than 3Z. The adduct 19Z (anti Z) is obtained with a high preference (98 %) when a mixture 3E + 3Z is used.

. 3Z can be added to p-bromobenzaldehyde under heating or under high pressure (entries i, k) but without a clear-cut stereoselectivity. An attempt to enhance the selectivity by trapping the transient alkoxytin with ethanol used as a solvent to avoid a possible retroallylstannation (23) failed : a mixture of the eight possible isomers was obtained (entry j).

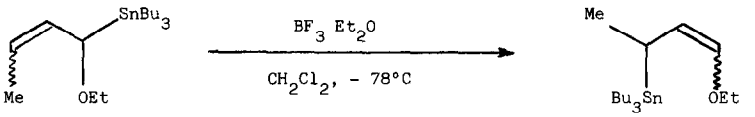
TABLE II : Reaction of p-bromobenzaldehyde with α-ethoxycrotyltributyltins (3)

Entry	Allyltins 3Z/3E	Stoichiometry 3/ArCHO	Experimental conditions	Overall yields	Products distribution				Remaining 3 (Z/E)
					16 (syn)	17 (anti)	18 (syn)	19 (anti)	
a	80/20	1,5	BF_3Et_2O, CH_2Cl_2, -78°C 0°C	95 %	93 (Z/E = 0/100)	7 (Z/E = 0/100)	0	0	nd
b	50/50	1,5	BF_3Et_2O, CH_2Cl_2, -78°C 0°C	80 %	94 (Z/E = 0/100)	6 (Z/E = 0/100)	0	0	nd
c	82/18	1	120°C, 120 h, neat	50 %	4.4 (Z/E = 47/53)	13.6 (Z/E = 84/16)	43.9 (Z/E = 58/42)	38.1 (Z/E = 70/30)	nd
d	82/18	1	150°C, 24 h, neat	75 %	9.1 (Z/E = 21/79)	10.9 (Z/E = 76/24)	53.4 (Z/E = 54/46)	26.6 (Z/E = 53/47)	nd
e	50/50	1	150°C, 24 h, neat	80 %	10.5 (Z/E = 5/95)	8.5 (Z/E = 82/18)	37.5 (Z/E = 53/47)	43.5 (Z/E = 59/41)	(Z/E = 58/42)
f	50/50	2	150°C, 24 h, neat	100 %	1.8 (Z/E 11/89)	4.2 (Z/E = 77/23)	20.5 (Z/E = 66/34)	73.5 (Z/E = 83/17)	(Z/E = 75/25)
g	82/18	1	100°C, 6 h, neat	22 %	2 (Z/E 5/95)	1 (Z/E 70/30)	22 (Z/E = 57/43)	75 (Z/E = 94/6)	(Z/E = 100/0)
h	50/50	2	100°C, 6 h, neat	50 %	0	0	2 (Z/E = 60/40)	98 (Z/E = 98/2)	(Z/E = 68/32)
i	100/0	1	100°C, 6 h, neat	8 %	0	0	59 (Z/E = 67/33)	41 (Z/E = 79/21)	(Z/E = 100/0)
j	100/0	1	100°C, 6 h, EtOH (5 eq)	10 %	7.3 (Z/E = 44/56)	22.7 (Z/E = 76/24)	30 (Z/E = 65/35)	40 (Z/E = 85/15)	(Z/E = 100/0)
k	82/18	1	1000 MPa, 50°C, CH_2Cl_2	50 %	0	0	40 (Z/E = 65/35)	60 (Z/E = 85/15)	(Z/E = 100/0)

