On the mechanism of remote induction using (5-alkoxypent-2-enyl)stannanes: trapping the intermediate allyltin trihalides by phenyllithium and the X-ray crystal structure of [(2*SR*,3*RS*)-1-(4-bromobenzoyloxy)-2-methylpent-3-yl]-(triphenyl)stannane

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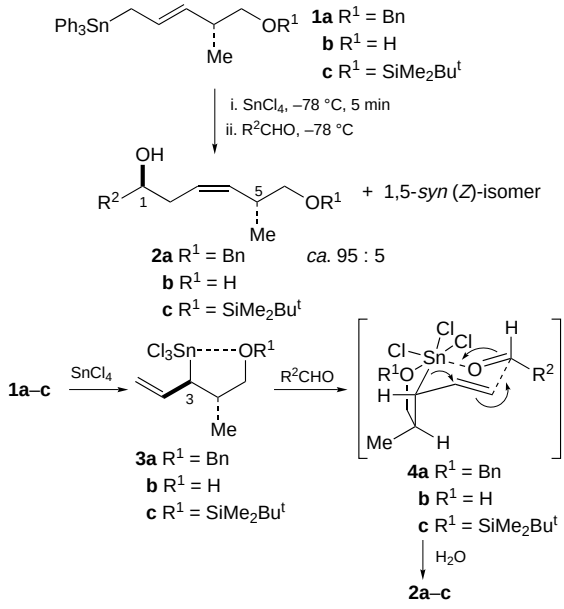
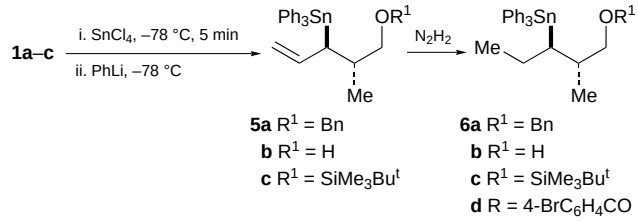
Allyltin trihalides, intermediates in tin(IV) halide promoted reactions of 5-alkoxy-4-methylpent-2-enyl(triphenyl)-stannanes with aldehydes which proceed with 1,5-induction, have been trapped by phenyllithium to give [(3*RS*,4*SR*)-5-alkoxy-4-methylpent-1-en-3-yl](triphenyl)stannanes.

Useful levels of 1,5-, 1,6- and 1,7-asymmetric induction have been found in reactions of (alkoxyalk-2-enyl)stannanes with aldehydes promoted by tin(IV) halides.[1] For example, treatment of [(4*R*)-5-benzyloxy-4-methylpent-2-enyl](triphenyl)stannane **1a** with tin(IV) chloride followed by addition of an aldehyde gives the 1,5-*anti* (*Z*)-alkenol **2a** (1,5-*anti* : 1,5-*syn* = 95 : 5) (Scheme 1).[2] To explain the stereo- and regio-selectivity of this reaction, it was suggested that transmetallation of the allylstannane **1a** is stereoselective and generates the allyltin trichloride **3a** in which the methyl and vinyl groups are *trans*-disposed about the oxastannane ring formed by coordination of the electron deficient tin by the oxygen of the benzyloxy group. This allytin trichloride then reacts with the aldehyde *via* the cyclic, chair-like transition structure **4a** in which the axial preference of the group next to tin determines the facial selectivity of the reaction with the aldehyde and introduces the double-bond into the product with (*Z*)-geometry.[1,3] Similar results were obtained using the 5-hydroxy- and 5-(*tert*-butyldimethylsilyloxy)-pent-2-enylstannanes **1b** and **1c** (1,5-*anti* : 1,5-*syn* = 80 : 20).[4] We now report evidence for the participation of allyltin trichlorides **3** in these reactions.

It was decided to attempt the conversion of the allyltin trichlorides into isolable products using a reaction which would



Scheme 1



Scheme 2

retain their C(3)–Sn bonds. It was found that addition of an excess of phenyllithium to the reaction mixture formed by treatment of the racemic pentylstannanes **1a**–**c** with tin(IV) chloride for 5 min gave the pent-2-en-3-yl(triphenyl)stannanes **5a**–**c** with excellent stereoselectivity (*ca*. 95 : 5) (Scheme 2). These allylstannanes were isolated and characterised, and reduced using diimide to give the pentan-3-ylstannanes **6a**–**c** to avoid problems associated with 1,3-migration of the tin.[5]

The structure of the (hydroxypentan-3-yl)stannane **6b** was established by an X-ray crystal structure of its 4-bromobenzoate **6d**.† Fig. 1 shows a projection of a molecule of the 4-bromobenzoate which illustrates its stereochemistry. Benzylation and silylation of **6b** gave the benzyloxy- and silyloxypentan-3-ylstannanes **6a** and **6c**, confirming their structures.

