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The Effect of a *tert*-Butyldimethylsilyl Substituent on the 1,5-Asymmetric Induction Found in Reactions of 4- and 5-Alkoxyallylstannanes with Aldehydes and Imines

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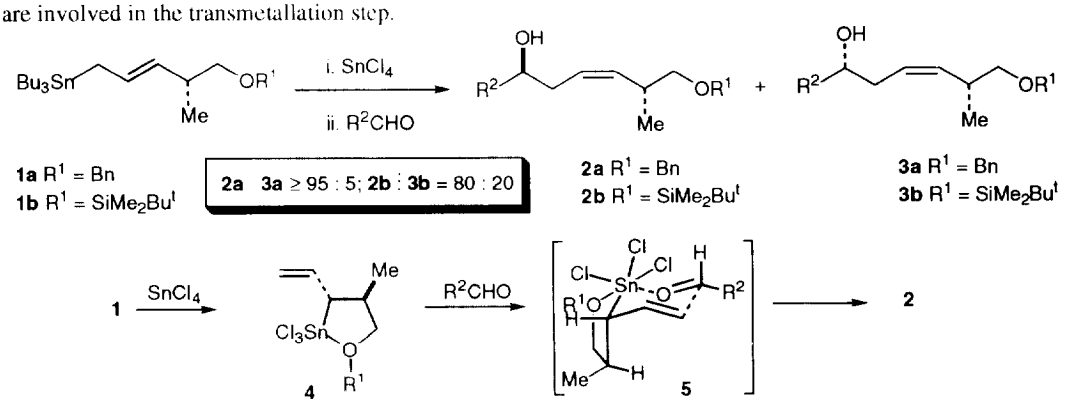
Abstract: The 4-benzyloxy- and 4-*tert*-butyldimethylsilyloxy-pent-2-enylstannanes **6a** and **6b** show different stereoselectivity in tin(IV) chloride promoted reactions with aldehydes and imines.

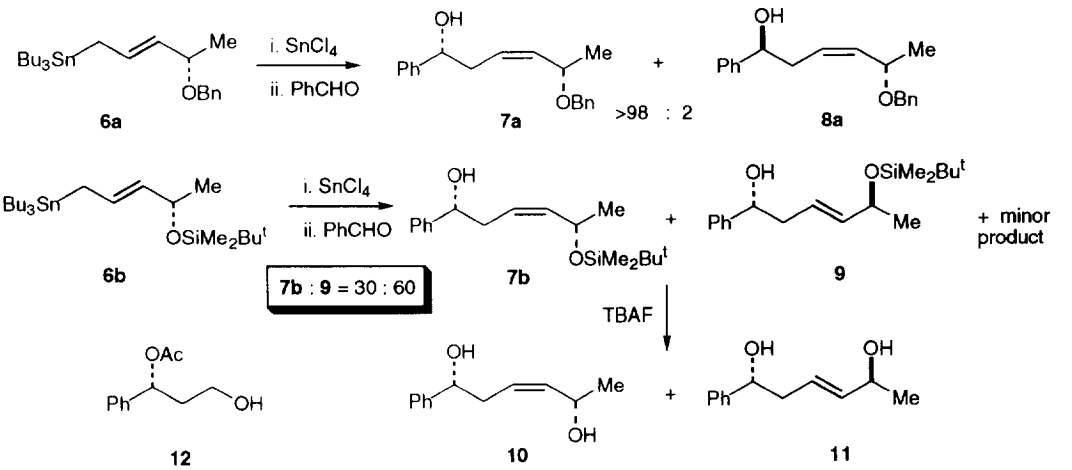
The intermediate generated by treatment of 5-benzyloxypent-2-enylstannane **1a** with tin(IV) chloride, reacts with aldehydes with excellent stereoselectivity to give the 1,5-*anti*-products **2a** containing less than 5% of their 1,5-*syn*-diastereoisomers **3a**.[1] Similar, albeit reduced, stereoselectivity was observed for the corresponding 5-*tert*-butyldimethylsilyloxypentenylstannane **1b**, which, with benzaldehyde, gave rise to the formation of the 1,5-*anti*- and 1,5-*syn*-diastereoisomers **2b** and **3b**, ratio *ca.* 80 : 20.[2] These reactions have been interpreted in terms of stereoselective transmetallation of the allylstannanes to generate a reactive allyltin trichloride **4** which reacts with aldehydes *via* a chair-like, cyclic, transition state **5**. We now wish to report that the stereoselectivity found for the 4-benzyloxypent-2-enylstannane **6a** is *reversed* for the *tert*-butyldimethylsilyloxypent-2-enylstannane **6b**, in reactions with aldehydes and imines, perhaps because different processes are involved in the transmetallation step.