4 - Discussion

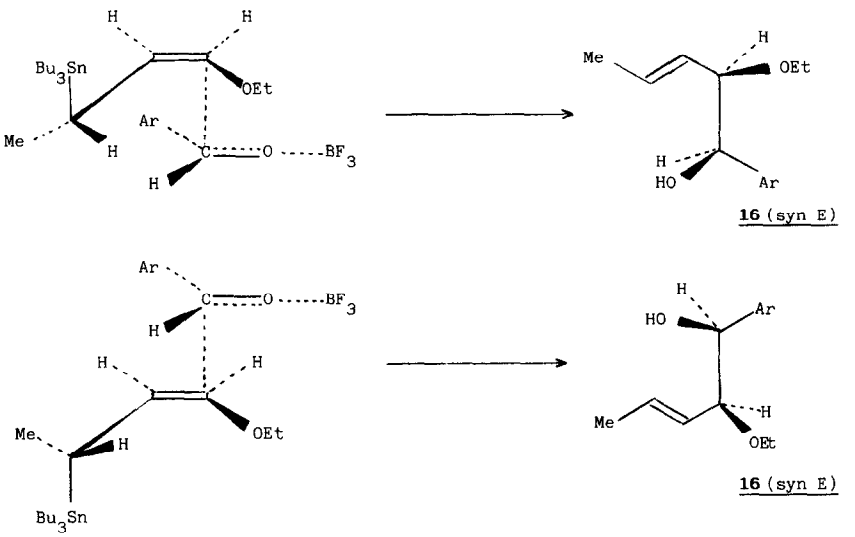
Boron trifluoride promoted reactions

The obtention of α-glycol monoethers under these experimental conditions can be rationalized by an initial isomerization of α-ethoxycrotyltributyltins **3** in γ-ethoxy derivatives as already observed for **1** (13) :

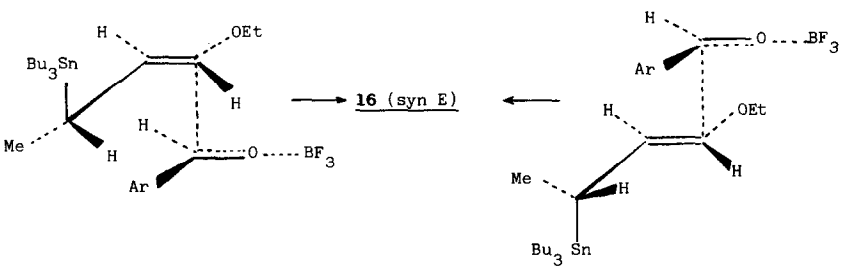


3 Z/E = 80/20 or 50/50 **20** Z/E = 83/17

The new allyltin reagent **20** reacts with the complexed aldehyde via an allylic rearrangement to give mainly the syn α-glycol monoether **16** in agreement with the open transition state proposed by **YAMAMOTO** and **MARUYAMA** in the crotyltin series (17, 24, 25). However the complete **E** selectivity for **16** and **17** cannot be explained by the relative thermodynamic stability of E isomers compared to Z isomers. Starting from **20Z** and taking into account the propensity of the allylic tin-carbon bond to be orthogonal to the allylic system (26-28), the less hindered transition states should be the following ones in relation to the absolute configuration of the α-carbon atom (the methyl group must be as far as possible from the entering carbonyl group) :

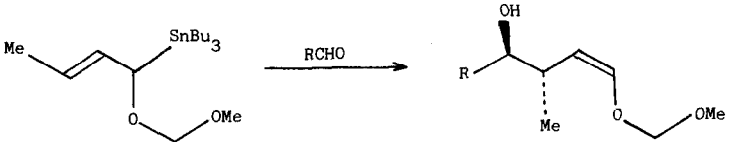


Starting from **20E** similar arguments justify the preferential obtention of the syn E isomer.



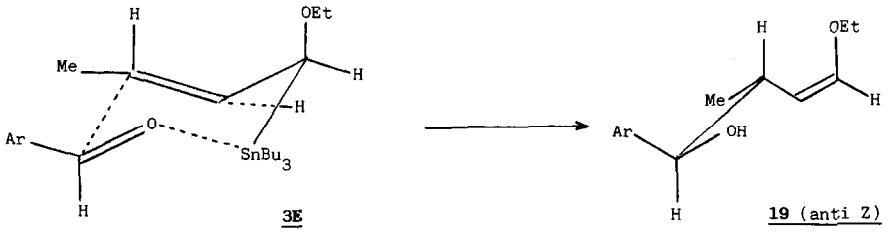
Thermic reactions and reactions under high pressure

On the basis of previous reports concerning addition of (Z)- and (E)-crotyltributyltin on aldehydes, a stereospecific reaction occurring via a cyclic transition state can be expected in both cases (25, 29-32). Such speculation has been corroborated by the formation of the anti Z isomer in the reaction of aldehydes with E-α-(methoxymethyloxy)-crotyltributyltin (21).

