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Addition of lactate-derived chiral allyltrichlorostannanes to chiral aldehydes

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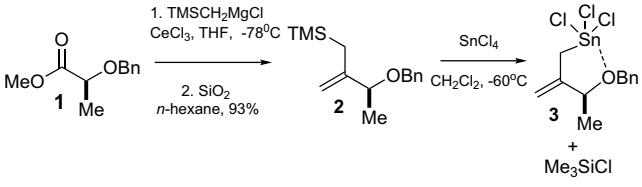
This paper is dedicated to Professor Edmundo A. Rúveda on the occasion of his 70th birthday

Abstract—Chiral lactate-derived allyltrichlorostannanes reacted with chiral α-methyl β-alkoxy and *syn* and *anti* α-methyl-β-alkoxy aldehydes to give the corresponding homoallylic alcohols with moderate to high 1,4-*syn*-diastereoselectivities.

The Lewis-acid mediated reaction of allylsilanes and allylstannanes with aldehydes is a well-known procedure for the preparation of homoallylic alcohols.[1] Because these reactions complement the aldol reactions, allylsilanes and allylstannanes are among the most important groups of organometallic-type reagents available for the control of acyclic stereochemistry.[2] The addition of enolates or analogs bearing a stereogenic center is of great importance in the application of the aldol addition to synthesis. We recently communicated that in situ prepared chiral allyltrichlorostannanes react with chiral α-methyl, chiral β-alkoxy as well as *syn* and *anti* α-methyl-β-alkoxy aldehydes to give 1,4-*syn* homoallylic alcohols that are key intermediates for the preparation of polyacetate and polypropionate-derived natural products.[3–11] We have described also that chiral and achiral allyltrichlorostannanes react with *N*-Boc-α-aminoaldehydes to give 1,2-*syn* *N*-Boc-α-aminoalcohols that are important intermediates for the preparation of hydroxyethylene dipeptide isosteres.[3–11]

We wish to describe here a divergently stereocontrolled reaction between chiral aldehydes and chiral lactate-derived allyltrichlorostannanes to give homoallylic alcohols with moderate to high diastereoselectivities.[12] In this part of the investigation, we have examined the interplay between 1,2-(Felkin–Anh),[13] 1,3- and 1,4-asymmetric induction in lactate-derived allyltrichlorostannane reactions with β-alcoxy and α-methyl-β-alkoxy aldehydes under conditions that preclude internal chelation with the aldehyde β-alkoxy substituent. This study details our efforts to understand the double stereodifferentiating stereocontrol elements involved in chiral allyltrichlorostannane additions to chiral aldehydes. Chiral allylsilane (*S*)-**2** and (*R*)-**2** were prepared from benzyl-protected methyl lactate ester **1**, both enantiomers of which are commercially available (Scheme 1).[14,15] According to previously established experimental procedures, allylsilane **2** was mixed with $SnCl_4$ before the addition of a solution of the aldehyde in order to promote the ligand exchange reaction leading to the corresponding allyltrichlorostannane **3** (Scheme 1).[5]

Aldehydes (*S*)-**4** and (*S*)-**5** were prepared in excellent yields from (3*S*)-1,3-butanediol and methyl 3-hydroxy-(2*S*)-methyl-propionate, respectively.[11] The 1,2-*syn* and 1,2-*anti* aldehydes (2*R*,3*S*)-**6** and (2*S*,3*S*)-**7** were easily prepared by using *syn*[16] and *anti*[17] selective aldol reactions, respectively, as the key steps.[11] These substrates



Scheme 1.

