Tetrahedron Letters,Vol.29,No.20,pp 2479-2482,1988 0040-4039/88 $3.00 + .00
Printed in Great Britain Pergamon Press plc

# An Observation of Diastereoface Selectivity in Thermal Reactions between δ-Alkoxyallylstannanes and Aldehydes

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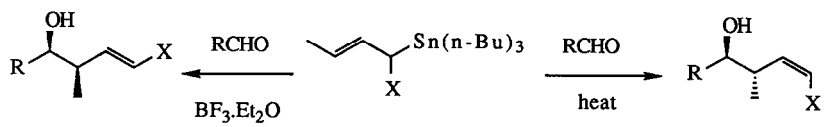
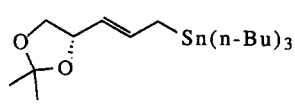
The δ-alkoxyallylstannanes (4) and (5) react stereoselectively on heating with p-nitrobenzaldehyde to provide the homoallylic alcohols (14) - (17), with (14) : (15) = 82 : 18; (16) : (17) = 73 : 27.

The chemistry of allylstannanes has been widely investigated over the last few years, and their reactions with aldehydes developed into useful, stereoselective procedures for the synthesis of homoallylic alcohols.[1] Of particular interest is the dependence of the stereoselectivity of these reactions upon the reaction conditions. Thus on heating with aldehydes, the (E)-crotylstannane (1; X = H) reacts to give anti-products (2; X = H),[2] whereas under Lewis acid catalysed conditions, syn-products (3; X = H) are formed,[3] and α-substituted allylstannanes (1; X = Me, OR) provide anti,cis-products (2) on heating with aldehydes, and syn,trans-products (3; X = Me) under Lewis acid catalysed conditions.[4]

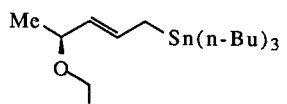



(3) (1) (2)

These observations have been explained in terms of six-membered ring, chair-like transition states for the thermal reactions, and open-chain transition states for the Lewis acid catalysed ones. However one aspect of the chemistry of allylstannanes which does not appear to have been investigated is the influence of remote allylic substituents on the stereoselectivity of their reactions. We now report syntheses of the δ-alkoxyallylstannanes (4) and (5) together with a study of the diastereoface selectivity of their thermal reactions with aldehydes.



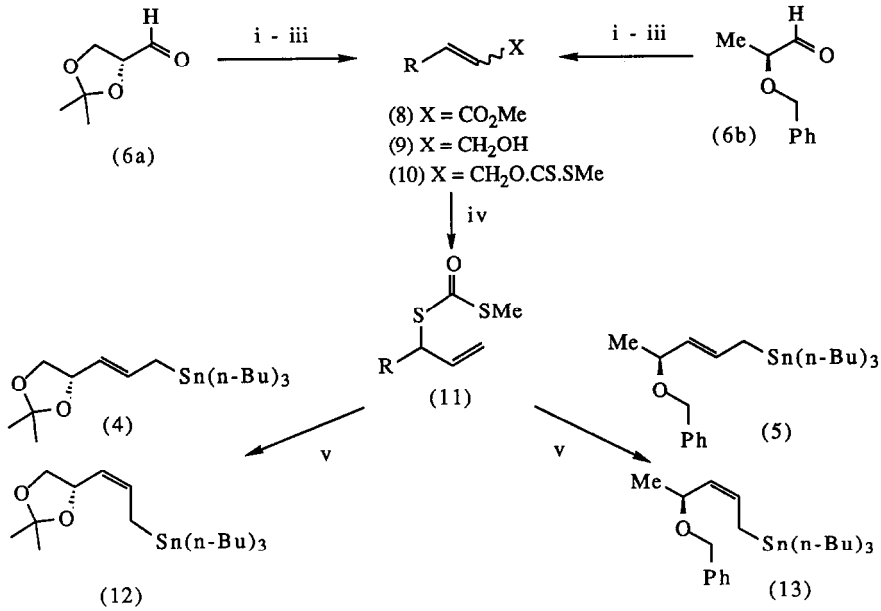

(4)




(5)