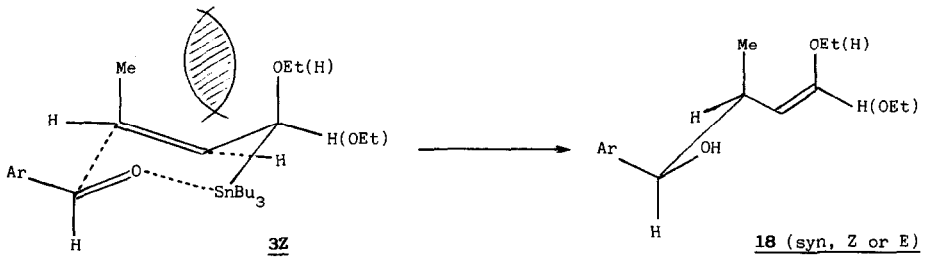


anti Z

In the reactions of α-ethoxycrotyltributyltins (3) with p-bromobenzaldehyde, the results can be also rationalized on the basis of a cyclic transition state. If one accept that a six-membered "chair-like" transition state is stabilized when an alkyl or an aryl group occupies a pseudo-equatorial position instead of a pseudoaxial position, the stereochemical results can be explained on the basis of the two following schemes related to **3E** and **3Z**.



3E **19** (anti Z)



3Z **18** (syn, Z or E)

The steric hindrance and the torsional interactions with the butyl groups on tin favour a pseudoaxial position of the ethoxy group in the absence of other interactions (isomer **3E**), while a subtle balance can be expected for isomer **3Z** (1-3 diaxial interaction between Me and OEt). The result is the nearly exclusive formation of the **anti Z** isomer from **3E** while a lower selectivity associated with a lower reactivity is expected for **3Z** (In practice mixtures of **18E**, **18Z**, **19E** and **19Z** were obtained in poor yields from **3Z**).

An attempt to quench the adducts with ethanol failed because ethanol is able to induce the isomerization **3E** ⇌ **3Z** through the isomeric γ-alkoxyderivatives **20E** and **20Z** (33). The intervention of cyclic transition states can subsequently justify the formation of the eight possible isomers and the exclusive presence of remaining **3Z** can be justified by its poor reactivity.

Under high pressure, a cyclic transition state is also expected (31) but while the yields are enhanced, the observed decrease in selectivity is also consistent with this type of experimental conditions.

III - EXPERIMENTAL SECTION

1 - General techniques

Gas-chromatography analyses have been performed on an Intersmat IGC 121 FL apparatus using one of the following columns :

column A : 10 % carbowax 20M on W chromosorb (aw - DMCS) 100-120 mesh, 3 m x 1/8" ; N_2 (20 ml/mn).
column B : capillary column, CP wax 52 CB (chrompack) 25 m x 0.22 mm ; N_2 (0.7 bar, split = 1.4/100).

^1H NMR spectra were recorded on an HITACHI-PERKIN ELMER R24B (60 MHz), a BRUKER WH 90 (90 MHz) or a BRUKER AC 200 (200 MHz) spectrometer using TMS as internal standard.

^{119}Sn NMR spectra were recorded on a BRUKER WH 90 apparatus (33.54 MHz) in "gated decoupling pulse modulated interrupted proton band decoupling" mode using tetramethyltin as external standard and C_6D_6 as solvent.

Mass spectra were obtained in GC-MS mode on VG Micromass 16F or 70-70F spectrometers using columns A or B and helium as carrier gas.

Infrared spectra were recorded between 600 and 4000 cm^{-1} on a PYE UNICAM SP 1100 apparatus.

2 - Starting materials

α -Ethoxyallyltins have been obtained by reaction of vinylic Grignard reagents with α-chloro-α-ethoxymethyltributyltin initially obtained from diethoxymethyltributyltin and acetyl chloride (34). The preparation of **3** will be reported herein. The same procedure applies for **4** and a similar one for **1** and **2** (the temperature must be -30°C).

Experimental procedure

A THF solution (0.03 mole in 30 ml) of freshly prepared crude α-chloro-α-ethoxymethyltributyltin (34) was added dropwise under nitrogen to a chilled solution (0°C) of propenylmagnesium bromide (0.045 mole) in THF (45 ml). After addition, the reaction mixture was stirred over a period of one hour and hydrolyzed at 0°C with an aqueous solution of ammonium chloride. The organic layer was extracted with ether and dried on magnesium sulfate. Subsequent elimination of solvents under vacuum and distillation afforded 8.2 g of **3E** + **3Z** ($b.p._{0.2}$ = 105°C, 70 % yield). The commercially available propenyl bromide (Z/E = 80/20) afforded **3E** and **3Z** in a similar ratio. When different isomeric mixtures were desired, the propenyl bromides were prepared by bromodemetallation of propenyltributyltins.

^1H NMR

In these organotin derivatives the usual absorptions of the butyl groups will not be mentioned. Note that the methylenic protons of the ethoxy groups are inequivalent.