Keywords: Allyltrichlorostannes; Chiral allylsilanes; 1,4-Asymmetric induction.
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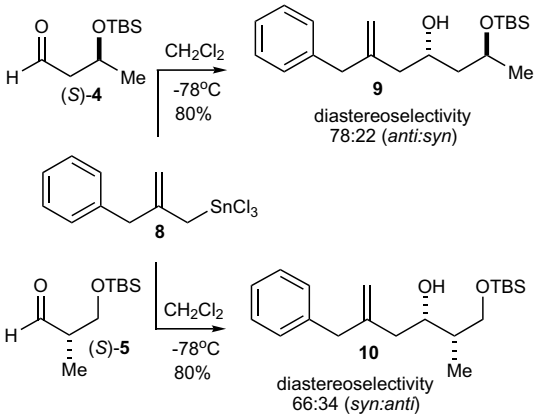
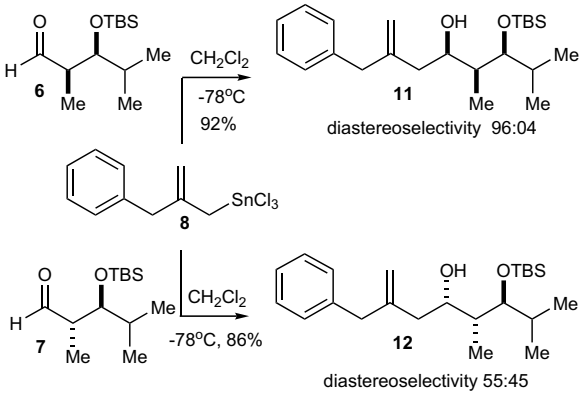
have been selected to be representative of the complex fragments that might be coupled in polyacetate and polypropionate-derived aldol-type reactions. For these aldehydes, internal chelation is presumably prevented by use of bulky silyl protecting groups since, with few exceptions, silyl ethers are generally recognized for their poor coordinating and chelating abilities.[18,19]

In order to check the facial selectivities of aldehydes **4**–**7**, we reacted them with achiral allyltrichlorostannane **8** (Schemes 2 and 3).[11] Achiral allyltrichlorostannane **8** reacted with chiral β-alkoxy aldehyde (*S*)-**4** in CH_2Cl_2 at −78 °C to give the corresponding 1,3-*anti* product **9** as the major isomer in good yield and with 78:22 diastereoselectivity (Scheme 2).[20,21] The stereoinduction observed in this reaction indicates that the intrinsic facial bias imposed by the resident β-OTBS substituent results in preferential formation of the 1,3-*anti* diastereomer, with a preference for aldehyde *Si*-face attack.

Achiral allyltrichlorostannane **8** reacted with chiral α-methyl aldehyde (*S*)-**5** in CH_2Cl_2 at −78 °C to give the corresponding 1,2-*syn* product **10** as the major product in good yield but with only 66:34 diastereoselectivity (Scheme 2).[11,21] The stereoinduction observed in this reaction indicates that the intrinsic facial bias imposed by the resident α-methyl group results in preferential formation of the 1,2-*syn* diastereomer, with a small preference for aldehyde *Si*-face attack (Felkin addition).[13]



Scheme 2.



Scheme 3.

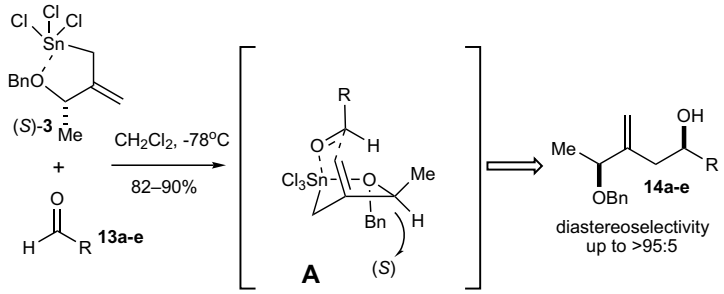
We next examined the stereochemical impact of both α and β-aldehyde substituents with chiral *syn*- and *anti*-disubstituted α-methyl-β-alkoxy aldehydes. Before starting the study described in Scheme 3, we expected that under conditions that preclude internal chelation, the carbonyl facial bias of *syn*- and *anti*-disubstituted aldehydes **6** and **7** should be highly predictable.[19] For 1,2-*anti* aldehyde **7**, we expected high levels of asymmetric induction since the factors which favor both 1,2- and 1,3-asymmetric induction mutually reinforce nucleophilic addition to this aldehyde to give the 1,2-*syn*-1,3-*anti* diastereomer.[19] However, we observed that this is not the case under the reaction conditions described here. Achiral allyltrichlorostannane **8** reacted with chiral *syn*-α,β-disubstituted aldehyde **6** to give the corresponding 1,2-*syn-1,3-syn* product **11** in 92% yield, with 96:04 diastereoselectivity (Scheme 3).[11,21] This example shows that under these conditions a 1,2-*syn* aldehyde has a preference to give the product with Felkin[13] addition as well as 1,3-*syn* addition. In the presence of an α-methyl stereocenter, 1,3-asymmetric induction imposes an intrinsic facial bias on the carbonyl that results in the formation of a 1,3-*syn*-dioxygen relationship. This is not observed when the α-methyl stereocenter is absent.

