Tetrahedron Vol. 45, No. 4, pp. 1053 to 1065, 1989
Printed in Great Britain.

0040-4020/89 $3.00+.00

STEREOCHEMICAL AND SPECTROSCOPIC STUDIES ON THE REACTION OF ALLYLSTANNANES WITH ALDEHYDES

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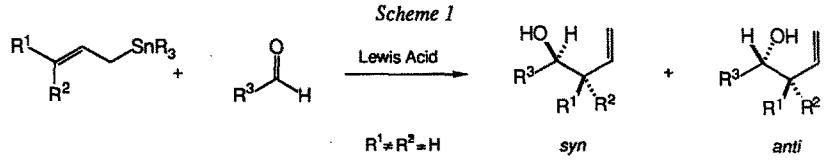
(*Received in Japan* 12 *December* 1988)

Abstract. - The orientational preference for the reacting double bonds in the Lewis acid-induced reaction of allylic stannanes and aldehydes has been examined. Model system **1** shows a strong and Lewis-acid independent preference for the synclinal orientation of double bonds. A possible stereoelectronic basis for this preference is discussed. A ^{13}C-NMR spectroscopic study of the reaction between crotyltrialkylstannanes (**9**) and acetaldehyde (**10**), pivaldehyde (**11**) and 4-*t*-butylbenzaldehyde (**12**) in the presence of $BF_3{\cdot}OEt_2$ and $SnCl_4$ is described. The spectroscopic study reveals that with $BF_3{\cdot}OEt_2$ only direct addition occurs while with $SnCl_4$ the pathway (addition vs. metathesis) is stoichiometry and aldehyde dependent. The mechanism of metathesis and chlorostannane isomerization is discussed.

INTRODUCTION

The ascension of organotin reagents into the domain of synthetic organic chemistry has been dramatically documented over the past decade.[1] In their central role as reagents for carbon-carbon bond construction they have demonstrated remarkable virtuosity in the myriad of reaction pathways available. Among these several stand out for their generality and utility such as 1) tin-lithium exchange,[2] 2) transition metal-catalyzed coupling,[3] and 3) radical reactions.[4] While many different organotins will engage in these processes, the *allyltin* derivatives have enjoyed widespread application due presumably to their enhanced reactivity and latent functionality. Indeed, allylation of organic substrates has been effectively carried out via tin-lithium exchange,[5a] Pd-catalyzed coupling,[5b] radical addition[5c] and even high pressure.[5d] In recent years the most popular method for allylation has been the Lewis acid-induced addition of allylstannanes to carbonyls,[6] Scheme 1.

Scheme 1



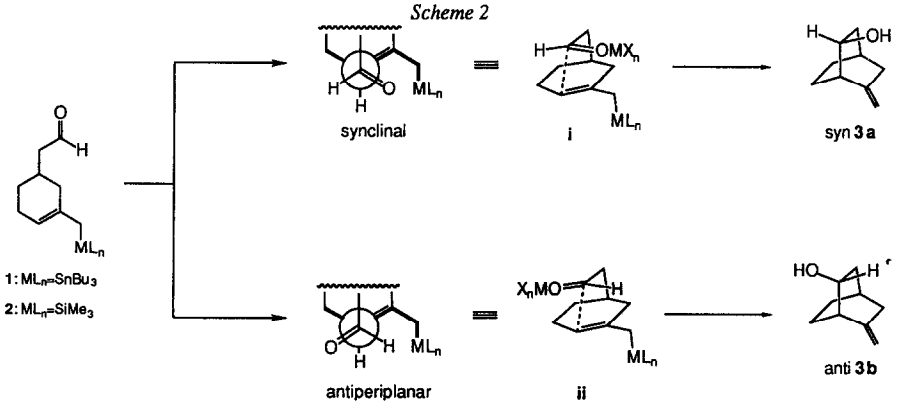
Although first demonstrated by Neumann,[7] the utility of Lewis acids as promoters of this reaction is credited to a 1978 report by Maruyama.[8] Since then there have been extensive studies on the scope of carbonyl electrophiles (aldehydes,[6] ketones,[9a] acetals,[9b] enones,[9c] acid chlorides[9d]), nature of the Lewis acid (most commonly $BF_3{\cdot}OEt_2$, $TiCl_4$, $SnCl_4$) and various aspects of regio- and stereocontrol. From the vantage of acyclic stereoselection three features of the reaction with aldehydes are noteworthy:

