

On the origin of 1,5-induction in tin(IV) halide-promoted reactions of 4-alkoxyalk-2-enylstannanes with aldehydes

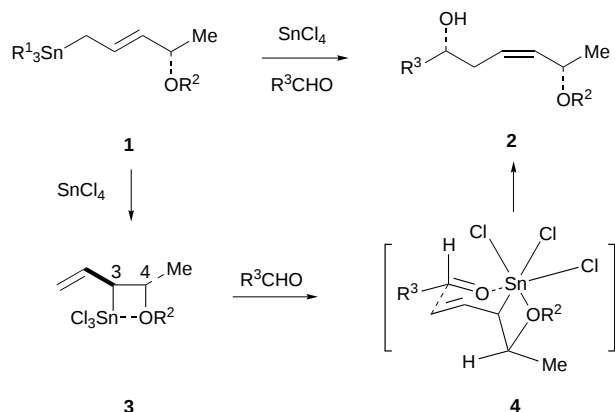
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A combination of experiment and theory has identified both the allyltin trichlorides **3** ($R^2 = \text{Bn}, \text{H}$) as key intermediates in tin(IV) chloride-promoted reactions of allylstannanes **1** ($R^2 = \text{Bn}, \text{H}$) and the transition structures that are involved in their reactions with aldehydes.

Useful levels of 1,5-, 1,6- and 1,7-asymmetric induction are obtained in tin(IV) halide-promoted reactions of 4-, 5- and 6-alkoxyalk-2-enylstannanes and aldehydes.¹ For example, tin(IV) chloride-promoted reactions between aldehydes and the (4-benzyloxypent-2-enyl)stannane **1** ($R^2 = \text{Bn}$) (Scheme 1) give the 1,5-*syn*(*Z*)-alkenols **2** with excellent stereoselectivity (*syn*:*anti* ≥ 97 :3).² Similar results are obtained using the 4-hydroxypent-2-enylstannane **1** ($R^2 = \text{H}$).³

This stereoselectivity is consistent with generation of the allyltin trichlorides **3**, which react with the aldehydes *via* the chair-like transition structures **4**.² However, alternative explanations are possible, notwithstanding the results from trapping the allyltin trichlorides generated from the 5-alkoxyalk-2-enylstannanes **5**.^{4,5} For example, participation of the C(3)-epimers of the allyltin trichlorides **3** and boat-like transition structures for the reactions with aldehydes, would account for the overall 1,5-*syn* (*Z*)-stereoselectivity. We now report confirmation of the involvement of the allyltin trichlorides **3** in these reactions, together with high level modelling of the transition structure **4**.

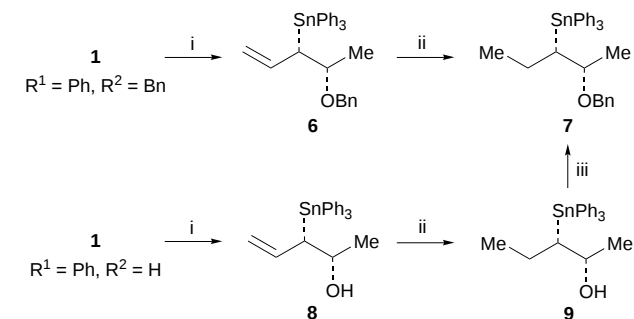


Scheme 1

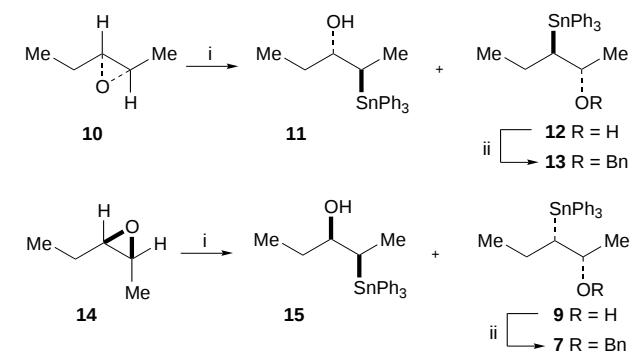
Tin(IV) chloride was added to a solution of the 4-benzyloxypent-2-enylstannane **1** ($R^2 = \text{Bn}$) at -78°C followed by an excess of PhLi . From this mixture the *syn*-4-benzyloxypent-1-en-3-yl(triphenyl)stannane **6**, containing less than 5% of its *anti* diastereoisomer, was isolated (see Scheme 2.) To avoid 1,3-migration of the triphenyltin moiety,⁶ the alkenylstannane **6** was reduced using diimide to give (2*S*,3*S*)-2-benzyloxypent-3-yl(triphenyl)stannane **7**. The same sequence of reactions

starting with the 4-hydroxypent-2-enylstannane **1** ($R^2 = \text{H}$) gave the 3-triphenylstannylpentan-2-ol **9** which was benzylated to give the *syn*-benzyl ether **7**.

