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Remote Asymmetric Induction in Reactions of 5-Alkoxyalk-2-enylsilanes and Aldehydes Promoted by Tin(IV) Chloride

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Abstract: Following observations on remote asymmetric induction using allylstannanes, 5-benzyloxy-4-methylpent-2-enylsilanes are also found to react with aldehydes with modest levels of 1,5-induction after treatment with tin(IV) chloride. Transmetallation to give intermediate allyltin trihalides may be involved.
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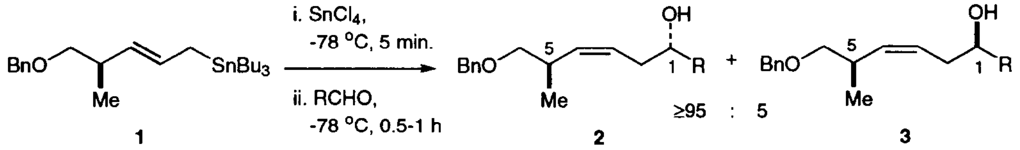
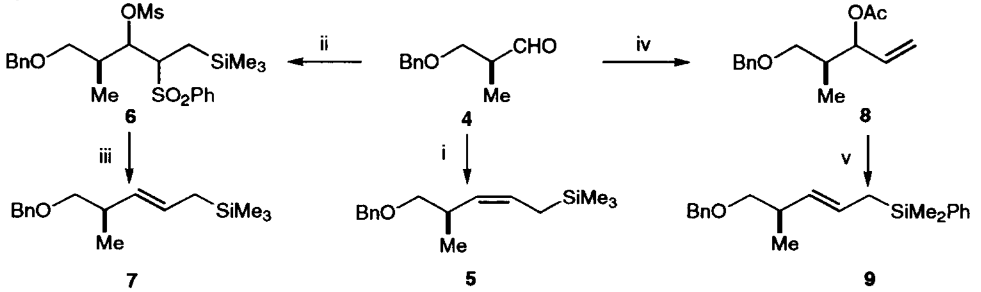
Alkoxy-substituted allylstannanes are transmetallated on treatment with tin(IV) halides to give allyltin trihalides which react with aldehydes with effective remote asymmetric induction.[1] For example, the 5-benzyloxy-4-methylpent-2-enylstannane **1** gives predominantly the 1,5-*anti*-products **2** with useful levels of stereoselectivity, **2** : **3** $\geq$ 95 : 5.[2] We now report analogous reactions of allylsilanes.[3]



The allylsilanes **5**, **7** and **9**, which are silyl analogues of the allylstannane **1**, were prepared from (*S*)-3-benzyloxy-2-methylpropanal **4** following well-established procedures for allylsilane synthesis involving a Wittig condensation, a Julia reaction, and a silyl cuprate displacement of an allyl acetate, as shown in the **Scheme**.[4-7] In each case, mixtures of (*E*)- and (*Z*)-isomers, ratio *ca.* 90(15) : 10(85), were obtained and used directly.



Scheme ***Reagents:*** i, $Ph_3P^+Me\ Br^-$, BuLi, 1 h, ICH_2SiMe_3, 1 h, BuLi then add **4** [36%: (*Z*) : (*E*) = 85 : 15]; ii, $PhSO_2CH_2CH_2SiMe_3$, BuLi, 0.5 h, then $MeSO_2Cl$; iii, disodium hydrogen phosphate, Na/Hg, MeOH [58% from **4**; (*E*) : (*Z*) = 90 : 10]; iv, $H_2C{=}CHMgCl$, tetrahydrofuran, then acetic anhydride, triethylamine (76%); v, lithium wire, $Me_2PhSiCl$, copper(I) cyanide, tetrahydrofuran [96%, (*E*) : (*Z*) = 85 : 15].

