Tetrahedron Letters, Vol.31, No.43, pp 6239-6242, 1990
Printed in Great Britain

0040-4039/90 $3.00 + .00
Pergamon Press plc

1,5-Asymmetric Induction in Reactions between δ-Alkoxyallylstannanes and Aldehydes induced by Tin (IV) Chloride

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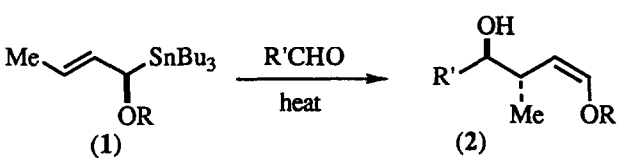
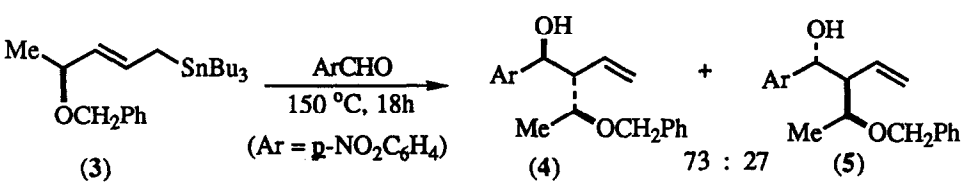
Abstract *Treatment of (S)-4-benzyloxypent-(2E)-2-enyl(tributyl)stannane (3) with tin (IV) chloride at -78 °C, followed by the addition of an aldehyde, gives 1,5-diol derivatives (6) with excellent 1,5-diastereoselectivity.*

Allylstannanes undergo stereoselective reactions with aldehydes to give homoallylic alcohols, both on heating and in the presence of Lewis acids,[1] e.g. 1-alkoxybut-2-enyl(tributyl)stannane (1) reacts with aldehydes at 120-140 °C to give the *anti, cis*-enol ethers (2), although the reaction is effectively limited to aromatic and secondary aliphatic aldehydes because of the high temperatures required.[2] δ-Alkoxyallylstannanes have been found to show modest diastereofacial selectivity on heating with aldehydes, e.g. (*S*)-4-benzyloxypent-(2*E*)-2-enyl(tributyl)stannane (3) reacts with p-nitrobenzaldehyde to give homoallylic alcohols (4) and (5) in the ratio 73:27.[3] We now report that if premixed at -78 °C with tin (IV) chloride, the (*S*)-4-benzyloxypentenylstannane (3) undergoes highly stereoselective reactions with a range of aldehydes.

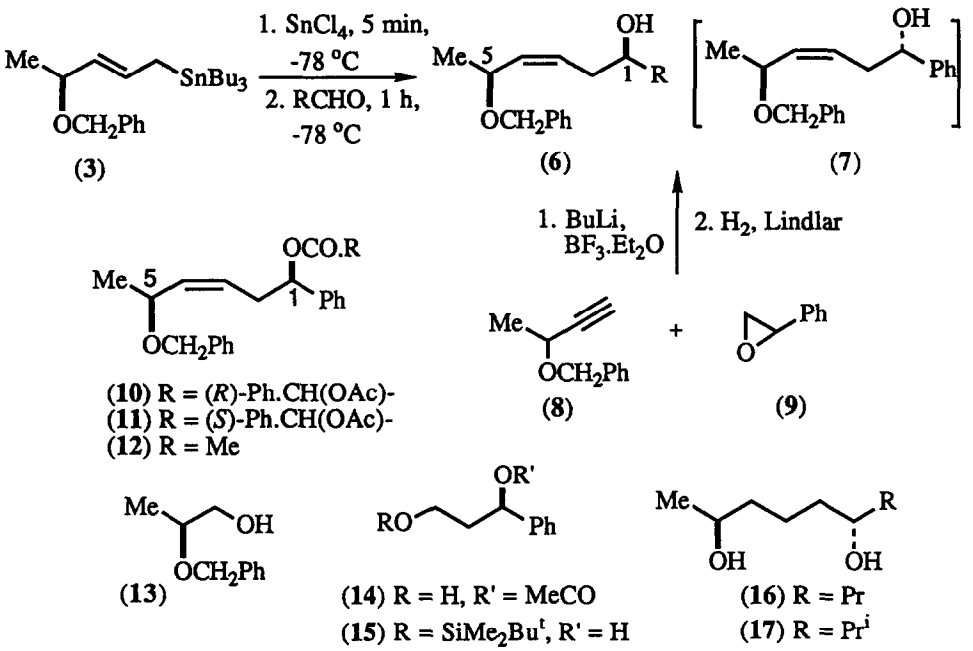


(1) (2)



