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Stereospecificity in the Lewis Acid Promoted Allylation Reaction of 3,3-Disubstituted Allyltins toward Aldehydes

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Abstract

The Lewis acid-promoted reaction of 3,3-disubstituted allyltins toward aldehydes was found to be stereospecific; the (*E*)-reagent gave *syn*-products and the (*Z*)-one gave *anti*-products. This is in contrast to that of 3-monosubstituted congeners which are known to react *syn*-stereoselectively regardless of their double bond geometry. The reaction was assumed to proceed via an acyclic *syn*-synclinal transition state.

Keywords: allylation; diastereoselection; stereospecificity; tin and compounds

Allyltin compounds are attracting the interest of many chemists as very effective synthetic tools in view of their unique reactivity and selectivity [1]. One widely applied reaction is the Lewis acid-promoted allylation of carbonyl compounds [2]. When 3-*mono*substituted allyltins and aldehydes are employed, high *syn*-stereoselectivity is usually realized regardless of the *cis/trans*-isomerism of the tin reagents [3,4]. This is a reason why various 3-substituted allyltin reagents are often utilized in synthetic chemistry. In spite of their usefulness, their mechanistic description has not been well established. The *syn*-selectivity is most commonly explained by the acyclic antiperiplanar transition state minimizing the steric interaction between the substituents of an aldehyde (R) and an allyltin (R') (Scheme 1) [3].

On the other hand, the reactions of 3,3-*di*substituted allyltin reagents are not well investigated. One example is the reaction of geranyltin reported by Koreeda and Tanaka [5], where high *syn*-stereoselectivity was again realized. This was explained by the major contribution of the bulkier group at the 3-position of geranyltin to the above transition state to dictate the mode of the reaction [5].

Herein we describe that the Lewis acid-promoted reaction of 3,3-disubstituted allyltins actually proceeded in a stereo*specific* (not just stereoselective) manner which can be explained by the major contribution of a *syn*-synclinal transition state.

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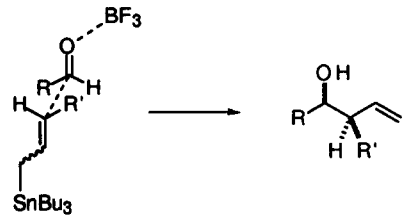
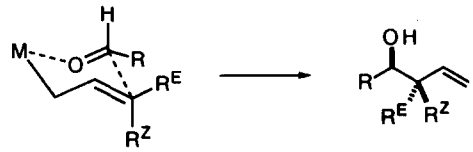


Scheme 1. Acyclic antiperiplanar transition state



Scheme 2. Chair-like six-membered cyclic transition state

Because we had previously developed a stereoselective preparation of (*E*)-3-methyl-2-pentenyltin, (*E*)-**1** [6], we first attempted its reaction toward benzaldehyde in the presence of $BF_3{\cdot}OEt_2$. The two alkyl substituents (ethyl and methyl) of the reagent **1** are similar in their steric bulk compared with the geranyltin. Therefore, the stereoselectivity was expected to be considerably lower, if the antiperiplanar transition state would be operative as reported before. To our surprise, however, the stereoselectivity was rather high as shown in Table 1. In addition, the reactions toward various other aldehydes also showed high selectivity, thus demonstrating its generality. As the major products were found to be *syn*-**2**,[1] this might be due to the fact that the steric size of the ethyl group was large enough to exceed that of the methyl group.

Accordingly, to check this possibility, the reaction of (*Z*)-**1** was also conducted under the same conditions. In contrast to the reaction above, the major product was *anti*-**2**[1] in every case as can be seen in Table 1. This means that the selectivity is not controlled by the steric bulkiness of the substituents. Moreover, it should be stressed that the present reaction showed stereospecificity unlike that of 3-monosubstituted congeners. It is also noteworthy that this specificity is opposite to that for the reaction of allylmetals which proceeds via a 6-membered cyclic transition state (Scheme 2); e.g., in the boron- [7] and the chromium [8] -mediated reactions, it has been reported that the *E*-reagent gave *anti*-products and the *Z*-reagent gave *syn*-products.

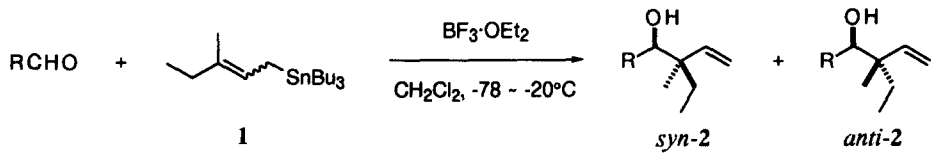
This stereospecificity is not special to the reaction of **1**. Similar stereospecificity was observed in the reactions of geranyltin, (*E*)-**3**, and neryltin, (*Z*)-**3**, [9] as well. Results are summarized in Table 2. As reported [5], geranyltin showed *syn*-selectivity with various aldehydes. On the other hand, neryltin preferentially gave *anti*-products in most cases. In the reagents **3**, the two terminal substituents are considerably different in size and yet the stereospecificity is similar to that for the reaction of **1**. Therefore, this fact further supports the assumption that the bulkier substituent does not control the stereoselectivity. Now, it is obvious that the antiperiplanar transition model can not account for the present stereospecificity.