The results obtained during preliminary studies of reactions between the allylsilanes **5**, **7**, and **9** and aldehydes, promoted by tin(IV) chloride, are summarised in the **Table**. In all cases, the tin(IV) chloride was added to a solution of the allylsilane in dichloromethane at -78 °C followed by the aldehyde. The major products were identified as the 1,5-*anti*- and 1,5-*syn*-alkenols **2a-d** and **3a-d** with only minor amounts of the regioisomeric alkenols **10** being obtained.[8]

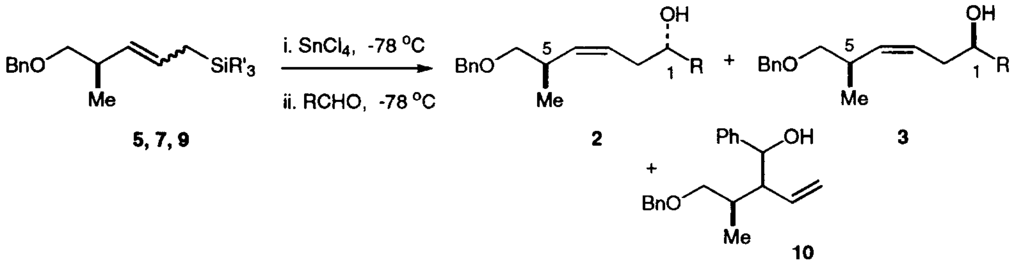


Table: Summary of Reactions of Allylsilanes 5, 7, and 9 with Aldehydes Promoted by Tin(IV) Chloride

Entry	Silane	Aldehyde R	Transmetallation Time (h)[a]	Yield (%)[b]	Products	Product Ratio **2** : **3**[c]
1	**5**	Ph	0.3	13	**2a**, **3a** (R = Ph)	77 : 23
2	"	"	1	65	"	85 : 15
3	"	"	2	67	"	86 : 14
4	"	"	5.5	72	"	69 : 31
5	**7**	"	1	64	"	72 : 28
6	"	"	2	73	"	73 : 27
7	"	*i*-Pr	"	80	**2b**, **3b** (R = *i*-Pr)	73 : 27
8	"	*p*-$O_2NC_6H_4$	"	71	**2c**, **3c** (R = Ar)[d]	82 : 18
9	"	Et	"	77	**2d**, **3d** (R = Et)	74 : 26
10	**9**	Ph	"	56	**2a**, **3a** (R = Ph)	77 : 23

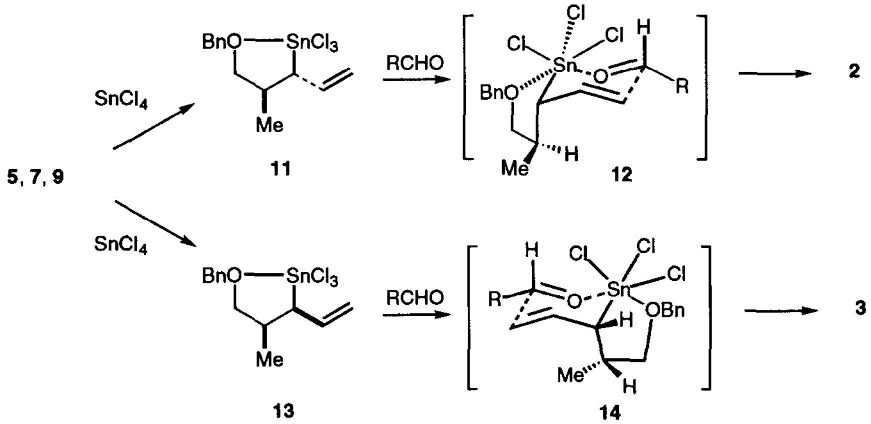
[a] The time between the additions of tin(IV) chloride and the aldehyde to the reaction. In all cases, the reaction mixture was stirred for 0.75 h at -78 °C after the addition of the aldehyde before work-up. [b] Yields of products isolated after flash chromatography. [c] Estimated by integration of the OCH_2Ph signals in the ^1H NMR spectra of the products. [d] Ar = *p*-$O_2NC_6H_4$.

