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Reinvestigation of the Lewis Acid-mediated Reaction of 3-Aryl-substituted Allyltin Reagents toward Aldehydes. Divergent Stereocontrol of the Product by Lewis Acids

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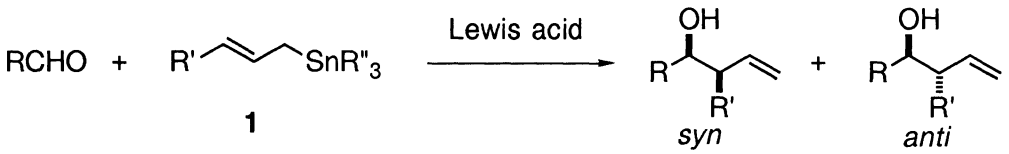
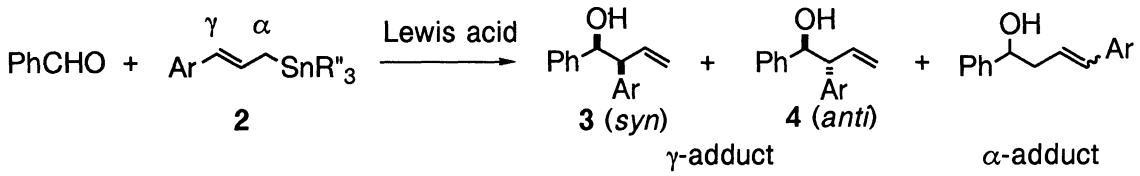
3-Arylallyltin reagents including cinnamyltin stereoselectively gave *anti*-adducts in the $ZnCl_2$-mediated reaction toward aldehydes in a donating solvent via the 6-membered cyclic transition state. In contrast, the BF_3-mediated reaction gave *syn*-adducts via the acyclic transition state. The present result corrects the previously reported stereochemical determination of the BF_3-mediated product.

3-Substituted allylic tin compounds (**1**) are synthetically important reagents for they undergo stereoselective addition reaction toward aldehydes to give the corresponding homoallyl alcohols.[1] When this reaction is promoted by a Lewis acid such as $BF_3{\cdot}OEt_2$, the *syn*-stereoselectivity is known to appear regardless of the stereochemistry of the applied allylic tin reagent via the acyclic antiperiplanar transition state.[2] However, if the 3-substituent is a phenyl group (**1** : R' = Ph, R" = Bu or Ph; cinnamyltin), the stereoselectivity has been reported to change oppositely *anti* by Koreeda and Tanaka.[3] They attributed the exceptional selectivity to the cyclic transition state caused by the increased ionic property of the C-Sn bond of cinnamyltin. Coxon *et al.* also explained it because the electron-withdrawing property of the phenyl groups on the allyl moiety and on the tin atom increased the coordinativity (Lewis acidity) of the tin atom to favor the 6-membered cyclic transition state even in the presence of a Lewis acid.[4]



In the course of our study on the reaction of allylic tin reagents in the presence of various metal salts,[5] we came interested in this fact and reinvestigated the reaction of (*E*)-cinnamyltin (**2** : Ar = Ph, R" = Bu) and aldehydes. Thus, we found that the $ZnCl_2$-mediated reaction toward benzaldehyde in ether gave the *anti*-adduct (**4** : Ar = Ph) with a good diastereoselectivity (Table 1, entry 1), judging from NMR spectroscopic data.[4,6] Strange to say, however, this product had the different stereochemistry from that of BF_3-mediated one (entry 2). This means that the BF_3-mediated reaction prefers *syn*-product, which is contrary to the previous report.[3] Thus, we tried to confirm the stereochemistry of the BF_3-mediated product by a couple of ways[7] while finding that the BF_3-mediated product indeed has *syn*-configuration as indicated by the compound **3** (Ar = Ph). In addition, the major product in the BF_3-mediated reaction toward acetaldehyde was also confirmed to have *syn*-configuration.[8] The previous stereochemical outcome[3] should be corrected.

Table 1. Lewis Acid-mediated Reactions between Benzaldehyde and 3-Arylallyltins[a)]