Achiral allyltrichlorostannane **8** addition to chiral *anti*-α,β-disubstituted aldehyde **7** gave the corresponding 1,2-*syn*-1,3-*anti*-product **12** as the major isomer in 86% yield, although with only 55:45 diastereoselectivity (Scheme 3).[11,21]

This example shows that *anti* aldehyde **7** has no facial preference under these conditions, since the Felkin addition to give 1,2-*syn* isomer competes with the β-alkoxy stereocenter to give the 1,3-*syn* isomer. Once again, we observed that under these allyltrichlorostannane conditions in the presence of an α-methyl stereocenter, the β-OTBS has a strong preference to give the 1,3-*syn* isomer. One might project that the transition states of these reactions exhibit less charge separation than the aldol processes, and are, accordingly, less subject to the electrostatic influence of the β-OTBS function.

In order to check the facial selectivity of allyltrichlorostannane (*S*)-**3** we reacted it with achiral aldehydes **13a**–**e** and observed the formation of 1,4-*syn* products **14a**–**e** as the major isomers (up to >95:5 diastereoselectivity) (Scheme 4 and Table 1).

The stereoselectivity of these reactions is consistent with an intermediate allyltin trichloride, which is stabilized by tin–oxygen interaction (Scheme 4). These reactions proceed through a closed, chair-like transition structure (**A**) where good information transfer from the resident stereogenic center on the allyltrichlorostannane was expected. In order to avoid steric interactions with the methyl group, the benzyl substituent at the oxygen would adopt a *trans* orientation in the five-member ring. This intermediate reacts with the aldehyde via a chair-like six-member ring transition state (**A**) in which the



Scheme 4.

Table 1. Chiral allyltrichlorostannane additions to achiral aldehydes[20]

Entry	Aldehydes (R)	ds* **14a–e**	Yield (%)
1	^{i}Pr	>95:5	82
2	Ph	>95:5	89
3	2-Furyl	>95:5	88
4	–CH=CHPh	85:15	89
5	–C(Me)=CH$_2$	84:16	90

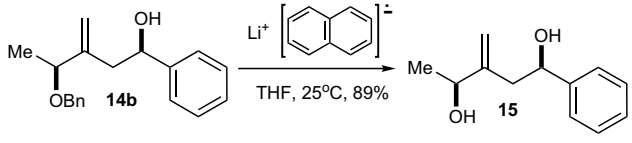
*ds=diastereoselectivity.

aldehyde approaches the complex from the side opposite to the benzyl group at the oxygen (Scheme 4). A chair-like arrangement is proposed, as it avoids steric interactions between the aldehyde substituent and the axial groups in the chair structure. The preference of the alkyl group of the aldehyde to adopt an equatorial position controls the aldehyde facial selectivity, resulting in the favored 1,4-*syn* stereochemistry in the adduct.

The 1,4-*syn* relative stereochemistry for adducts **14a–e** was confirmed, after conversion of homoallylic alcohol **14b** (R = Ph) to the corresponding 1,4-*syn*-diol **15**, by comparison of ^{1}H- and ^{13}C NMR data as well as its optical rotation with literature values (Scheme 5).[2c,22] Treatment of benzyl ether **14b** with in situ prepared lithium naphthalenide (5 equiv) in THF at rt gave the desired diol **15** in 89% yield (Scheme 5).

At this point we initiated a double stereodifferentiating study.[23] Allyltrichlorostannane (*S*)-**3** reacted with aldehyde[24] (*S*)-**4** to give 1,3-*syn*-1,4-*syn* product **16** as the major product (75:25 diastereoselectivity) (Scheme 6).

The facial bias of this chiral allyltrichlorostannane is dominated by the α-methyl stereocenter and tends to give the 1,4-*syn* isomer with *Si*-face attack, but the facial bias of this particular aldehyde is to give the 1,3-*anti* product. Apparently, this represents a 'partially *matched* case' of double stereodifferentiation.[23,24]



Scheme 5.