The stereospecificity can be most rationally explained by the major contribution of a *syn*-synclinal acyclic transition state as shown by **A** in Scheme 3. In the Lewis acid-promoted reaction, it would be reasonable to assume that the tin atom can not coordinate the oxygen of the aldehyde due to the preferential BF_3-coordination; thus, acyclic transition states have been proposed. Scheme 3 shows three possible acyclic transition conformations that give the major

[1] The notation of *syn*/*anti* is defined here as follows: *syn* indicates both the OH group and the prior group of R^E and R^Z are on the same side when the carbon chain derived from the aldehyde and the allyl moiety is placed in zig-zag form, and *vice versa*.

product. The steric demand of 3,3-disubstituted allyltins seems to be similar in each case. But as for the molecular orbital interaction, only *syn*-synclinal **A** allows the interaction between Sn-C and the oxygen, as pointed out earlier by Denmark [10] and recently by Keck [11]. It is not possible for other models, antiperiplanar **B** and *anti*-synclinal **C**, to obtain such an advantage.

Table 1
Stereospecific Reactions of (*E*)- and (*Z*)-1 toward Aldehydes

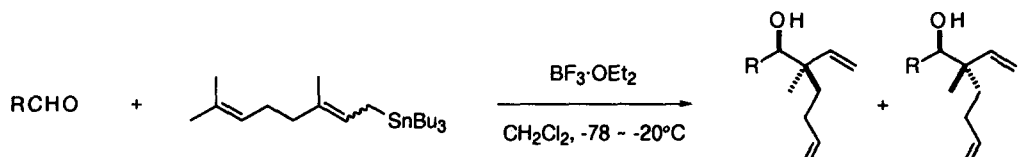


1 *syn*-2 *anti*-2

Aldehyde	Product ratio[a] *syn*-2/*anti*-2 (yield/%)	
R	from (*E*)-1[b]	from (*Z*)-1
Ph	87/13[c] (87)	20/80 (93)
PhCH=CH	83/17[d] (20)	27/73 (21)
n-C_6H_{13}	98/ 2[e] (91)	7/93 (86)
cyclo-C_6H_{11}	>99/ 1[f] (94)	5/95 (97)

[a] The isomeric ratios were determined by ^1H NMR (270 MHz) and/or ^{13}C NMR (68 MHz).
[b] The tin reagent contained 15% of (*Z*)-isomer [6]. The product ratios are corrected based on this isomeric ratio (85/15).
[c] Uncorrected ratio: 77/23. [d] Uncorrected ratio: 75/25. [e] Uncorrected ratio: 85/15. [f] Uncorrected ratio: 89/11.

Table 2
Stereospecific Reactions of (*E*)- and (*Z*)-3 toward Aldehydes

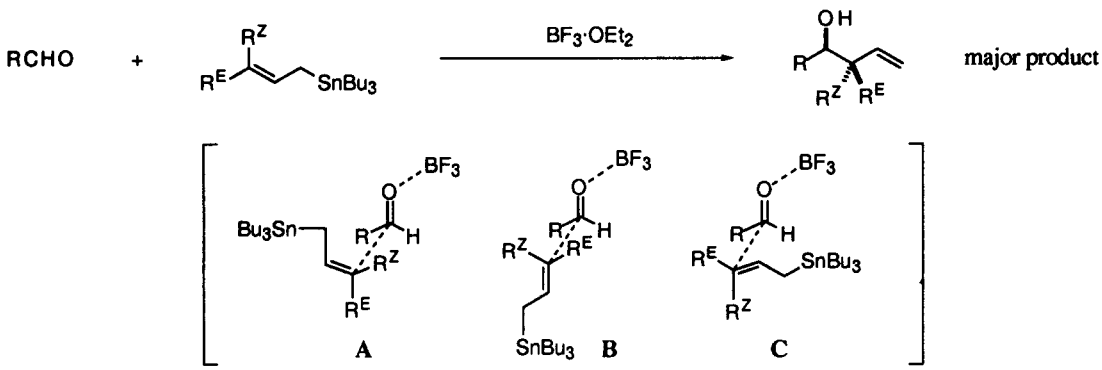


3 *syn*-4 *anti*-4

Aldehyde	Product ratio[a] *syn*-4/*anti*-4 (yield/%)	
R	from (*E*)-3 (geranyltin)	from (*Z*)-3 (neryltin)
Ph	78/22 (88)	27/73 (75)
PhCH=CH	72/28 (48)	42/58 (36)
n-C_6H_{13}	91/ 9 (82)	8/92 (75)
cyclo-C_6H_{11}	82/18 (85)	23/77 (64)

[a] The isomeric ratios were determined by ^1H NMR (270 MHz) and/or ^{13}C NMR (68 MHz).

The present stereospecific reaction shows the general and critical contribution of a synclinal open transition state toward controlling the stereoselectivity in the Lewis acid-promoted intermolecular allylstannation for the first time as far as we know, though it has been already elucidated in the intramolecular systems [10,11]. This reaction is important not only from a mechanistic viewpoint but also from a synthetic viewpoint because the stereoselectivity of the product is at an acceptable level and complementary to that attained by the usual coordinating allylic metals via the cyclic transition state. Further investigation of such allylic tin reagents and application to the reagents with other substituents, including hetero atoms, are under way.



Scheme 3. Possible acyclic transition states giving the major product

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