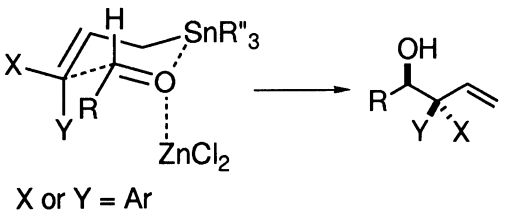
Entry	3-Arylallyltin 2	Lewis acid	Isomeric ratio of γ-adduct 3 / 4 (*syn* / *anti*)	Yield of γ-adduct %
1	Ph, $SnBu_3$	$ZnCl_2$	19 / 81	90
2		$BF_3{\cdot}OEt_2$	98 / 2	92
3	Ph, $SnMe_3$	$ZnCl_2$[b)]	9 / 91	quant
4		$BF_3{\cdot}OEt_2$	97 / 3	97
5	MeO, $SnBu_3$	$ZnCl_2$	28 / 72	59
6		$BF_3{\cdot}OEt_2$	95 / 5	55
7	α-Np, $SnBu_3$	$ZnCl_2$	21 / 79	quant
8		$BF_3{\cdot}OEt_2$	>99 / 1	quant
9	$SnBu_3$	$ZnCl_2$	81 / 19	43[c)]
10		$BF_3{\cdot}OEt_2$	50 / 50	87

a) The $ZnCl_2$-mediated reaction was carried out in ether at room temperature for 12 h with use of 3.5 mol $ZnCl_2$ per 1 mol of the aldehyde. The BF_3-mediated reaction was carried out in dichloromethane at -78 °C for 2 h with use of 2 mol of $BF_3{\cdot}OEt_2$. b) DMF was used as a solvent instead of ether. c) The α-adduct was also obtained in 53% yield.

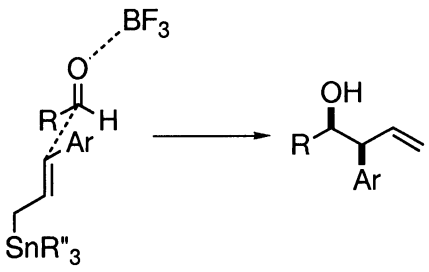
Accordingly, we investigated whether the stereoselective reaction of other (*E*)-3-aryl-substituted allyltins (2) could be controlled by the applied Lewis acid and solvent. The results of the reaction toward benzaldehyde are also collected in Table 1 as representatives. All (*E*)-allyltins attempted (Ar = 4-methoxyphenyl and α-naphthyl) showed similar divergent selectivity; $ZnCl_2$ gave *anti*-products (entries 5 and 7) with high selectivity and BF_3 gave *syn*-products (entries 6 and 8) with very high selectivity. When more polar and donating *N*,*N*-dimethylformamide (DMF) was used instead of ether as a solvent for the $ZnCl_2$-mediated reaction of cinnamyltrimethyltin, the *anti*-selectivity was much increased (entry 3). For the reaction toward an aliphatic aldehyde, similar divergent stereocontrol was also realized[9)] though acetaldehyde was an exception.[8)]

From a mechanistic viewpoint, (*Z*)-3-aryl-substituted allyltin was also investigated (entries 9 and 10). The $ZnCl_2$-mediated reaction stereoselectively produced the *syn*-γ-adduct though the regio-isomer (α-adduct) was the major product (entry 9). Comparing with the result in entry 1, it was proved that there was stereospecificity in the $ZnCl_2$-mediated reaction, which indicated that the reaction proceeded through a 6-membered cyclic transition state (Scheme 1). On the other hand, in the BF_3-mediated reaction, the stereoselectivity was much decreased

(entry 10). This feature is very similar to those observed in the reactions of (*Z*)-allylsilanes[10] and (*Z*)-allyltins,[11] where acyclic transition states[12] have been proposed. Together with the *syn*-selectivity of the (*E*)-allyltins, the BF_3-mediated reaction of 3-arylallyltins also proceeds via an acyclic transition state as shown in Scheme 2 just like those of other 3-substituted allyltins.



Scheme 1.



Scheme 2.

In conclusion, we should say that the present result includes a synthetic importance because the stereoselectivity can readily be controlled by simply changing the Lewis acid and the solvent applied. It is also noteworthy that $ZnCl_2$ as a Lewis acid can unprecedentedly promote the cyclic transition state in a donating solvent unlike a conventional Lewis acid such as BF_3.

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References

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3) M. Koreeda and Y. Tanaka, *Chem. Lett.*, **1982**, 1299.

4) J. M. Coxon, S. J. van Eyk, and P. J. Steel, *Tetrahedron Lett.*, **26**, 6121 (1985); *Tetrahedron*, **45**, 1029 (1989).

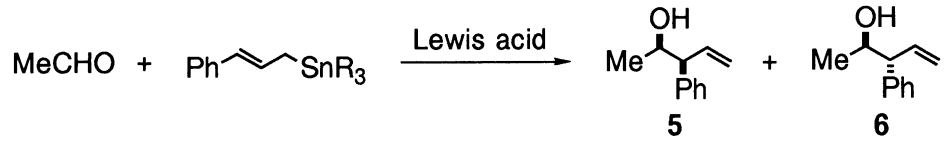
5) Y. Nishigaichi, A. Takuwa, K. Iihama, and N. Yoshida, *Chem. Lett.*, **1991**, 693; Y. Nishigaichi, N. Nakano, and A. Takuwa, *J. Chem. Soc., Perkin Trans. 1*, **1993**, 1203.