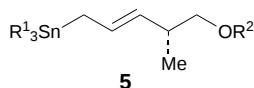
The hydroxyalkylstannane **9** could not be converted into a crystalline material suitable for X-ray diffraction and so its structure was confirmed by comparison with an authentic sample (see Scheme 3.) The racemic (*E*)- and (*Z*)-epoxides **10** and **14** were obtained from the corresponding alkenes using NBS and KOH .⁷ Ring-opening using triphenylstannyl lithium then gave the regioisomeric hydroxystannanes **11/12** and **15/9** which were separated and characterised spectroscopically. The configurations of these products were assigned on the basis that analogous epoxide ring-openings are known to proceed with inversion of configuration.⁸ The *syn*-hydroxyalkylstannane **9** obtained from the *cis*-epoxide **14** was spectroscopically and chromatographically identical to that obtained from the trapping reaction of the hydroxystannane **1** ($R^2 = \text{H}$). Moreover, *O*-benzylation gave a benzyl ether which was identical to that prepared by reduction of the alkenylstannane **6**. The *anti*-hydroxyalkylstannane **12** obtained from the *trans*-epoxide **10** was distinctly different from that obtained from the trapping reaction of the hydroxystannane **1** ($R^2 = \text{H}$), and benzylation gave the *anti*-benzyloxystannane **13** which was clearly distinguishable from its *syn*-diastereoisomer **7** by ^1H and ^{13}C NMR spectroscopy.



Scheme 2 Reagents and conditions: i, SnCl_4 , -78°C , 5 min, then PhLi (**6**, 54%; **8**, 35%); ii, diimide (**7**, 68%; **9**, 69%); iii, NaH , BnBr (68%)



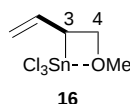
Scheme 3 Reagents and conditions: i, Ph_3SnLi (**11**, 30%; **12**, 20%; **15**, 20%; **9**, 20%); ii, NaH , BnBr (**13**, 61%; **7**, 72%)



It would appear that transmetalation of the 4-benzyloxy- and 4-hydroxy-pent-2-enylstannanes **1** ($R^2 = \text{Bn}, \text{H}$) with tin(IV) chloride gives the (3*S*,4*S*)-4-benzyloxy- and (3*S*,4*S*)-4-hydroxy-pent-1-en-3-yltin trichlorides **3** ($R^2 = \text{Bn}, \text{H}$) as originally postulated. By analogy with the transmetalation of the 5-alkoxypent-2-enylstannanes **5**,⁵ it is likely that this transmetalation is due to kinetic control. However only low yields of products were obtained on attempted transmetalation of the pent-1-en-3-ylstannane **6** using either tin(IV) chloride or bromide, and so the interconversion of regioisomeric allyltin trichlorides could not be investigated in this case.

The formation of the 1,5-*syn* (*Z*)-products from the reactions between the tin trichlorides **3** and aldehydes is consistent with participation of chair-like transition structures akin to **4**. However, why does the C(3)–C(4) bond prefer to be axial rather than equatorial, *i.e.* why are (*Z*)-alkenes obtained as the dominant products from these reactions rather than their (*E*)-isomers? To probe the factors involved in this stereoselectivity, high level electronic structure calculations have been carried out on the allyltin trichloride **16** and the transition structures for its reactions with formaldehyde which would lead to (*E*)- and (*Z*)-alkenols. A split valence basis was employed,⁹ with electron correlation included at the density functional theory level (B3LYP), using GAUSSIAN94.¹⁰ Stationary structures were identified as minima or saddle points by the calculation of harmonic frequencies.

We find two conformations of the allyltin trichloride **16**, corresponding to rotamers about the C(2)–C(3) bond, to be energy minima with Sn–O bond lengths of 2.457 and 2.531 Å. Transition states for reactions of **16** with formaldehyde leading



to both *cis*- and *trans*-double-bonded products have been located and identified as saddle points on the potential energy surfaces. These are summarised in Fig. 1.

There are considerable differences in the transition state structures and energy barriers leading to the two different stereoisomers. The transition structure leading to the *cis*-double-bonded product [Fig. 1(a)] has a considerably lower barrier (1.9 kcal mol^{−1}) and different structure, particularly about the tin atom, than the transition structure leading to the

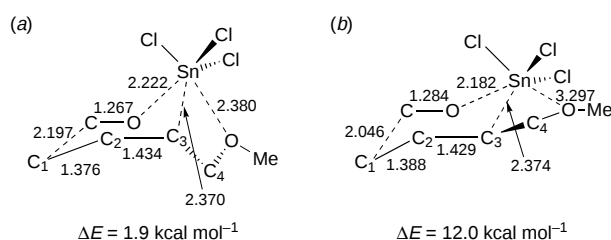


Fig. 1 Transition structures leading to (a) *cis* and (b) *trans* products. Bond lengths are in Å.

trans-isomer [Fig. 1(b)], which has a barrier of 12.0 kcal mol^{−1}. The favoured structure has a six-coordinated tin atom, with Sn–C and Sn–O bond lengths in the range 2.2–2.4 Å. The transition structure leading to the unfavoured *trans*-isomer has one of its Sn–O bond lengths considerably longer than normal (3.3 Å), so that the tin is effectively five-coordinated.

Two factors favour the transition structure shown in Fig. 1(a). Firstly, there is greater steric repulsion between the C(3)–C(4)–OMe entity and the chlorine atoms in the transition structure for formation of the unfavoured *trans*-isomer. Secondly, the different orientations of the C(3)–C(4) bond in the two transition structures leads to the long Sn–O bond in the disfavoured transition structure.

This work confirms the participation of the allyltin trichlorides **3** in tin(IV) chloride-promoted reactions of the allylstannanes **1**. The theoretical studies provide an insight into the factors which favour the formation of *cis*-alkenes in reactions of these allyltin trichlorides with aldehydes and complement recently reported computational studies into reactions between allylsilanes and aldehydes.^{11,12}

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Notes and References

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