1 : 1.13 ppm (3H, ^3J2H = 6.7 Hz), 3.18 and 3.69 ppm (1H + 1H, ^2J1H = - 8.7 Hz, ^3J3H = 6.7 Hz), 4.21 ppm (1H, ^3J1H = 5.7 Hz, ^4J2H 1.4 Hz), 4.69 ppm (1H, ^3J1H = 10 Hz, ^2J1H ^4J1H 1.4 Hz), 4.87 ppm (1H, ^3J1H = 17.1 Hz, ^2J1H ^4J1H 1.4 Hz), 5.91 ppm (1H, ^3J1H = 5.7 Hz, ^3J1H = 10 Hz, ^3J1H = 17.1 Hz).

2 : 1.15 ppm (3H, ^3J2H = 6.6 Hz), 1.87 ppm (3H, s), 3.30 and 3.72 ppm (1H + 1H, ^2J1H = - 8.3 Hz, ^3J3H = 6.6 Hz), 4.11 ppm (1H, s), 4.73 ppm (2H, m).

3 : Common signals for **3E** and **3Z** : 1.13 ppm (3H, ^3J2H = 6.9 Hz), 1.57 ppm (3H, ^3J1H = 7.15 Hz, ^4J1H 1.6 Hz), 3.16 and 3.61 ppm (1H + 1H, ^2J1H = - 8.8 Hz, ^3J3H = 6.9 Hz).

Specific signals

3E : 4.25 ppm (1H, ^3J1H = 7.15 Hz, ^4J1H = 1.4 Hz), 5.46 ppm (1H, ^3J3H = 7.15 Hz, ^3J1H =

15.4 Hz, $^{4}J1H$ = 1.4 Hz), 5.68 ppm (1H, $^{3}J1H$ = 7.15 Hz, $^{3}J1H$ = 15.4 Hz, $^{4}J3H$ 1.4 Hz).

3Z : 4.66 ppm (1H, $^{3}J1H$ = 9.35 Hz, $^{4}J1H$ = 1.65 Hz), 5.24 ppm (1H, $^{3}J1H$ = 11 Hz, $^{3}J3H$ = 7.15 Hz, $^{4}J1H$ = 1.65 Hz), 5.82 ppm (1H, $^{3}J1H$ = 9.35 Hz, $^{3}J1H$ = 11 Hz, $^{4}J3H$ = 1.65 Hz).

4 : 1.08 ppm (3H, $^{3}J2H$ = 6.9 Hz), 1.59 ppm (3H, s), 1.70 ppm (3H, s), 3.24 and 3.51 ppm (1H + 1H, $^{2}J1H$ = - 9.2 Hz, $^{3}J3H$ = 6.9 Hz), 4.52 ppm (1H, $^{3}J1H$ = 10.2 Hz, $^{2}JSnH$ = 22.2 Hz), 5.44 ppm (1H, $^{3}J1H$ = 10.2 Hz with small allylic couplings, $^{3}JSnH$ = 18 Hz).

^{119}Sn NMR

1 : - 38.4 ppm, **2** : - 36.8 ppm, **3E** : - 39.0 ppm, **3Z** : - 33.4 ppm, **4** : - 34.2 ppm

3 - Substitution of organic halides

All these reactions have been achieved in similar experimental conditions according to the general procedure used previously by **MIGITA** (35). 0.05 mmole of palladium catalyst ($Pd(PPh_3)_4$ for aryl bromides or $BnPdCl(PPh_3)_2$ for benzoyl chloride), 5 mmoles of α-ethoxyallyltin derivative and 5 mmoles of halide were successively added under an inert atmosphere (argon) in a tube which was sealed and then warmed at 110-120°C over a period of 10 to 20 hours. A hexane/acetonitrile partition of organotin and organic products was performed and the organic compounds (extracted in acetonitrile) purified on florisil or silica gel (eluent = pentane).

Aldehydes were obtained under gentle warming (50°C) of vinylethers (5 mmoles) with a 30 % sulfuric acid solution (10 ml) over a period of one hour followed by extraction with diethyl ether.

The Z/E ratio for compounds **5-14** were determined by G.C. analysis (column A) and the identifications subsequently corroborated using IR, MS and ^{1}H NMR spectroscopies.

^{1}H NMR data for compounds **5-15**

5 (E-isomer) 1.18 ppm (3H, $^{3}J2H$ = 6.7 Hz), 3.12 (2H, $^{3}J1H$ = 7.3 Hz), 3.58 ppm (2H, $^{3}J3H$ = 6.7 Hz), 4.72 ppm (1H, $^{3}J1H$ = 7.3 Hz, $^{3}J1H$ = 12.7 Hz), 6.15 ppm (1H, $^{3}J1H$ = 12.7 Hz), 7.02 ppm (5H, s).