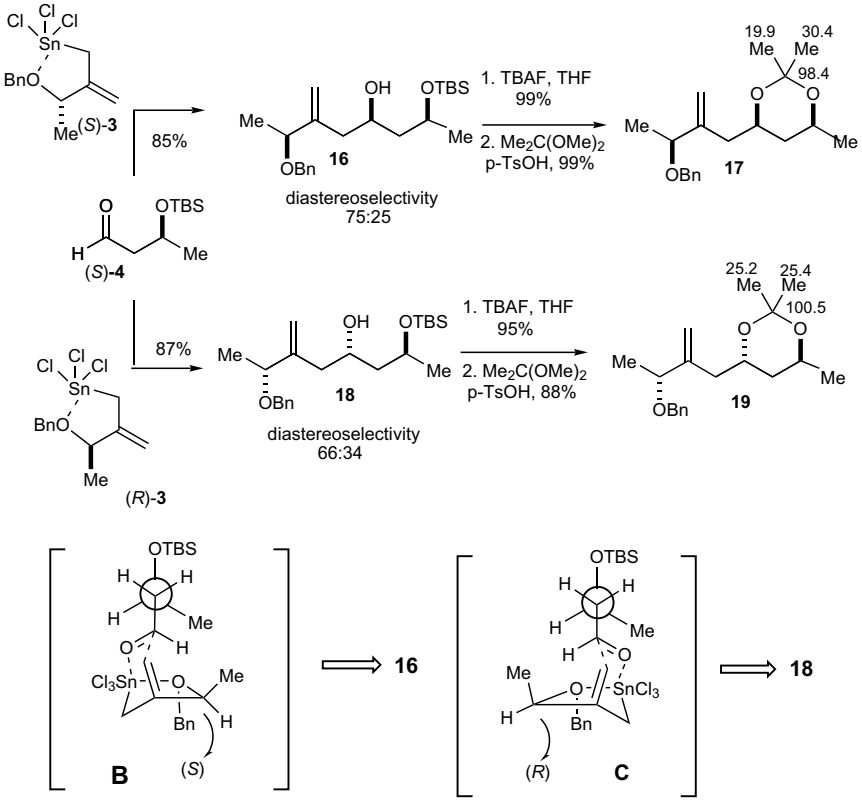
Addition of the enantiomeric allyltrichlorostannane (*R*)-**3** to aldehyde (*S*)-**4** led to a 67:34 mixture favoring the 1,4-*syn*-1,3-*anti* product **18** (Scheme 6). It is interesting to point out that as the facial bias of the aldehyde is to give the 1,3-*anti* product, we expected a *matched* case and higher levels of diastereoselectivity in the reaction of (*R*)-**3** with (*S*)-**4**. We were surprized to see that was not the case.

The stereoselectivity of these reactions can be explained by chair-like six-membered ring transition states (**B** and **C**) (Scheme 6). The relative stereochemistry for homoallylic alcohols **16** and **18** was unambiguously established on the basis of the ^{13}C NMR analysis of their respective acetonides **17** and **19** (Scheme 6).[25,26] Treatment of **16** and **18** with TBAF at rt followed by treatment of the corresponding diols under acidic conditions with 2,2-dimethoxypropane gave acetonides **17** (99%) and **19** (88%), respectively. Observed ^{13}C NMR resonances at 19.9, 30.4 and 98.4 for **17** are characteristic of a *syn*-1,3-diol-acetonide and ^{13}C NMR resonances at 25.2, 25.4 and 100.5 for **19** are consistent with an *anti*-1,3-diol-acetonide.[25]

