Stereochemical Studies on the Addition of Allylstannanes to Aldehydes. The S_E' Component

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Summary: The disposition of the tin electrofuge in the cyclization of (*l*)-**1** and (*u*)-**1** has been established to be anti S_E' under Lewis and Bronsted acid promotion and syn S_E' under thermal conditions.

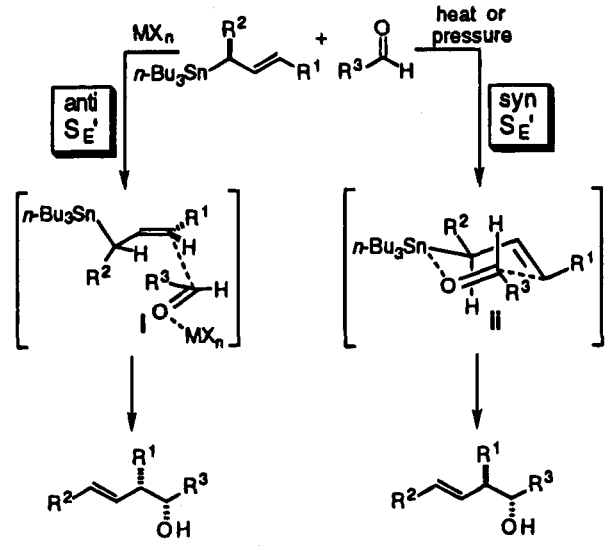
Among the modern reagents for allylation of carbonyl compounds and their derivatives, allylboranes, -silanes, and -stannanes are among the most synthetically useful.[1] Within this triumvirate, the latter two enjoy the additional advantage of potential asymmetric catalysis by the use of chiral Lewis acids.[2] For the design of new and selective protocols for the use of these reagents, a detailed understanding of the transition structures for additions to aldehydes is critical.

In the preceding paper[3] we demonstrated unambiguously that under Lewis acid catalysis, the addition of an allylsilane to an aldehyde proceeds exclusively by an anti S_E' pathway independent of Lewis acid and synclinal/antiperiplanar orientation of double bonds. For the allylation of aldehydes with allylstannanes, a similar conclusion had been reached by several authors,[4] all of whom correlate starting stannane and product alcohol configurations to reconstruct plausible transition structures (**i**, Scheme 1). Moreover, a stereochemical reversal to a syn S_E' pathway (**ii**, Scheme 1) is proposed to take place in the absence of Lewis acids under purely thermal[5] or hyperbaric[6] conditions.[7]

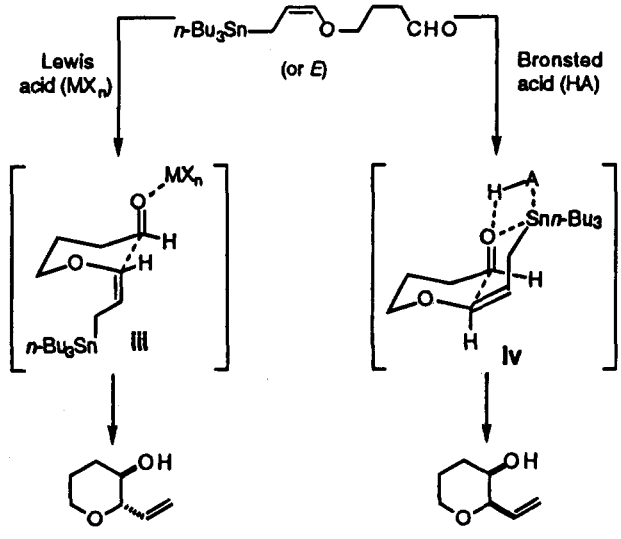
We were therefore intrigued by a recent proposal from Yamamoto[8] of a third mechanism (called a "push–pull" mechanism) operative under *Bronsted acid catalysis* wherein the acid serves to bridge the aldehyde and tin moieties (**iv**, Scheme 2). These authors found complementary stereochemical outcomes for Bronsted versus Lewis acid catalysis for both *E* and *Z* isomers of the allylstannane shown, Scheme 2.