6 (E+Z) 1.19 ppm (3H, $^{3}J2H$ = 6.6 Hz), 1.97 ppm (3H, ~s), 3.13 ppm (2H, ~s), 3.61 ppm (2H, $^{3}J3H$ = 6.6 Hz), 6.19 ppm (1H, ~s), 7.07 ppm (5H, ~s).

7 (E-isomer) 1.27 ppm (3H, $^{3}J2H$ = 6.7 Hz), 1.29 ppm (6H, s), 3.64 ppm (2H, $^{3}J3H$ = 6.7 Hz) ; 4.79 ppm (1H, $^{3}J1H$ = 12.8 Hz), 6.09 ppm (1H, $^{3}J1H$ = 12.8 Hz) ; 7.13 ppm (5H, s).

8 (E-isomer) 1.20 ppm (3H, $^{3}J2H$ = 6.7 Hz), 3.11 ppm (2H, $^{3}J1H$ = 7.3 Hz), 3.62 ppm (2H, $^{3}J3H$ = 6.7 Hz), 4.71 ppm (1H, $^{3}J2H$ = 7.3 Hz, $^{3}J1H$ = 13.3 Hz), 6.21 ppm (1H, $^{3}J1H$ = 13.3 Hz), 7.12 ppm (4H, m).

(Z-isomer) 1.20 ppm (3H, $^{3}J2H$ = 6.7 Hz), 3.28 ppm (2H, $^{3}J1H$ = 6.9 Hz), 3.62 ppm (2H, $^{3}J3H$ = 6.7 Hz), 4.42 ppm (1H, $^{3}J2H$ = 6.9 Hz, $^{3}J1H$ = 6.7 Hz), 5.91 ppm (1H, $^{3}J1H$ = 6.7 Hz), 7.15 ppm (4H, m).

9 (E-isomer) 1.27 ppm (3H, $^{3}J2H$ = 6.7 Hz), 3.16 ppm (2H, $^{3}J1H$ = 7.1 Hz), 3.63 ppm (2H, $^{3}J3H$ = 6.7 Hz), 4.83 ppm (1H, $^{3}J1H$ = 12.2 Hz, $^{3}J2H$ = 7.1 Hz), 6.36 ppm (1H, $^{3}J1H$ = 12.2 Hz), 7.10 ppm (4H, m).

(Z-isomer) 1.26 ppm (3H, $^{3}J2H$ = 6.7 Hz), 3.38 ppm (2H, $^{3}J1H$ = 7.6 Hz), 3.66 ppm (2H, $^{3}J3H$ = 6.7 Hz), 4.58 ppm (1H, $^{3}J1H$ = 6.2 Hz, $^{3}J2H$ = 7.6 Hz), 6.07 ppm (1H, $^{3}J1H$ = 6.2 Hz), 7.10 ppm (4H, m).

10 (E-isomer) 1.21 ppm (3H, $^{3}J2H$ = 6.7 Hz), 3.14 ppm (2H, $^{3}J1H$ = 6.9 Hz), 3.58 ppm (3H, s), 3.65 ppm (2H, $^{3}J3H$ = 6.7 Hz), 4.79 ppm (1H, $^{3}J2H$ = 6.9 Hz, $^{3}J1H$ = 13.8 Hz), 5.98 ppm (1H, $^{3}J1H$ = 13.8 Hz), 7.11 ppm (4H, m).

(Z-isomer) 1.25 ppm (3H, $^{3}J2H$ = 6.7 Hz), 3.28 ppm (2H, $^{3}J1H$ = 6.8 Hz), 3.58 ppm (3H, s), 3.61 ppm (2H, $^{3}J3H$ = 6.7 Hz), 4.38 ppm (1H, $^{3}J2H$ = 6.8 Hz, $^{3}J1H$ = 6.5 Hz), 5.87 ppm (1H, $^{3}J1H$ = 6.5 Hz), 7.11 ppm (4H, m).

11 (E-isomer) 1.22 ppm (3H, $^{3}J2H$ = 6.7 Hz), 2.12 ppm (3H, s), 3.12 ppm (2H, $^{3}J1H$ = 7.4 Hz), 3.60 ppm (2H, $^{3}J3H$ = 6.7 Hz), 4.76 ppm (1H, $^{3}J2H$ = 7.4 Hz, $^{3}J1H$ = 13.6 Hz), 6.19 ppm (1H, $^{3}J1H$ = 13.6 Hz), 7.13 ppm (4H, m).