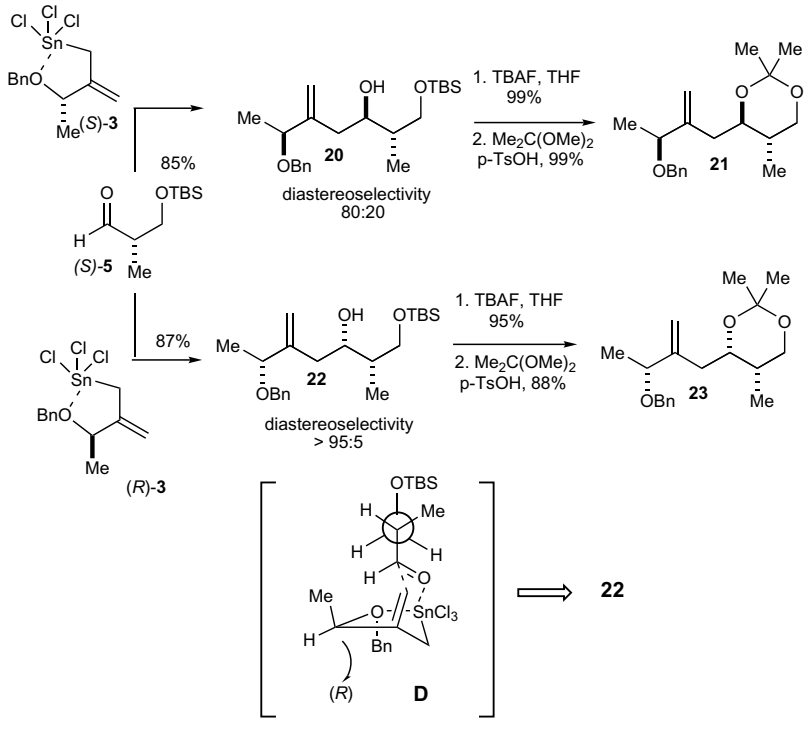
Allyltrichlorostannane (*S*)-**3** reacted with aldehyde (*S*)-**5** to give 1,2-*anti*-1,4-*syn* product **20** as the major product (80:20 diastereoselectivity) (Scheme 7). The facial bias of the chiral allyltrichlorostannane is dominated by the α-methyl stereocenter and tends to give the 1,4-*syn* isomer with *Si*-face attack. However, the facial bias of this aldehyde is to give the 1,2-*syn* product. This is another example of a partially *matched* reaction.[23]

Allyltrichlorostannane (*R*)-**3** was next employed in anticipation that its preference for forming the **22** adduct, combined with the same intrinsic preference of the substrate, would lead to high selectivity. Indeed, this was found to be the case. The reaction of chiral allyltrichlorostannane (*R*)-**3** with aldehyde (*S*)-**5** gives homoallylic alcohol **22** (all-*syn* product) as the major isomer (Felkin addition, *matched case*) (Scheme 7). The stereoselectivity of this latter reaction is consistent with a chair-like six-member-ring transition state (**D**) (Scheme 7).

We next examined the addition of allylstannanes **3** to chiral *syn*- and *anti*-disubstituted α-methyl-β-alkoxy aldehydes **6** and **7**. Allyltrichlorostannane (*S*)-**3** reacted with aldehyde **6** to give a 88:12 ratio favoring the all-*syn* isomer **24**, in a *matched case* (Scheme 8).