Given the mechanistic novelty and obvious implications for asymmetric catalysis, we have tested this hypothesis with the tri-*n*-butylstannyl analog **1** of the silicon model **2**, employed in the preceding paper, Scheme 3. The divergent pathways proposed by Yamamoto for Lewis and Bronsted acid catalysis are readily distinguished by the

Scheme 1



Scheme 2



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(1) Reviews: (a) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207. (b) Yamamoto, Y. *Acc. Chem. Res.* **1987**, *20*, 243. (c) Yamamoto, Y. *Aldrichim. Acta* **1987**, *20*, 45. (d) Nishigaichi, Y.; Takuwa, A.; Naruta, Y.; Maruyama, K. *Tetrahedron* **1993**, *49*, 7395. (e) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 489. (f) Roush, W. R. In *Comprehensive Organic Synthesis, Vol. 2, Additions to C–X Bonds, Part 2*; Heathcock, C. H., Ed.; Pergamon Press: Oxford, 1991; pp 1–53. (g) Fleming, I. In *Comprehensive Organic Synthesis, Vol. 2, Additions to C–X Bonds, Part 2*; Heathcock, C. H., Ed.; Pergamon Press: Oxford, 1991; pp 563–593. (h) Fleming, I.; Dunoguès, J.; Smithers, R. *Org. React.* **1989**, *37*, 57. (i) Marshall, J. A. *Chemtracts* **1992**, *5*, 75.

(2) (a) Costa, A. L.; Piazza, M. G.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. *J. Am. Chem. Soc.* **1993**, *115*, 7001. (b) Keck, G. E.; Tarbet, K. H.; Geraci, L. S. *J. Am. Chem. Soc.* **1993**, *115*, 8467. (c) Ishihara, K.; Mouri, M.; Gao, Q.; Maruyama, T.; Furuta, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1993**, *115*, 11490.

(3) Denmark, S. E.; Almstead, N. G., preceding paper in this issue.

(4) (a) Marshall, J. A.; Crooks, S. L.; DeHoff, B. S. *J. Org. Chem.* **1988**, *53*, 1616. (b) Marshall, J. A.; Gung, W. Y. *Tetrahedron* **1989**, *45*, 1043. (c) Marshall, J. A.; Gung, W. Y. *Tetrahedron Lett.* **1989**, *30*, 2183. (d) Marshall, J. A.; Welmaker, G. S.; Gung, B. W. *J. Am. Chem. Soc.* **1991**, *113*, 647. (e) Young, D.; Jones, M.; Kitching, W. *Aust. J. Chem.* **1986**, *39*, 563. (f) Young, D.; Kitching, W. *Aust. J. Chem.* **1985**, *38*, 1767.

(5) (a) Servens, C.; Pereyre, M. *J. Organomet. Chem.* **1972**, *35*, C20. (b) Daudé, G.; Pereyre, M. *J. Organomet. Chem.* **1980**, *190*, 43. (c) Hull, C.; Mortlock, S. V.; Thomas, E. J. *Tetrahedron Lett.* **1987**, *28*, 5343. (d) Pratt, A. J.; Thomas, E. J. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1521. (e) Jephcote, V. J.; Pratt, A. J.; Thomas, E. J. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1529.

(6) (a) Yamamoto, Y.; Maruyama, K.; Matsumoto, K. *J. Chem. Soc., Chem. Commun.* **1983**, 489. (b) Yamamoto, Y.; Saito, K. *J. Chem. Soc., Chem. Commun.* **1989**, 1676.

(7) For a recent review on the mechanism of allylstannane aldehyde additions see: Yamamoto, Y.; Shida, N. In *Advances in Detailed Reaction Mechanisms*; Coxon, J., Ed.; JAI Press: Greenwich, 1994; Vol. 3, pp 1–44.

(8) Gevorgyan, V.; Kadota, I.; Yamamoto, Y. *Tetrahedron Lett.* **1993**, *34*, 1313.

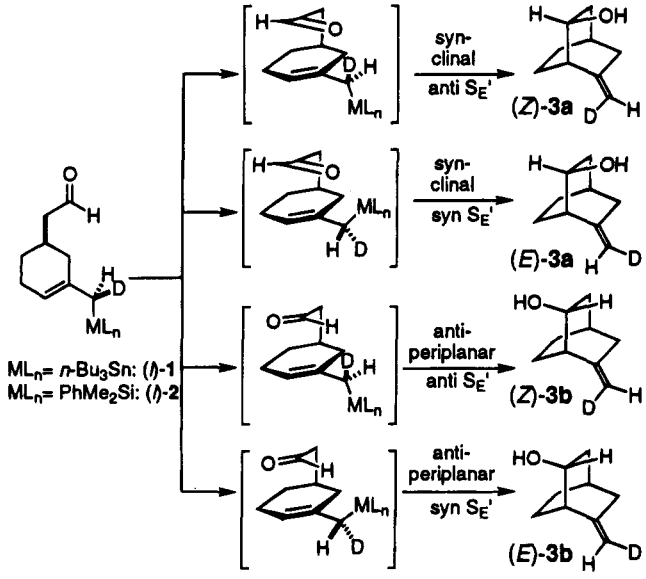
0022-3263/94/1959-5133$04.50/0

Table 1. Cyclization of Model (*l*)-1[a]