(Z-isomer) 1.24 ppm (3H, $^{3}J2H$ = 6.7 Hz), 2.12 ppm (3H, s), 3.32 ppm (2H, $^{3}J1H$ = 7.1 Hz), 3.63 ppm (2H, $^{3}J3H$ = 6.7 Hz), 4.47 ppm (1H, $^{3}J2H$ = 7.1 Hz, $^{3}J1H$ = 6.5 Hz), 5.94 ppm (1H, $^{3}J1H$ = 6.5 Hz), 7.13 ppm (4H, m).

12 (E-isomer) 1.10 ppm (3H, $^{3}J2H$ = 6.7 Hz), 1.27 ppm (3H, $^{3}J1H$ = 6.1 Hz), 2.23 ppm (3H, s), 3.37 ppm (1H, $^{3}J1H$ = 6.1 Hz, $^{3}J1H$ = 7.3 Hz), 3.54 ppm (2H, $^{3}J3H$ = 6.7 Hz), 4.78 ppm (1H, $^{3}J1H$ = 7.3 Hz, $^{3}J1H$ = 12.7 Hz), 6.10 ppm (1H, $^{3}J1H$ = 12.7 Hz), 7.02 ppm (4H, m).

13 (E-isomer) 1.22 ppm (3H, $^{3}J2H$ = 7.5 Hz), 1.35 ppm (3H, $^{3}J1H$ = 6.9 Hz), 2.60 ppm (3H, s), 3.50 ppm (1H, m), 3.70 ppm (2H, $^{3}J3H$ = 7.5 Hz), 4.80 ppm (1H, $^{3}J1H$ = 13 Hz, $^{3}J1h$ = 7.7 Hz), 6.15 ppm (1H, $^{3}J1H$ = 13 Hz, $^{4}J1H$ 0.7 Hz), 7.65 ppm (4H, m).

(Z-isomer) 1.22 ppm (3H, $^{3}J2H$ = 7.5 Hz), 1.30 ppm (3H, $^{3}J1H$ = 6.9 Hz), 2.60 ppm (3H, s), 3.50 ppm (1H, m), 3.70 ppm (2H, $^{3}J3H$ = 7.5 Hz), 4.35 ppm (1H, $^{3}J1H$ = 6 Hz, $^{3}J1H$ = 9 Hz), 5.80 ppm (1H, $^{3}J1H$ = 6 Hz, $^{4}J1H$ = 1 Hz), 7.65 ppm (4H, m).

14 (E-isomer) 1.22 (3H, $^{3}J2H$ = 7.5 Hz), 1.40 ppm (3H, $^{3}J1H$ = 7.0 Hz), 3.60 ppm (1H, m), 3.72 ppm (2H, $^{3}J3H$ = 7.5 Hz), 4.95 ppm (1H, $^{3}J1H$ = 8.2 Hz, $^{3}J1H$ = 13 Hz), 6.40 ppm ($^{3}J1H$ = 13 Hz, $^{4}J1H$ 1 Hz), 7.64 ppm (4H, m), 9.95 ppm (1H, s).

(Z-isomer) 1.22 ppm (3H, $^{3}J2H$ = 7.5 Hz), 1.31 ppm (3H, $^{3}J1H$ = 7.0 Hz), 3.81 ppm (2H, $^{3}J3H$ = 7.5 Hz), 4.00 ppm (1H, m), 4.54 ppm (1H, $^{3}J1H$ = 6.5 Hz ; $^{3}J1H$ = 9.2 Hz), 6.05 ppm (1H, $^{3}J1H$ = 6.5 Hz), $^{4}J1H$ 1 Hz), 7.60 ppm (4H, m), 9.95 ppm (1H, s).

15 1.12 ppm (3H, $^{3}J1H$ = 7.5 Hz), 2.42 ppm (1H, $^{3}J1H$ = 6.1 Hz, $^{2}J1H$ = -17.9 Hz), 3.04 ppm (1H, $^{3}J1H$ = 7.9 Hz, $^{2}J1H$ = -17.9 Hz), 3.88 ppm (1H, $^{3}J3H$ = 7.5 Hz, $^{3}J1H$ = 6.1 Hz, $^{3}J1H$ = 7.9 Hz), 7.15 to 8 ppm (5H, m), 9.71 ppm (1H, bs).