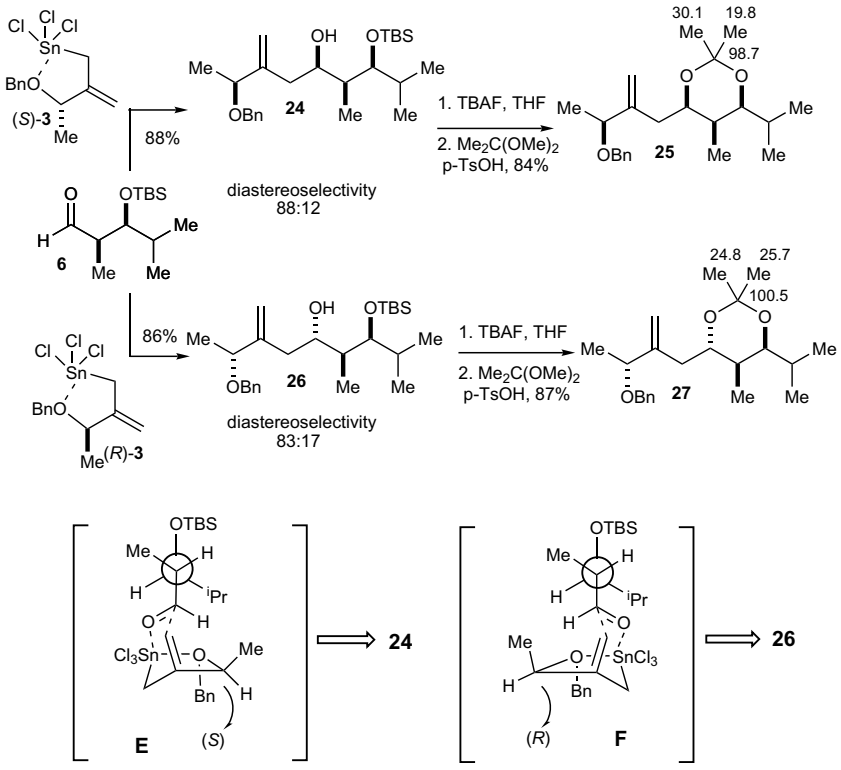


Scheme 6.



Scheme 7.

Under the same conditions described before, allyltrichlorostannane (*R*)-**3** reacted with aldehyde **6** to give isomer **26** with 83:17 diastereoselectivity (Scheme 8). In this latter case, the α-methyl stereocenter in allyltrichlorostannane (propensity for 1,4-*syn* addition) exerts a dominant influence on aldehyde facial selectivity, by



Scheme 8.

overriding the intrinsic bias imposed by the α and β-stereocenters in the aldehyde, to give the 1,2-*syn*-1,3-*syn* product. Although *matched* and *mismatched* cases were again observed, the selectivity in the *matched* case was somewhat disappointing, given the high selectivity observed in the reaction of aldehyde **6** with allyltrichlorostannane **8** (Scheme 3).

The stereochemical assignment of compounds **24** and **26** was determined by ^{13}C NMR analysis of acetonides **25** and **27**, respectively (Scheme 8). ^{13}C NMR resonances at 19.8, 30.1, and 98.7 for **25** are characteristic of a *syn*-1,3-diol-acetonide and the ^{13}C NMR resonances at 24.8, 25.7, and 100.5, observed for **27**, are consistent with an *anti*-1,3-diol-acetonide.[25,26]

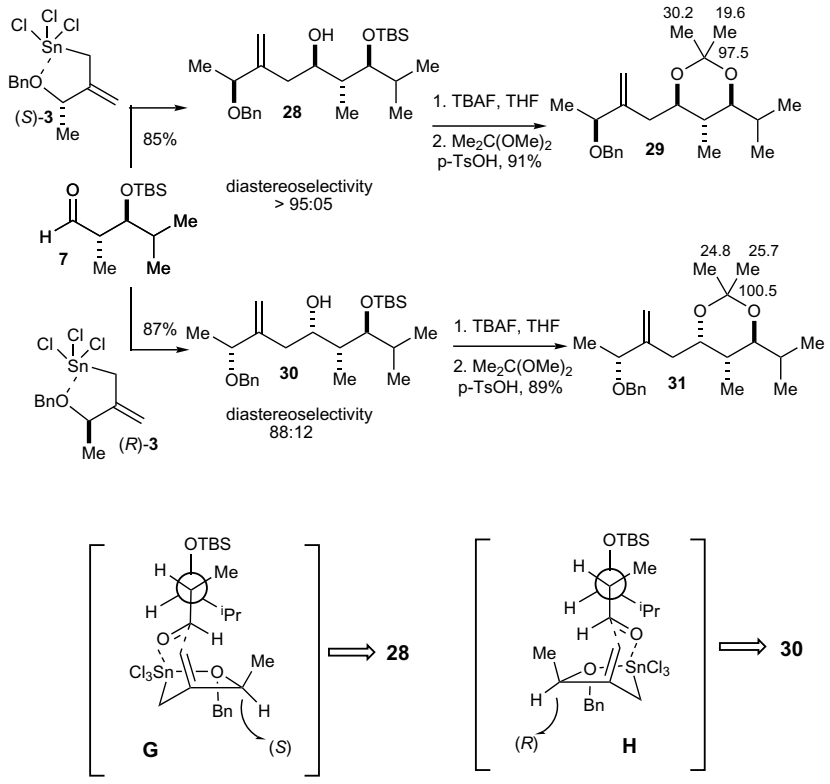
The reaction of allyltrichlorostannane (*S*)-**3** with aldehyde **7** gave homoallylic alcohol **28** as the major isomer in >95:5 diastereoselectivity (1,4-*syn*-1,3-*syn*, *anti*-Felkin addition) (Scheme 9).