During initial studies using the (*Z*)-allylsilane **5**, it was found that the yields and stereoselectivities of the reactions depended on the time allowed for the allylsilane to react with the tin(IV) chloride before the addition of the aldehyde. When benzaldehyde was added to the reaction mixture 20 min after the tin(IV) chloride, only a low yield (13%) of the 1,5-*anti*- and *syn*-products **2a** and **3a** was obtained, entry 1. However, when the allylsilane was allowed to react with the tin(IV) chloride for 1 - 2 h before addition of the aldehyde, both the yields and stereoselectivity increased, **2a** : **3a** ~ 85-86 : 15-14 (65-67%), entries 2 and 3. If the addition of the aldehyde was delayed, slightly better yields were obtained, but the stereoselectivity decreased, entry, 4.

Allowing 1 - 2 h for the reaction between the allylsilane and tin(IV) chloride, the reactions of the (*E*)-allylsilane **7** and a range of aldehydes were studied, see **Table**, entries 5 - 9. Reasonable yields of the alkenols **2a-d** and **3a-d** were obtained with modest diastereoselectivity in favour of the 1,5-*anti*-products, *anti* : *syn* ~ 72-82 : 28-18. The allyl(dimethyl)phenylsilane **9** gave similar results, entry 10, showing that the size of the groups on the silicon did not have a marked effect on the stereoselectivities of the reactions.

It would appear that both the regio- and stereoselectivities observed for the tin(IV) halide promoted reactions of the allylstannane **1** with aldehydes are observed for the analogous allylsilanes **5**, **7**, and **9**. The stereoselectivity observed for the allylsilanes is less than that observed for the allylstannanes. The (*Z*)-allylsilane **5** would appear to react with benzaldehyde with slightly better stereoselectivity than its (*E*)-isomer **7**, 85-86 : 15-14 *cf.* 72-73 : 28-27 (entries 2/3 and 5/6 in the Table).

The formation of the *anti*-(*Z*)-alkenols **2** as the major products from these reactions is inconsistent with the tin(IV) chloride simply acting as a Lewis acid and promoting the reactions by co-ordination to the carbonyl oxygen of the aldehyde. This process would be expected to give rise to the formation of the regioisomeric terminal alkenols **10**, which were only observed as minor products of the reactions. However, the formation of the internal alkenols **2** and **3** as the major products can be explained by transmetallation of the allylsilane by the tin(IV) chloride to generate the allyltin trichlorides **11** and **13**.[9] These would react with the aldehyde *via* the 'chair-like' transition structures **12** and **14** to give the 1,5-*anti*-(Z)- and 1,5-*syn*-(Z)-alkenols **2** and **3**, respectively.[10] The preference for formation of (Z)-alkenes in reactions of co-ordinated allyltin trichlorides with aldehydes has been explained in terms of the stabilities of the initially formed medium-ring products.[1]



The transmetallation of the allylsilanes would appear to be less stereoselective than transmetallation of the corresponding allylstannanes. However, since the allylsilane transmetallation is a much slower process, requiring 1 - 2 h at -78 °C in comparison to the < 5 min required for transmetallation of the allylstannane, it is not clear whether the transmetallation of the allylsilane is intrinsically less stereoselective, or whether the intermediate allyltin trichlorides have time to interconvert under the conditions of their formation.[11]

Further work will be required to confirm the participation of the allyltin trichlorides **11** and **13** in these reactions. Nevertheless, the observation of remote asymmetric induction in reactions of allylsilanes and aldehydes is of interest and may be of use in synthesis since the allylsilanes are more accessible than the corresponding allylstannanes and their use avoids the problems associated in separating products from organotin residues.[12]