4 - Addition of 3 on p-bromobenzaldehyde

$BF_3.Et_2O$ promoted reactions

In a Schlenk reactor containing p-bromobenzaldehyde (10 mmoles), in methylene chloride (50 ml) and maintained at -78°C under an inert atmosphere were successively added by syringe method boron trifluoride etherate (20 mmoles) and **3** in methylene chloride (15 mmoles in 10 ml). The reaction mixture was stirred at -78°C and allowed to reach 0°C over a period of two hours. After subsequent hydrolysis (HCl, 2N), extraction, drying and evaporation of solvents the hexane/acetonitrile partition provided the mixture of adducts **16** + **17**.

Thermic reaction

A mixture of **3** (10 mmoles) and p-bromobenzaldehyde (10 mmoles) was warmed in a sealed tube under an inert atmosphere without solvent (for details concerning temperature and heating period see table II). After hydrolysis, the hexane/acetonitrile partition afforded the mixture of isomers **16-19**.

High pressure induced reactions

A solution of p-bromobenzaldehyde (2 mmoles) and **3** (2 mmoles) in methylene chloride (1 ml) was compressed in the teflon cell of the high pressure equipment previously described (36). The pressure was allowed to reach 1000 MPa at room temperature and the whole apparatus was warmed to 50°C. After 20 hours, the pressure was released, CH_2Cl_2 removed under vacuum and the products submitted to the usual workup (see above).

G.C./M.S. analyses

The gas-chromatography analyses were performed on column B at 200°C. The relative retention times for the eight isomers are the following ones : **16E** (1≡ 13.5 mn), **16Z** (1.04), **17E** (1.13), **17Z** (1.21), **19Z** (1.23), **18Z** (1.86), **19E** (2.60) and **18E** (2.67).

The mass spectra of the eight isomers obtained in G.C./M.S. mode are very similar (M^+ = 284 for ^{79}Br) with a highly preferential benzylic scission (higher abundancy for m/z = 99).

^{1}H NMR data (200 MHz/$CDCl_3$) for compounds **16-19**

16E 1.22 ppm (3H, ^{3}J2H 7 Hz), 1.62 ppm (3H, ^{3}J1H = 6.3 Hz, ^{4}J1H = 1.4 Hz), 3.35 ppm (1H, ^{2}J1H = -9.35 Hz, ^{3}J3H = 6.98 Hz), 3.37 ppm (hydroxyl, ^{3}J1H = 1.6 Hz), 3.57 ppm (1H, ^{3}J1H = 7.9 Hz, ^{3}J1H = 7.6 Hz), 3.64 ppm (1H, ^{2}J1H = -9.35 Hz, ^{3}J3H = 7.06 Hz), 4.44 ppm (1H, ^{3}J1H = 7.9 Hz, ^{3}J1H = 1.6 Hz), 5.21 ppm (1H, ^{3}J1H = 7.6 Hz, ^{3}J1H = 15.4 Hz, ^{4}J3H = 1.4 Hz), 5.43 ppm (^{3}J1H = 15.4 Hz, ^{3}J3H = 6.3 Hz, ^{4}J1H 0.2 Hz), 7.33 ppm (4H, m).

16Z less abundant compound. A full set of NMR parameters could not be measured. However a triplet has been observed at 4.10 ppm (J∿ 8 Hz) and assigned to the tertiary hydrogen near the ethoxy group.

17E 1.15 ppm (3H, ^{3}J2H 7 Hz), 1.67 ppm (3H, ^{3}J1H = 6.3 Hz, ^{4}J1H = 1.4 Hz), 2.67 ppm (hydroxyl, ^{3}J1H = 3.64 Hz), 3.35 ppm (1H, ^{2}J1H = -9.5 Hz, ^{3}J3H = 7 Hz), 3.59 ppm (1H, ^{2}J1H = -9.5 Hz, ^{3}J3H = 7.1 Hz), 3.78 ppm (1H, ^{3}J1H = 4.8 Hz, ^{3}J1H = 7.9 Hz, ^{4}J1H = 0.4 Hz), 4.71 ppm (1H, ^{3}J1H = 4.8 Hz, ^{3}J1H = 3.64 Hz), 5.29 ppm (1H, ^{3}J1H = 15.4 Hz, ^{3}J1H = 7.9 Hz, ^{4}J3H = 1.4 Hz), 5.59 ppm (1H, ^{3}J1H = 15.4 Hz, ^{3}J3H = 6.3 Hz, ^{4}J1H = 0.4 Hz), 7.33 ppm (4H, m).