The reaction of allyltrichlorostannane (*R*)-**3** with aldehyde **7** gave homoallylic alcohol **30** as the major isomer in >95:5 diastereoselectivity (1,4-*syn*-1,3-*anti*, Felkin addition, partially *matched case*) (Scheme 9).

The results described in Scheme 9 can be rationalized with dominant acyclic 1,4-asymmetric induction from the chiral allyltrichlorostannane. These are examples of partially *matched* reactions, with the chiral allyltrichlorostannanes (*S*)-**3** and (*R*)-**3** being responsible for control of the observed diastereoselectivities, through transition states analogous to **G** and **H**, respectively. This reaction with 1,2-*anti* β-OTBS aldehydes is characterized by poor levels of diastereoselectivity only when an achiral allyltrichlorostannane is used.

As before, the relative stereochemistry for compounds **28** and **30** was determined by analysis of the ^{13}C NMR of the corresponding acetonides **29** and **31** (Scheme 9). ^{13}C NMR resonances at 19.6, 30.2 and 97.5 for **29** are characteristic of a *syn*-1,3-diol-acetonide and ^{13}C NMR resonance's at 24.8, 25.7, and 100.5, observed for **31**, are characteristic of an *anti*-1,3-diol-acetonide.[25,26]

The examples presented in this work show that the levels of π-facial selection are dependent on the absolute stereochemistries of the aldehydes as well as of the allyltrichlorostannanes. The results from these experiments suggest that the stereochemical relationships between the α and β aldehyde substituents may confer either a reinforcing (*matched*) or opposing (*mismatched*) facial bias on the carbonyl moiety. In this complex scenario, the chiral allyltrichlorostannane may adopt either a reinforcing or nonreinforcing relationship. One possible reason for this result could be attributed to the involvement of energetically similar chair and twist-boat pericyclic transition states that lead to diastereomeric product formation. Another possibility to consider in these reactions is that nonbonded interactions between the allyltrichlorostannane and aldehyde α substituents may not be significant in pericyclic transition states leading to either Felkin or *anti*-Felkin addition products.[13] We believe that this chemistry is truly significant in the context of acyclic diastereoselection and will prove to be



Scheme 9.

useful in the synthesis of more complex molecules, like polyacetate and polypropionate-derived natural products.[27,28]

Acknowledgements

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20. (a) The ratios were determined by ^{1}H and ^{13}C NMR spectroscopic analysis of the purified product mixture; (b) The *syn* and *anti*-products could not be separated and were characterized as mixtures. We have been able to separate both *syn* and *anti* diols originating from most of the homoallylic alcohols and they were characterized individually; (c) All of the percentage values represent data obtained from at least three individual trials.
21. The relative stereochemistry for compounds **9**–**12** has been confirmed after conversion to the corresponding acetonides. See Ref. 11.
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26. Having confirmed the relative (*syn* or *anti*) relationship between allylstannane-derived stereogenic centers, the absolute stereochemistry of the newly formed hydroxyl substituent was determined by ascertaining its relationship to the stereocenter originating from the aldehydes, which are of known configuration.
27. All new compounds were isolated as chromatographically pure materials and exhibited acceptable ^{1}H NMR, ^{13}C NMR, IR, MS, and HRMS spectral data.
28. *General procedure for allyltrichlorostannane coupling reactions*: To a solution of 2.5 mmol of allylsilane **2** in 7 mL of dry CH_2Cl_2 at −78 °C was added 2.5 mmol of $SnCl_4$. The resulting solution was stirred at −78 °C for 30 min when 2.7 mmol of aldehyde in 2 mL of H_2Cl_2 was added. This mixture was stirred at −78 °C for 1 h and quenched by the slow addition of 0.2 mL of Et_3N, followed by 10 mL of saturated NH_4Cl solution. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2×5 mL). The combined organic layer was dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification by flash chromatography on silica gel (30% EtOAc/hexanes) gave the corresponding homoallylic alcohols.