6) J. M. Coxon, G. W. Simpson, P. J. Steel, and V. C. Trenerry, *Aust. J. Chem.*, **37**, 65 (1984).

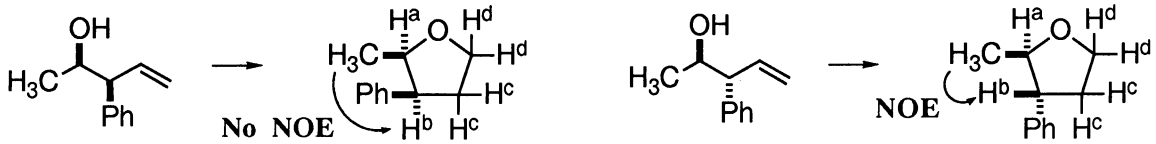
7) The BF_3-mediated product, 1,2-diphenyl-3-buten-1-ol, was identical in respect to ^1H and ^{13}C NMR spectra and to the melting point (77.5 - 79 °C) with the reported *syn*-isomer,[4] of which stereochemistry was confirmed by the X-ray analysis of its oxirane derivative.[6]

8) We also investigated the reaction between acetaldehyde and cinnamyltins. The results are shown below. The both γ-adduct **5** and **6** in BF_3- and $ZnCl_2$-mediated reactions were converted to the corresponding tetrahydrofuran derivatives **7** and **8**, respectively, following Ref. 3 (^1H NMR data of **7** and **8** are listed below). From 2D NMR experiments, an NOE was observed between Me and H^b of **8**, but not of **7**. This result appears contrary to the previous one,[3] but we found that in Ref 3, there had been confusion between H^b (δ=3.33) and H^d (δ=3.86) of **7**. Thus, the stereochemistries of **5** and **6** were lead to be *syn* and *anti*, respectively. The ring current effect of the phenyl group can explain the difference between the

chemical shifts of the methyl groups of **7** and **8**. In this respect, it is also apparent that the BF_3-mediated reaction is *syn*-selective.

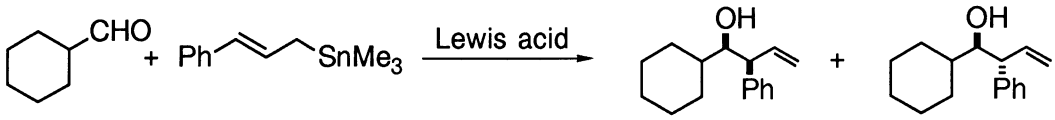


			Yield of γ-adduct
R = Ph	BF_3·OEt_2/CH_2Cl_2	99 : 1	67%
Bu		96 : 4	85%
Me	$ZnCl_2$/Et_2O	55 : 45	44%



^1H NMR ($CDCl_3$, 270 MHz) **7**: δ = 0.84 (3H, d, *J* = 6.4 Hz, Me), 2.17 (1H, dddd, *J* = 5.9, 7.6, 8.5, 13.0 Hz, H^c), 2.39 (1H, ddt, *J* = 4.4, 13.0, 8.3 Hz, H^c), 3.33 (1H, ddd, *J* = 5.9, 6.1, 8.3 Hz, H^b), 3.86 (1H, dt, *J* = 7.6, 8.6 Hz, H^d), 4.15 (1H, dq, *J* = 6.1, 6.4 Hz, H^a), 4.18 (1H, dt, *J* = 4.4, 8.8 Hz, H^d), 7.17 (2H, dd, *J* = 1.4, 6.9 Hz, Ph), 7.21-7.33 (3H, m, Ph). **8**: δ = 1.22 (3H, d, *J* = 6.1 Hz, Me), 2.09-2.21 (1H, m, H^c), 2.33-2.45 (1H, m, H^c), 2.80 (1H, q-like, *J* = 8.8, 9.0 Hz, H^b), 3.86 (1H, m, H^a), 4.02 (2H, dd, *J* = 6.0, 8.1 Hz, H^d), 7.20-7.35 (5H, m, Ph).

9) The reaction of cinnamyltrimethyltin toward cyclohexanecarbaldehyde was attempted.



		Yield of γ-adduct
BF_3·OEt_2/CH_2Cl_2	98:2	66%
$ZnCl_2$/Et_2O	8:92	55%

10) T. Hayashi, K. Kabeta, I. Hamachi, and M. Kumada, *Tetrahedron Lett.*, **24**, 2865 (1983).

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12) As a reason for the decreased selectivity in the (*Z*)-allylic reagents, contribution of synclinal transition states has been considered.[10,11]

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