17Z 1.16 ppm (3H, ^{3}J2H = 7 Hz), 1.40 ppm (3H, ^{3}J1H = 6.95 Hz, ^{4}J1H = 1.8 Hz), 2.87 ppm (hydroxyl, ^{3}J1H = 4.5 Hz), 3.35 ppm (1H, ^{2}J1H = -9.3 Hz, ^{3}J3H = 7 Hz), 3.56 ppm (1H, ^{2}J1H = -9.3 Hz, ^{3}J3H = 7 Hz), 4.22 ppm (1H, ^{3}J1H = 4 Hz, ^{3}J1H = 9.3 Hz, ^{4}J1H = 0.9 Hz), 4.76 ppm (1H, ^{3}J1H = 4 Hz, ^{3}J1H = 4.5 Hz), 5.28 ppm (^{3}J1H = 11.2 Hz, ^{3}J1H = 9.3 Hz, ^{4}J1H = 1.8 Hz), 5.71 ppm (1H, ^{3}J1H = 11.2 Hz, ^{3}J3H = 6.95 Hz, ^{4}J1H = 0.9 Hz), 7.33 ppm (4H, m).

18E 0.93 ppm (3H, ^{3}J1H = 6.9 Hz), 1.24 ppm (3H, ^{3}J2H = 7 Hz), 2.42 ppm (1H, ^{3}J3H = 6.9 Hz, ^{3}J1H = 5.2 Hz, ^{3}J1H = 8.5 Hz, ^{4}J1H = 0.3 Hz), 2.70 ppm (hydroxyl), 3.67 ppm (2H, ^{3}J3H = 7 Hz), 4.49 ppm (1H, ^{3}J1H = 5.2 Hz), 4.55 ppm (1H, ^{3}J1H = 12.7 Hz, ^{3}J1H = 8.5 Hz), 6.19 ppm (1H, ^{3}J1H = 12.7 Hz, ^{4}1H = 0.3 Hz), 7.33 ppm (4H, m).

18Z 0.95 ppm (3H, ^{3}J1H = 6.9 Hz), 1.21 ppm (3H, ^{3}J2H = 7.1 Hz), 2.80 ppm (hydroxyl, ^{3}J1H = 3.2 Hz), 3.05 ppm (1H, ^{3}J1H = 5 Hz, ^{3}J1H = 9 Hz, ^{3}J3H = 6.9 Hz, ^{4}J1H = 1 Hz), 3.73 ppm (2H, ^{3}J3H = 7.1 Hz), 4.09 ppm (1H, ^{3}J1H = 6.3 Hz, ^{3}J1H = 9 Hz), 4.60 ppm (1H, ^{3}J1H = 5 Hz, ^{3}J1H = 3.2 Hz), 5.95 ppm (^{3}J1H = 6.3 Hz, ^{4}J1H = 1 Hz), 7.32 ppm (4H, m).

19E 0.85 ppm (3H, ^{3}J1H = 6.8 Hz), 1.28 ppm (3H, ^{3}J2H = 7 Hz), 2.22 ppm (1H, ^{3}J1H = 7.9 Hz, ^{3}J1H = 9.1 Hz, ^{3}J3H = 6.8 Hz), 2.70 ppm (hydroxyl), 3.74 ppm (2H, ^{3}J3H = 7 Hz), 4.20 ppm (1H, ^{3}J1H = 7.9 Hz), 4.61 ppm (1H, ^{3}J1H = 12.5 Hz, ^{3}J1H = 9.1 Hz), 6.35 ppm (1H, ^{3}J1H = 12.5 Hz, ^{4}J 0), 7.33 ppm (4H, m).

19Z 0.80 ppm (3H, ^{3}J1H = 6.9 Hz), 1.24 ppm (3H, ^{3}J2H = 7 Hz), 2.75 ppm (1H, hydroxyl), 2.90 ppm (1H, ^{3}J1H = 7.9 Hz, ^{3}J1H = 9.3 Hz, ^{3}J3H = 6.9 Hz, ^{4}J1H = 0.8 Hz), 3.80 ppm (2H, ^{3}J3H = 7 Hz), 4.27 ppm (1H, ^{3}J1H = 6.3 Hz, ^{3}J1H = 9.3 Hz), 4.28 ppm (1H, ^{3}J1H = 7.9 Hz), 6.12 ppm (1H, ^{3}J1H = 6.3 Hz, ^{4}J1H = 0.8 Hz), 7.33 ppm (4H, m).

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