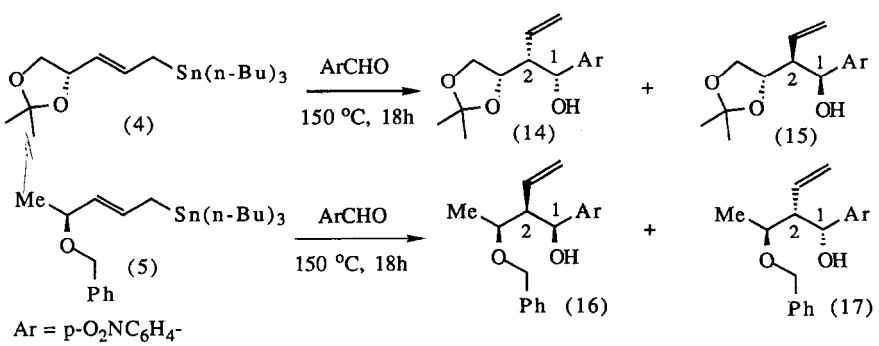
The δ-alkoxyallylstannanes (4) and (5) were prepared from the (2R)-glyceraldehyde acetal (6a) and (2S)-2-benzyloxypropanal (6b), respectively, as shown in Scheme 1. Thus Wittig condensation with (methoxycarbonylmethylene)triphenylphosphorane (7) gave mixtures of alkenes (8) [(E)-(8a) : (Z)-(8a) = 55 : 45; (E)-(8b) : (Z)-(8b) : 70 : 30], which were reduced using diisobutylaluminium hydride to give mixtures of allyl alcohols (9). These

were not separated, instead they were treated sequentially with NaH, $CS_2$, and MeI, to provide the xanthates (10), which were rearranged to the isomeric dithiocarbonates (11) by heating under reflux, in benzene for xanthate (10a), and in toluene for xanthate (10b). Treatment of the dithiocarbonates with tri-n-butyltin hydride in the presence of azobisisobutyronitrile (ABIBN) then gave the (E)-allylstannanes (4) and (5) together with small amounts of their (Z)-isomers (12) and (13), which were separated by flash chromatography.[5]



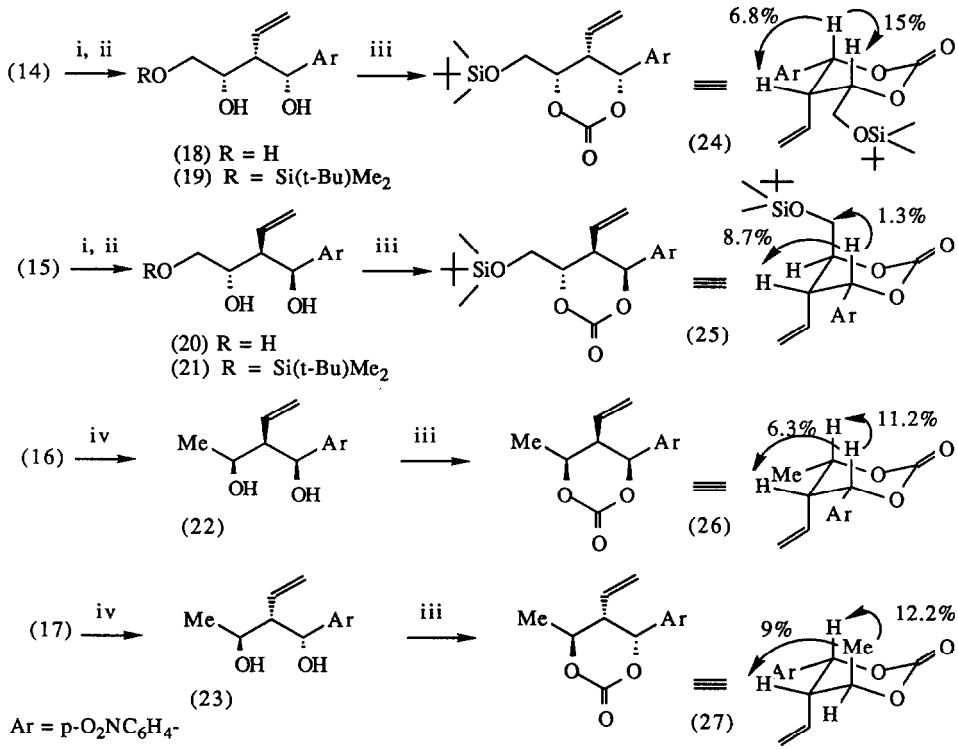

**Scheme 1** Reagents: i. $Ph_3P{=}CH.CO_2Me$ (7), benzene, 20°C (85%); ii. diisobutylaluminium hydride (85 - 90%); iii. NaH, $CS_2$, MeI (80%); iv. benzene, 80°C for (10a), toluene, 115°C for (10b) (both ca. 100%); v. n-$Bu_3SnH$, ABIBN, benzene (65 -75%); (4) : (12) = 80 : 20; (5) : (13) = 90 : 10.