entry	reagent	T,[b] °C (time, min)	proximal/distal (**3a/3b**)[c]	(**3a**) *Z*/*E*[d]	(**3b**) *Z*/*E*[d]	proximal anti/syn S_E'[e]	distal anti/syn S_E'[e]
1	$TiCl_4$	−85 (10)	88/12	89/11	95/5	94/6	>99/1
2	$SnCl_4$	−70 (5)	94/6	86/14	95/5	91/9	>99/1
3	$SnCl_4$[f]	−70 (5)	94/6	88/12	95/5	93/7	>99/1
4	$BF_3{\cdot}OEt_2$	−70 (15)	86/14	92/8	95/5	97/3	>99/1
5	CF_3SO_3H	−70 (10)	97/3	93/7		98/2	
6	CF_3CO_2H	−70 (10)	>99/1	93/7		98/2	
7	CCl_3CO_2H	−70 (30)	99/1	93/7		98/2	
8[g]		90	>99/1	5/95		<1/99	

[a] All cyclizations (in duplicate) were performed in CH_2Cl_2 at 0.05 M with 1.05 equiv of Lewis acid. [b] Internal temperature. [c] Ratios determined by GC analysis with cyclododecane as an internal standard. Complete conversion to **3** was observed. [d] Ratios determined by ^{1}H-NMR analysis. [e] Anti/syn S_E' based on 94.5% d_1-(*l*)-**1**. [f] 5.0 equiv of $SnCl_4$ were used. [g] Reaction run in benzene at 0.05 M.

Scheme 3

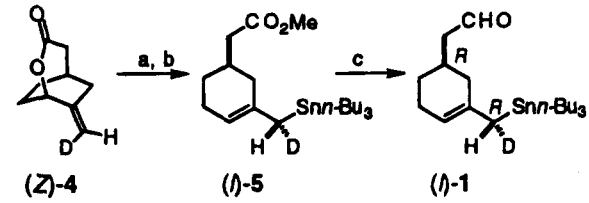


S_E' component of the addition reaction. The stereospecific placement of the deuterium label in (*l*)-**1** allows this feature to be discerned under various reaction conditions for either synclinal or antiperiplanar orientation of the double-bonded groups. Thus, under Lewis acid catalysis, we anticipate a similar outcome as was seen for (*l*)-**2** in which an anti S_E' pathway led to the formation of (*Z*)-**3a** and (*Z*)-**3b**. However, with Bronsted acids, if a push–pull mechanism were operative, the transition structure must constitute a synclinal/syn S_E' pathway leading to the formation of product (*E*)-**3a**. In this paper we disclose the syntheses of (*l*)- and (*u*)-**1** and the stereochemical course of their cyclizations under activation by Lewis acids, Bronsted acids, and heat.

The synthesis of (*l*)-**1** follows directly by modification of the previously described preparation of the unlabeled allylstannane[9] along the lines detailed for the labeled allylsilane (*l*)-**2**,[3] Scheme 4.[10] Starting with the stereospecifically labeled lactone (*Z*)-**4**,[10] the S_N2' opening[11] with a tin cuprate[12] afforded allystannane ester (*l*)-**5**[10] after diazomethane esterification. Controlled reduction of (*l*)-**5** with DIBAL-H at −78 °C afforded the model (*l*)-**1**[10,13] after purification on activity V, basic alumina at −37 °C.