The formation of the [(3*RS*,4*SR*)-pentenyl](triphenyl)stannanes **5a**–**c** in these reactions is consistent with stereoselective formation of the allyltin trichlorides **3a**–**c**, which are trapped by phenyllithium.‡§ To probe the mechanism of transmetallation, the [(3*RS*,4*SR*)-5-benzyloxypent-2-en-3-yl]stannane **5a** was treated with tin(IV) chloride followed by the addition of an aldehyde (Scheme 3). The 1,5-*syn* diastereoisomers **7a**–**c** were the major products from these reactions if 2 min was allowed between the addition of the tin(IV) chloride and addition of the aldehyde, although the yields were modest and the stereoselectivity varied with the aldehyde. The stereoselectivity was also dependent upon the time allowed between the addition of the tin(IV) chloride and addition of the aldehyde, *e.g.* with

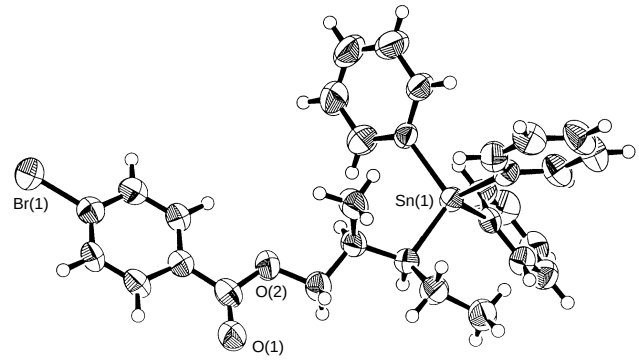
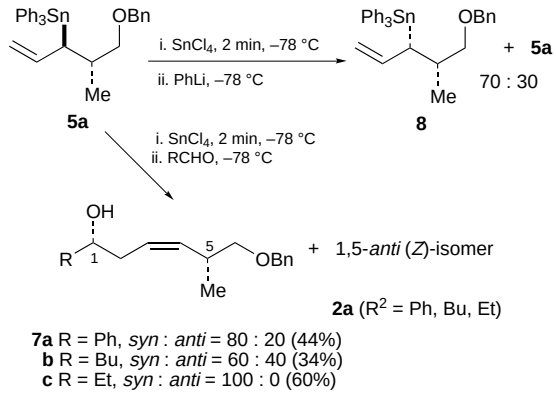


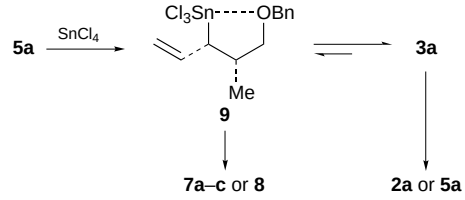
Fig. 1 Projection of a molecule of the 4-bromobenzoate **6d** as determined by X-ray crystallography



Scheme 3

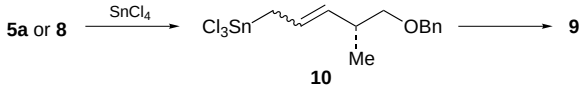
benzaldehyde the stereoselectivity of 80 : 20 in favour of the 1,5-*syn* product **7a** was reduced to 60 : 40 if 5 min was left before addition of the aldehyde, and reversed to 80 : 20 in favour of the 1,5-*anti* product **2a** (R^2 = Ph; 40%) if the mixture was left for 10 min before the addition of the aldehyde. Addition of phenyllithium to the allyltin trichloride generated by transmetallation of the 5-benzyloxypentenylstannane **5a** for 2 min gave the (3*RS*,4*RS*)-5-benzyloxypentenylstannane **8** as the major product together with its (3*RS*,4*SR*)-isomer **5a** (ratio 70 : 30).¶

It would appear that the (3*RS*,4*RS*)-allyltin trichloride **9** is the major, kinetically-formed intermediate from transmetallation of the allylstannane **5a** (Scheme 4) and leads to the formation of the 1,5-*syn* products **7a**–**c** and the (3*RS*,4*RS*)-allylstannane **8** if 2 min only is allowed before addition of the aldehyde or phenyllithium. If, however, the addition of the aldehyde or phenyllithium is delayed, equilibration of **9** to **3a** takes place, leading to increased amounts of the 1,5-*anti* products **2a**.