The δ-alkoxystannanes (4) and (5) were found to require more vigorous conditions for their thermal reactions with aldehydes than unsubstituted allylstannanes, possibly due to the electron-withdrawing inductive effect of the alkoxy substituents, however the reactions did show significant diastereoface selectivity. Thus with p-nitrobenzaldehyde, the acetal-stannane (4) reacted on heating in a sealed tube at 150°C for 18h to give a mixture



of two adducts which were separated and identified as (14) and (15), ratio 82 : 18, combined yield (60%). The δ-benzyloxyallylstannane (5) similarly gave adducts (16) and (17), ratio 73 : 27 (48%).

Structures were assigned to these products on the basis of spectroscopic data and by conversion to the corresponding cyclic carbonates. Thus acid hydrolysis of the acetal adducts (14) and (15) gave triols (18) and (20) which were selectively protected using t-butyldimethylsilyl chloride, and converted into carbonates (24) and (25) by treatment with carbonyl 1,1'-diimidazole. The analogous carbonates were prepared from the benzyloxy-adducts (16) and (17) by debenzylation using $BF_3.Et_2O$ - EtSH, followed by treatment of diols (22) and (23) again with carbonyl 1,1'diimidazole.

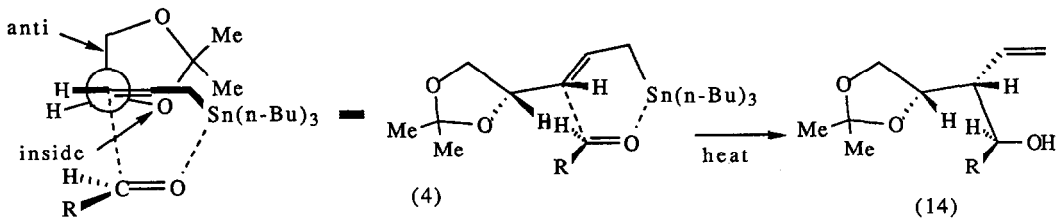



**Scheme 2** Reagents: i. 5% HCl, MeOH (70 - 75%); ii. t-$BuMe_2SiCl$, imidazole, DMF (60%); iii. $CO(imid)_2$, benzene, cat. NaH (70 - 90% crude, 30 - 40% after flash chromatography); iv. $BF_3.Et_2O$, EtSH, dichloromethane (55 - 70%).

Selected n.O.e. data for carbonates (24) - (27) are given in Scheme 2. In particular for carbonates (24) and (26) derived from the major adducts (14) and (16), irradiation of the benzylic protons caused significant n.O.e. enhancement of the other six-membered ring protons, and so established the relative configurations of all three chiral centres as shown. For the carbonate (27) derived from the minor benzyloxystannane adduct (17), irradiation of the methyl group caused significant n.O.e. enhancement of the six-membered ring protons which once again established the configuratiuons of the three chiral centres.

The optical purity of the major adduct (14) was found to correspond to an enantiomeric excess of 93% ($^{19}F$ n.m.r. of its Mosher's derivative).

The stereochemistry of adducts (14) - (17) at C(1) and C(2) is consistent with product formation via chair-like, six-membered ring, transition states. However of additional interest here is the influence of the δ-allylic oxygen substituent on the diastereoface selectivity exhibited by stannanes (4) and (5). The selectivity observed, 3 - 4 : 1, in favour of adducts (14) and (16) is consistent with reaction taking place preferentially via a conformation in which the allylic oxygen adopts an 'inside' position with the alkyl or alkoxyalkyl group in an 'anti' position, with respect to the double-bond,[6] as shown in the Figure. The increased stereoselectivity of the acetalstannane (4) may be due to the influence of the remote oxygen lone-pair electrons.




Figure

Lewis acid catalysed reactions between the stannanes (4) and (5) were briefly investigated but only very low yields of products were obtained. Treatment of the stannane (5) with $BF_3.Et_2O$ resulted in complete elimination of benzyl alcohol in under two hours at -78°C, and this elimination competed with aldehyde addition for a wide range of Lewis acid catalysts investigated. However in so far as the products that were obtained from the benzyloxystannane (5) appeared to be diastereoisomers of the thermal products (16) and (17), it may be that open-chain reactions leading to syn-products were being observed.

The high temperatures required for the thermal reactions between the δ-alkoxyallylstannanes (4) and (5) and aldehydes limits their use in synthesis. However the diastereofacial selectivity observed in these reactions is of interest in its own right.[6]

**Acknowledgements**

We thank the S.E.R.C. for support (to S.V.M.), Mrs. McGuinness and Dr. A.E. Derome for n.m.r. spectra, and Dr. R.T. Aplin for mass spectra.

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**(Received in UK 11 March 1988)**