The results of cyclization of (*l*)-**1** are collected in Table 1.[14] To test the hypothesis of a push–pull mechanism

Scheme 4[a]



[a] Key: (a) (*n*-$Bu_3Sn)_2CuCNLi_2$, THF, −78 °C, 30 min; (b) CH_2N_2, Et_2O–MeOH, rt, 95% (two steps); (c) DIBAL-H, toluene, −78 °C, 10 min, 95%.

we surveyed three Lewis acids ($TiCl_4$, $SnCl_4$ and $BF_3{\cdot}OEt_2$) and three Bronsted acids (TfOH, CF_3CO_2H, CCl_3CO_2H) that were shown to give divergent results in the Yamamoto system. From our studies with the unlabelled substrate, we anticipated and found rapid and highly proximal-selective cyclization. Under all conditions examined, the proximal/distal ratios were very high and within experimental error to those reported previously.[9] Moreover, as expected, with all Lewis acids examined (entries 1–3) the anti S_E' pathway is strongly preferred regardless of the internal stereochemical outcome. The lower anti S_E' preference for $SnCl_4$ was suspected to arise from partial metathesis to an allyltrichlorostannyl species[1d,9b] which might react via a closed transition state. This was discounted by the observation that the anti selectivity did not change with 5.0 equiv of $SnCl_4$ (entry 4). *Most importantly, under promotion by all three Bronsted acids (entries 5–7) the anti S_E' pathway was again observed nearly exclusively.*[15] Finally, for completeness, and as a control to eliminate the possibility of idiosyncratic bias against a syn S_E' pathway, the thermolysis of (*l*)-**1** was carried out (entry 8). As expected, the cyclization afforded exclusively (*E*)-**3a** which is indicative of a synclinal/syn S_E' pathway, the signature of a closed, cyclic transition structure.[16]

If a push–pull mechanism is not the origin of the stereochemical switch observed by Yamamoto, then this

(9) (a) Denmark, S. E.; Weber, E. J. *J. Am. Chem. Soc.* **1984**, *106*, 7970. (b) Denmark, S. E.; Weber, E. J.; Wilson, T. M.; Willson, T. M. *Tetrahedron* **1989**, *45*, 1053.

(10) Both (*u*)-**1** and (*l*)-**1** were prepared and studied, but only (*l*)-**1** is depicted. All new compounds have been fully characterized by ^{1}H NMR, ^{13}C NMR, IR, mass spectrometry, and combustion analysis (±0.3%).

(11) The stereochemical course of the S_N2' opening of the allylic lactones by tin cuprates has not been established. We assume an anti S_N2' pathway as was established for the silicon cuprates in the preceeding study.

(12) (a) Piers, E.; Morton, H. E.; Chong, J. M. *Can. J. Chem.* **1987**, *65*, 78. (b) Barbero, A.; Cuadrado, P.; Fleming, I.; Gonzàlez, A. M.; Pulido, F. J. *J. Chem. Soc., Perkin Trans. 1* **1992**, 327.

(13) The deuterium content in the model systems were determined to be 94.5% d_1-(*l*)-**1** and 92.0% d_1-(*u*)-**1** by mass spectroscopy of the final product **1** as well as by ^{1}H NMR analysis of the precursor lactone, **4**.

(14) For of the reagents studied, the reactions went to completion as judged by TLC (basic alumina) analysis. An identical set of experiments was performed on (*u*)-**1** which gave the same results; see the supplementary material. For the assignment of structure of the products and methods of stereochemical analysis see ref 3.

(15) In these cases the distal product **3b** was formed in insufficient quantities to evaluate the S_E' component.

important result warrants closer scrutiny.[17] We have previously demonstrated that allylmetal aldehyde reactions intrinsically prefer synclinal geometries (as in **i**) but that this modest preference can be offset by the bulk of the Lewis acid aldehyde complex toward an antiperiplanar geometry (as in **iii**).[18] We suggest that the size difference between a protonated and complexed aldehyde is at the root of the observed stereochemical change.

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Supplementary Material Available: Full characterization of (*l*)-**1**, (*u*)-**1**, (*l*)-**5**, and (*u*)-**5**, a general procedure for reaction of **1**, and a table of the results with (*u*)-**1** (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(16) Yamamoto has also carried out thermal cyclization in a related system: Yamamoto, Y.; Yamada, J.; Kadota, I. *Tetrahedron Lett.* **1991**, *32*, 7069.

(17) Since the Yamamoto system is an acyclic enol ether, rigorously this compound could be deuterium labeled and the stereochemical course established. However, the results of the thermal reaction clearly show **1** has no bias against a closed transition structure.

(18) Denmark, S. E.; Henke, B. R.; Weber, E. J. *J. Am. Chem. Soc.* **1987**, *109*, 2512.