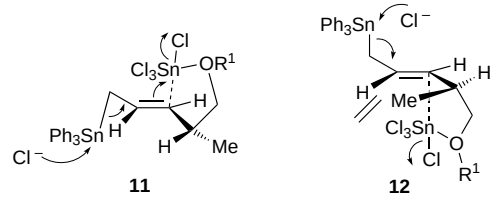


Scheme 4

The formation of the (3*RS*,4*RS*)-allyltin trichloride **9** from the allylstannane **5a** corresponds to an electrophilic substitution with inversion of configuration at the more substituted end of an allylstannane when an SE′ process might have been expected. However, treatment of the (3*RS*,4*RS*)-allylstannane **8** with tin(IV) chloride for 3 min followed by addition of benzaldehyde also gives the 1,5-*syn* alcohol **7a** as the major product (1,5-*syn* : 1,5-*anti* = 73 : 27, 60% combined yield), and trapping the intermediate allyltin trichloride with phenyllithium returns the (3*RS*,4*RS*)-allylstannane **8** together with its epimer **5a** (ratio 70 : 30). The (3*RS*,4*RS*)-allyltin trichloride **9** is therefore involved in reactions of both allylstannanes **5a** and **8**. Perhaps transmetallation of the allylstannanes **5a** and **8** proceeds *via* formation of the terminal allyltin trichloride **10** (Scheme 5), in which, for the (*Z*)-isomer, the electron deficient tin would be coordinated by the alkoxy group, followed by rapid isomerisation to the (3*RS*,4*RS*)-allyltin trichloride **9**. This is then trapped by the aldehyde or phenyllithium or isomerises to the (3*RS*,4*SR*)-allyltin trichloride **3a** on standing.



Scheme 5



Scheme 6

The high stereoselectivities in reactions of allylstannanes **1a**–**c** promoted by tin(IV) chloride would appear primarily to be due to kinetic control of the transmetallation. Perhaps the tin(IV) chloride is delivered by the oxygen of the 5-substituent to the allylstannane at C(3) with transition structure **11** being preferred over the alternative transition structure **12** (Scheme 6) because of increased steric interaction between the terminal methyl group and H(2) in **12**.

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Footnotes and References

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† *X-Ray crystal data* for **6d**: $C_{31}H_{31}BrO_2Sn$, M = 634.18, triclinic, space group $P\bar{1}$, a = 10.390(2), b = 17.643(3), c = 8.429(2) Å, α = 92.81(2), β = 113.88(1), γ = 90.83(1)°, U = 1410.2(4) Å^3 (by least-squares refinement on diffractometer angles of 25 automatically centred reflections), λ = 0.71069 Å, Z = 2, D_c = 1.493 g cm^{-3}, μ = 23.51 cm^{-1}, $F(000)$ = 636.00, colourless prism, crystal dimensions 0.2 × 0.2 × 0.25 mm. Data were collected at 293 K using a Rigaku AFC-5R diffractometer with graphite monochromated Mo-Kα radiation and a rotating anode generator. A total of 5290 reflections were measured in the ω–2θ scan mode to a $2\theta_{max}$ of 50.1°, which gave 4987 independent reflections (R_{int} = 0.024). A semi-empirical absorption correction was applied, based on the azimuthal scans of several reflections (transmission factors: 0.8958–1.00). A decay correction was also applied (3.16% decline). 3413 reflections had $I > 3\sigma(I)$. The structure was solved by Patterson methods using DIRDIF92 PATTY (ref. 6) and refined using full-matrix least-squares refinement using TEXSAN (ref. 7). All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in calculated positions. Refinement of the 316 variables converged with R = 0.040, R_w = 0.038 based on the 3413 reflections with $I > 3\sigma(I)$ and where $w = 1/[\sigma^2|F_o| + 0.00005|F_o|^2]$. Max/min peaks in the final difference map: 0.70/−0.38 eA^{-3}. CCDC 182/557.

‡ [(4*R*)-5-Benzyloxy-4-methylpent-2-enyl](tributyl)stannane also gave the triphenylstannane **5a** after transmetallation by tin(IV) chloride and addition of phenyllithium, so confirming that the phenyl substituents in **5a** are derived from the phenyllithium and not from the starting material **1a**. Trapping the allyltin trichloride **3a** with methyllithium also gave the trimethylstannyl analogue of **5a** (40%).

§ An alternative explanation would be that a mixture of rapidly equilibrating isomeric allyltin trichlorides is present after transmetallation of the pentenylstannanes **1a**–**c** but that the (2*SR*,3*RS*)-isomers are the most reactive. However this explanation is inconsistent with the formation of different products from the allyltin trichlorides **3a** and **9**.

¶ The isolation of both of the triphenylpentenylstannanes **5a** and **8** during this work meant that we knew we were able to distinguish them.

1 E. J. Thomas, *Chem. Commun.*, 1997, 411.
2 J. S. Carey and E. J. Thomas, *Synlett*, 1992, 585.
3 A. H. McNeill and E. J. Thomas, *Tetrahedron Lett.*, 1990, **31**, 6239; V. J. Jephcote, A. J. Pratt and E. J. Thomas, *J. Chem. Soc., Perkin Trans. 1*, 1989, 1521.
4 J. S. Carey, T. S. Coulter and E. J. Thomas, *Tetrahedron Lett.*, 1993, **34**, 3933.
5 V. J. Jephcote and E. J. Thomas, *J. Chem. Soc., Perkin Trans. 1*, 1991, 429.
6 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, The DIRDIF Program System, 1992, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.
7 TEXSAN: Crystal Structure Analysis Package, Molecular Structure Corporation, 1985 and 1992.

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