(3) (4) (5)

Preliminary investigations into Lewis acid catalysis of reactions between δ-alkoxyallylstannanes and aldehydes were restricted by competing decomposition of the stannane.[3] However it was found that if the (*S*)-4-benzyloxypentenylstannane (3)[3] was mixed with one mol. equivalent of tin (IV) chloride at -78 °C, followed after 5 min. by the addition of a precooled solution of benzaldehyde, a good yield, 90%, of a single product, identified as (1*R*,5*S*,3*Z*)-5-benzyloxy-1-phenylhex-3-en-1-ol (6; R = Ph), was obtained.



The structure of (**6**) was established by spectroscopic data, with the *cis*-geometry of the double-bond being confirmed by n.O.e. observations.† To confirm the absence of the (1*S*,5*S*)-diastereoisomer (**7**), a 1:1 mixture of both isomers was prepared by coupling the lithium acetylide of racemic 3-benzyloxybut-1-yne (**8**) with racemic styrene oxide (**9**), followed by hydrogenation in the presence of a Lindlar catalyst. The two isomers (**6**; R = Ph) and (**7**) could not be separated by chromatography, but were clearly distinguished by high field n.m.r. Re-examination of the product from the reaction between benzaldehyde and stannane (**3**) showed that less than 2% of the (1*S*,5*S*)-isomer (**7**) had been formed.

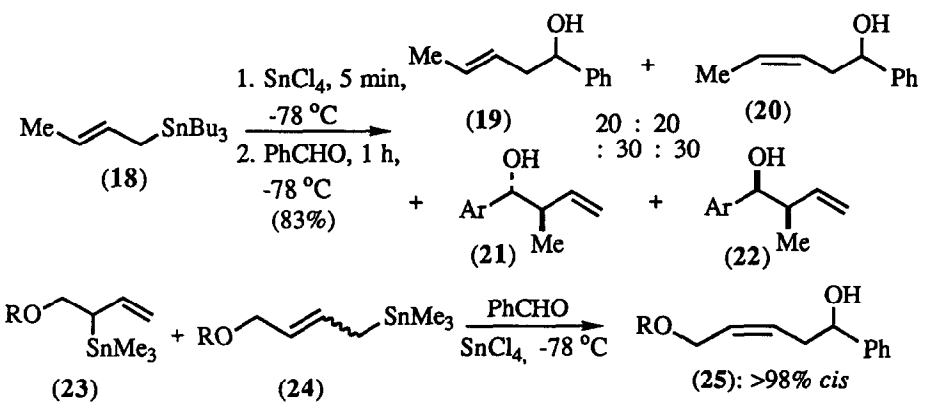
The stereochemistry of the product from the stannane reaction was initially assigned as (1*R*) on the basis of the relative chemical shifts of the 2-CH_2 protons of the (*R*)- and (*S*)-acetoxymandelates (**10**) and (**11**),[4] and was confirmed by ozonolysis of the acetate (**12**) followed by treatment with dimethyl sulphide and $NaBH_4$, which gave (*S*)-2-benzyloxypropanol (**13**) and the (+)-3-acetoxy-3-phenylpropan-1-ol (**14**), whose absolute configuration was established as (*R*) by correlation with the known (*R*)-1-phenylpropane-1,3-diol mono-t-butyldimethylsilyl ether (**15**).[5]¶

This stereoselective reaction between benzaldehyde and stannane (**3**) was found to be quite general. Thus good yields of products were obtained with a wide range of aromatic and aliphatic aldehydes as shown in the **Table**. In all cases the reactions were highly stereoselective, less than 2% of any other diastereoisomer being detected by ^1H n.m.r. Hydrogenation of the products from the butyraldehyde and isobutyraldehyde reactions gave the 1,5-diols (**16**) and (**17**), illustrating the usefulness of this procedure for the stereoselective synthesis of open-chain *anti*-1,5-diols.