The 4-benzyloxypent-2-enylstannane **6a** is known to generate an intermediate on transmetallation with tin(IV) chloride, which reacts with benzaldehyde with excellent 1,5-stereoselection in favour of the 1,5-*syn*-diastereoisomer **7a**.[3] In contrast, the corresponding reaction with the 4-*tert*-butyldimethylsilyloxypent-2-

Dedicated to the memory of Professor Hidemasa Takaya, deceased on 5 October 1995

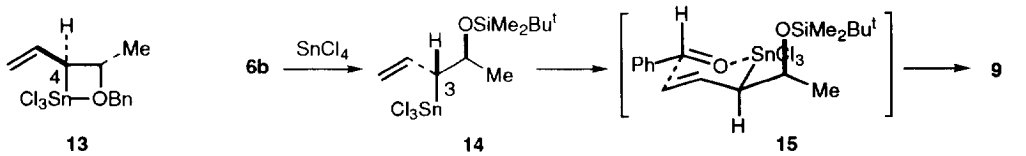
enylstannane **6b** was found to be far less stereoselective and gave rise to a mixture of the 1,5-*syn*-(*Z*)-hexenol **7b** and its 1,5-*anti*-(*E*)-stereoisomer **9**, together with a third minor product, which was not fully characterised, ratio 30 : 60 : 10, respectively. These products could not be separated. However, after treatment of the mixture with tetrabutylammonium fluoride, the two major diols **10** and **11** were separated and characterised. The configuration of the major diol **11** at C(1) was established by ozonolysis of its bis-acetate with a reductive work-up. This gave the dextrorotatory 3-acetoxy-3-phenylpropanol which is known to correspond to the (*R*)-enantiomer **12**.[4]



The formation of the 1,5-*anti*-(*E*)-alkenol **9** as the major product in the reaction between the 4-*tert*-butyldimethylsilyloxypent-2-enylstannane **6b** and benzaldehyde is surprising and contrasts with the stereoselectivity observed for the corresponding reaction with the 4-benzyloxystannane **6a**. As in the reactions of the stannanes **1a** and **1b**, transmetallation of the allylstannanes **6a** and **6b** to generate allyltin trichlorides which react with benzaldehyde *via* chair-like six-membered, cyclic transition states, is believed to be involved. However, the formation of the *anti*-(*E*)-alkenol **9** as the major product from the silyloxystannane **6b** requires that transmetallation of **6b** generates an allyltin trichloride which has the *opposite* configuration at the tin bearing carbon with respect to that generated from the benzyloxystannane **6a**. If the allyltin trichloride generated from **6b** had the same configuration at the tin bearing carbon as that obtained from **6a**, it could not give rise to the formation of an (*E*)-alkenol with the same configuration at C(1) as the (*Z*)-alkenol obtained from the benzyloxystannane **6a**, at least not *via* a chair-like, cyclic transition state, because the formation of the *trans*-double-bond would require the stannane to approach the aldehyde on its opposite face.

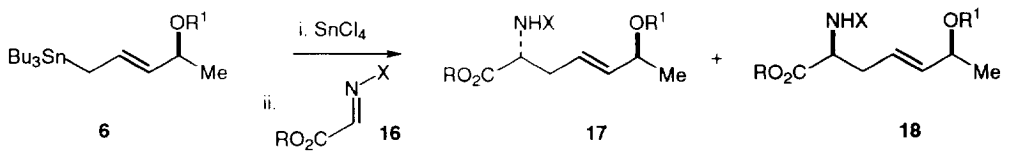
Transmetallation of the 4-benzyloxystannane **6a** may involve coordination of the tin(IV) chloride to the oxygen of the benzyloxy substituent followed by *intra*molecular transfer of the tin chloride to give the (4*S*)-allyltin trichloride **13** in which the electron deficient tin remains coordinated to the oxygenated functionality. For the silyloxystannane **6b**, it may be that prior coordination of the tin(IV) chloride to the silyloxy substituent is disfavoured by the presence of the bulky silyl group, and that transmetallation is *inter*molecular giving rise to the formation of the (3*R*)-allyltin trichloride **14** with only modest stereoselectivity induced by the allylic stereogenic centre. The allyltin trichloride **14** may then be reacting with the benzaldehyde *via* the chair-like transition state **15** in which the substituent α to tin is equatorial. Why

trans-double-bond formation is preferred in this case is not clear, but may be associated with the oxygen substituent not being coordinated to the electron deficient tin.[5]



13 **14** **15**

If transmetallation of the silyloxyallylstannane **6b** gives an intermediate allyltin trichloride with the *opposite* configuration at the tin bearing carbon from that formed by transmetallation of the benzyloxyallylstannane **6a**, then products with different configurations would be expected from their reactions with imines. This proves to be the case. The allyltin trichloride derived from the 4-benzyloxypent-2-enylstannane **6a** has been shown to react with 1-alkoxycarbonyl imines **16** with useful stereoselectivity in favour of the 1,5-*anti*-products **17**.[6,7] However, addition of an imine to the allyltin trichloride generated from the silyloxypent-2-enylstannane **6b**, gives the 1,5-*anti*- and 1,5-*syn*-products **17** and **18** in which the 1,5-*syn*-isomers predominate, ratio *ca.* 75 : 25, with both achiral and chiral imines.[8]