Acknowledgements

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7. **5**; (Found: M^+, 262.1759. $C_{16}H_{26}OSi$ requires *M*, 262.1753) δ_H ($CDCl_3$) 0.06 [9 H, s, $Si(CH_3)_3$], 1.06 (3 H, d, *J* 7, 4-CH_3), 1.56 (2 H, m, 1-H_2), 2.79 (1 H, m, 4-H), 3.27 (1 H, t, *J* 8, 5-H), 3.39 (1 H, dd, *J* 6, 9, 5-H'), 4.56 and 4.57 (each 1 H, d, J 12, HC*H*Ph), 5.13 (1 H, dd, *J* 10, 11, 3-H), 5.46 (1 H, m, 2-H), and 7.39 (5 H, m, aromatic H); δC -1.76, 17.96, 18.70, 32.04, 72.95, 75.26, 126.01, 127.44, 127.54, 128.33, 128.96, 138.81; *m/z* (CI) 280 (M^+ + 18, 12%), 263 (M^+ + 1, 50), and 262 (M^+ + 15).
   7; (Found: M^+ + H, 263.1831. $C_{16}H_{27}OSi$ requires *M*, 263.1831) υ_{max} /cm^{-1} 1247, 1096, 857, 845; δ_H ($CDCl_3$) 0.03 [9 H, s, $Si(CH_3)_3$], 1.06 (3 H, d, *J* 7, 4-CH_3), 1.47 (2 H, d, *J* 8, 1-H_2), 2.50 (1 H, m, 4-H), 3.29 (1 H, dd, *J* 7, 9, 5-H), 3.40 (1 H, dd, *J* 6, 9, 5-H'), 4.56 (2 H, s, CH_2Ph), 5.24 (1 H, dd, *J* 7, 15, 3-H), 5.50 (1 H, m, 2-H), and 7.38 (5 H, m, aromatic H); δC -1.99, 17.74, 22.78, 37.19, 72.92, 75.93, 126.10, 127.42, 127.57, 128.32, 131.29, 138.80; m/z (CI) 280 (M^+ + 18, 52%) and 263 (M^+ + 1, 100).
   9; (Found: M^+ + H, 325.1984. $C_{21}H_{29}OSi$ requires *M*, 325.1988) υ_{max} /cm^{-1} 1247, 1113, 831; δ_H ($CDCl_3$) 0.35 [6 H, s, $Si(CH_3)_2$], 1.07 (3 H, d, *J* 7, 4-CH_3), 1.75 (2 H, d, *J* 8, 1-H_2), 2.51 (1 H, m, 4-H), 3.29 and 3.40 (each 1 H, dd, *J* 6.5, 9, 5-H), 4.58 (2 H, s, CH_2Ph), 5.28 (1 H, dd, *J* 7, 15, 3-H), 5.53 (1 H, m, 2-H), and 7.49 (10 H, m, aromatic H): *m/z* (CI) 342 (M^+ + 18, 100%) and 325 (M^+ + 1, 28).
8. The alkenols **2** were identified by comparison with samples prepared using the allylstannane chemistry.[1,2] The major product **2a** was converted into **3a** by a Mitsunbobu procedure (*p*-nitrobenzoic acid, triphenylphosphine, diethyl azodicarboxylate, then saponification using methanolic aqueous sodium hydroxide; 80% of **3a** from **2a**).
9. The transmetallation of an unsymmetric allylsilane by tin(IV) chloride to generate an allyltin trichloride has been proposed to explain the regioselectivity of its reaction with ethylene oxide: Andersen, N. H.; McCrae, D. A.; Grotjjahn, D. B.; Gabbe, S. Y.; Theodore, L. J.; Ippolito, R. M.; Sarkar, T. K. *Tetrahedron*, **1981**, *37*, 4069-4079.
10. The intermediate **11** from the reactions of the allylstannane **1** has been intercepted by phenyl lithium to give the corresponding isolable triphenylallylstannane whose structure was established by X-ray diffraction of a derivative.[11]
11. A limited amount of isomerisation of the the minor allyltin trichloride **13** into the major isomer **11** has been observed at -78 °C in dichloromethane: Hobson, L.; Thomas, E. J. unpublished observations.
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