Table

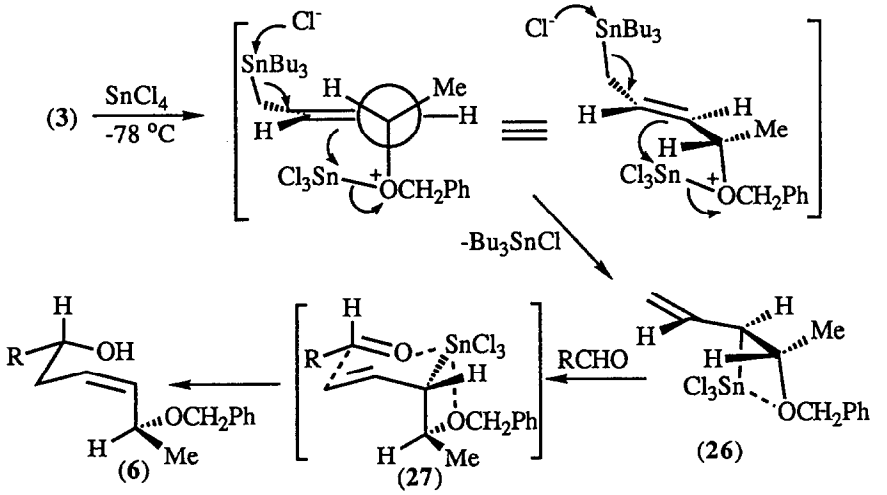
RCHO	Yield of (6) (%)
PhCHO	90
p-ClC_6H_4CHO	77
p-$NO_2C_6H_4CHO$	77
p-$MeOC_6H_4CHO$	77
furfural	72
$CH_3CH_2CH_2CHO$	84
$(CH_3)_2CHCHO$	78
$(CH_2)_5CH.CHO$	71
$CH_3CH{=}CH.CHO$	70
$MeO_2C.CHO$	57

The mechanism of this allylstannane - aldehyde reaction has not been investigated. However tin (IV) chloride induced reactions between but-2-enyl(tributyl)stannane (**18**) and aldehydes reported in the literature, give mixtures of stereo- and regio-isomers, the compositions of which depend upon the order of mixing of the reagents.[6] In our hands, the reaction between stannane (**18**) and benzaldehyde in the presence of tin (IV) chloride, under the *exact* conditions used for the selective synthesis of adducts (**6**), gave a mixture of all four possible products (**19**)-(**22**). This suggests that the benzyloxy substituent is important in controlling the regio- as well as the stereo-selectivity of our reaction. This view is supported by the selective formation of (3*Z*)-5-alkoxy-1-phenylpent-3-en-1-ol (**25**) from the tin (IV) chloride induced reaction of a *mixture* of allylstannanes (**23**) and (**24**) with benzaldehyde.[7]



Since tin (IV) chloride reacts at low temperatures with allyl(trialkyl)stannanes to generate allyl(trichloro)stannanes which are unstable, but which are very reactive towards aldehydes,[8] it is suggested that the selective formation of the product (**6**) involves participation of the allyl(trichloro)-stannane (**26**) which may be stabilized by a hypervalent Sn-O interaction.[9] The usual metallo 'ene' process with aldehydes *via* the six membered ring transition state (**27**), in which the substituent adjacent to the tin is in the preferred axial position,[2] would then give the observed products. The stereoselectivity of the overall process therefore depends upon the selectivity of formation of the

intermediate (**26**) which may be due to intramolecular delivery of the trichlorotin substituent to the double-bond by the benzyloxy group (see **Scheme**).



Scheme

It is proposed to study the mechanism of this reaction further, and to explore the generality of *in situ* generation of reactive allyl organometallic reagents for remote asymmetric induction.

Acknowledgements. We thank the S.E.R.C. for a studentship (to. A. H. McN.), and Dr. S. V. Mortlock for helpful preliminary investigations.

† (**6**; R = Ph) (Found: $M + NH_4^+$ 300.1974. $C_{19}H_{26}NO_2$ requires M, 300.1964); $\nu_{max.}$(film) 3 408, 1 071, and 699 cms^{-1}; $\delta_H(CDCl_3)$ 1.12 (3 H, d, J 7.5Hz, CH_3), 2.21 (1 H, J 2.5Hz, OH), 2.50 (2 H, m, 2-CH_2), 4.23 (1 H, m, 5-H), 4.36 and 4.51 (each 1 H, d, J 12Hz, C*H*HPh), 4.71 (1 H, m, 1-H), 5.58 (2 H, m, vinylic H), and 7.35 (10 H, m, aromatic H); *m/z* (c.i.) 300 (M^+ + 18, 36%) and 192 (M^+ - 90, 100%).

¶ (**15**) Found: $[\alpha]_D$ +27.4 °(*c* 0.76, $CHCl_3$) {lit.[5] $[\alpha]_D$ +24.7 °(*c* 0.76, $CHCl_3$)}.

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(Received in UK 1 August 1990)