6 **16** **17** **18**

Table 1: Reactions of Stannanes 6 with Imines 16

Stannane R^1	Imine	X	R	Yield (%)	1,5-*anti* (**17**) : 1,5-*syn* (**18**)
Bn	**16a**	SAr^a	Me	87	89 : 11
Bn	**16b**	$CHPh_2$	Bu	79	90 : 10
Bn	**16c**	CMe_2Ph	Bu	75	90 : 10
$SiMe_2Bu^t$	**16a**	SAr^a	Me	85	25 : 75
$SiMe_2Bu^t$	**16b**	$CHPh_2$	Bu	91	25 : 75
$SiMe_2Bu^t$	**16c**	CMe_2Ph	Bu	74	25 : 75
$SiMe_2Bu^t$	**16d**	$CHPh_2$	Me	76	25 : 75
$SiMe_2Bu^t$	**16e**	(*S*)-CHMePh	Bu	76	33 : 67
$SiMe_2Bu^t$	**16f**	(*R*)-CHMePh	Bu	93	25 : 75

[a]Ar = 2-$NO_2C_6H_4$-

For the 5-benzyloxy- and 5-silyloxypentenylstannanes **1a** and **1b**, it would appear that transmetallation gives allyltin trichlorides with the same stereochemistry at the tin bearing carbon, since these react to give products with the same stereochemistry at C(1) with aldehydes. For these stannanes it would be expected that the major products from reactions with imines would therefore have the same configuration at C(2), with better stereoselectivity being obtained using the benzyloxystannane **1a**. Again this proves to be the case. The 5-benzyloxypent-2-enylstannane **1a** has been found to react with 1-alkoxycarbonyl imines stereoselectively in favour of the 1,5-*syn*-products **19**, selectivity typically 95 : 5.[6,7] The major products formed from reactions

between the 5-*tert*-butyldimethylsilyloxypent-2-enylstannane **1b** and the allyltin trichloride generated from the imines **16a**, **16e** and **16f**, were found to correspond to the 1,5-*syn*-isomers. In these cases the stereoselectivity was influenced by the matching and mismatching in the cases of the chiral imines **16e** and **16f**, but the overall stereoselectivity was as expected.

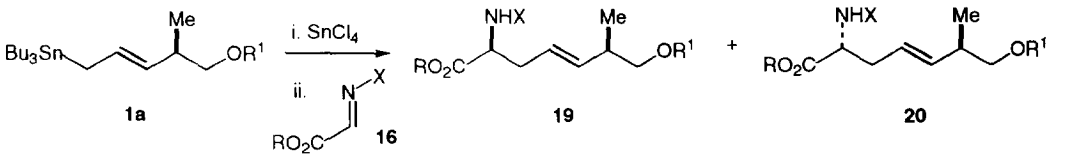


Table 2: Reactions of Stannanes 1 with Imines 16

Stannane R^1	Imine	X	R	Yield (%)	1,5-*syn* (**19**) : 1,5-*anti* (**20**)
Bn	16a	SAr[a]	Me	74	95 : 5
Bn	16b	$CHPh_2$	Bu	78	95 : 5
$SiMe_2Bu^t$	16a	SAr[a]	Me	77	80 : 20
$SiMe_2Bu^t$	16e	(*S*)-CHMePh	Bu	80	67 : 33
$SiMe_2Bu^t$	16f	(*R*)-CHMePh	Bu	74	75 : 25

[a]Ar = 2-$NO_2C_6H_4$-

This work shows an interesting effect of the nature of the Q-substituent on the direction of remote asymmetric induction observed in reactions of 4- and 5-alkoxyallylstannanes and aldehydes and imines. Although the mechanistic details of these processes remain to be clarified, the ability to switch the stereoselectivity of product formation in reactions of the 4-alkoxyallylstannanes is of interest particularly so in their reactions with imines. Further work in this area is concerned with the development of alternative traps for the intermediate allyltin trichlorides, which it is hoped will lead to proof of their stereochemistry.

Acknowledgements

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References and Notes

1. Carey, J. S.; Thomas, E. J. *Synlett*, **1992**, 585.
2. Carey, J. S.; Coulter, T. S.; Thomas, E. J. *Tetrahedron Lett.*, **1993**, *34*, 3933.
3. McNeill, A. H.; Thomas, E. J. *Synthesis*, **1994**, 207.
4. McNeill, A. H.; Thomas, E. J. *Tetrahedron Lett.*, **1990**, *31*, 6239.
5. The origin of the preference for *cis*-alkene formation in reactions between coordinated allyltin trichlorides and aldehydes is not clear, but may be due to the formation of medium ring systems as the initially formed products.[3] If the heterosubstituent is not coordinated to the tin, this constraint is no longer present.
6. Hallett, D. J.; Thomas, E. J. *J. Chem. Soc., Chem. Commun.*, **1995**, 657.
7. Hallett, D. J.; Thomas, E. J. *Tetrahedron Asymmetry*, preceding paper in this issue.
8. The structures of the products **17** and **18** were established by correlation with methyl (2*R*,6*S*)- and (2*S*,6*R*)-6-acetoxy-2-acetylaminoheptanoate.[7] Full details will be published in a full paper.

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