1) high syn[10]-diastereoselectivity with crotylstannanes independent of allyl geometry[6] (Type 2),[11]
2) significant relative diastereoselectivity[12] with α- and β-alkoxy aldehydes via chelation of the Lewis acid,[13]
3) high diastereoface selectivity with chiral, α-substituted allylstannanes in an anti S_E2' sense.[14]

Our studies on the Lewis acid-induced reaction of allylstannanes with aldehydes are focused on a fundamental understanding of the origin of the remarkable stereoselection. To glean information about transition structure in these reactions and understand the factors controlling stereochemical outcome we chose to undertake a study with two objectives:

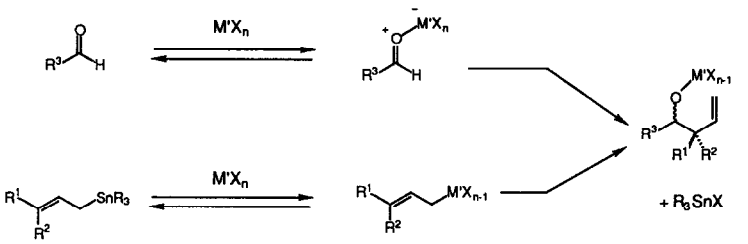
1) to elucidate any preference for specific double bond orientation in the transition state and 2) to establish the exact nature of the reactive species involved. The former objective would be addressed in a product study using the model **1**, Scheme 2. This model was designed to evaluate the relative importance of synclinal **i** and antiperiplanar **ii** transition structures by rigidly

Scheme 2



enforcing these two limiting orientations intramolecularly. In the absence of an intrinsic bias, the ratio of the epimeric products **3a/b** reflects the preference for double bond orientations. We have previously described a similar study with the related allylsilane **2**.[11a] In that case a dramatic dependence of stereochemical course on the Lewis acid was demonstrated (*syn/anti*: 99/1 ($SiCl_4$); 47/59 ($SnCl_4$). Furthermore, a later study with **2** established the stereochemical consequences of experimental variables such as concentration, stoichiometry and mode of complexation.[15] The second objective requires obtaining structural information regarding the activated aldehyde complex and the actual allylating reagent. *A priori* there are two limiting pathways available for addition as shown in Scheme 3. The upper pathway depicts Lewis acid activation of the carbonyl group followed by direct nucleophilic attack. The lower pathway involves a transmetallation of the allylstannane (metathesis) with the Lewis acid to generate a new reagent followed by addition.

Scheme 3



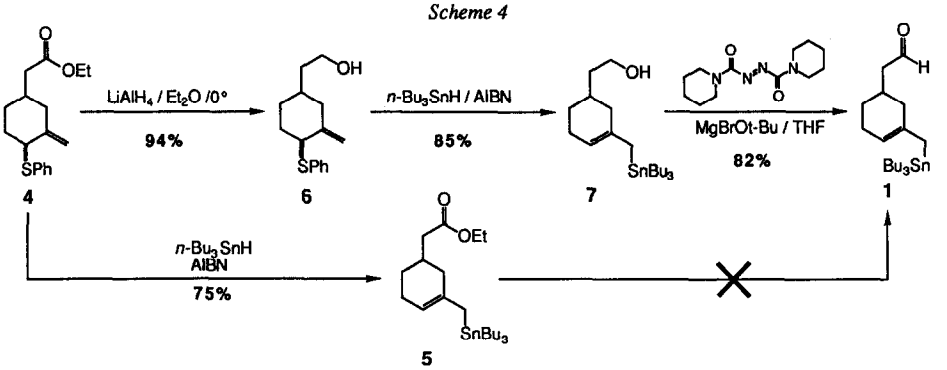
The possibility that metathetical processes are involved with allylic stannanes has been discussed by Tagliavini,[16a,c] Keck,[17] Yamamoto[18] and Maruyama.[19] Moreover, Tagliavini,[16b] Marshall[20] and Keck[17a] have demonstrated the stereochemical consequences of mixing order with various Lewis acids in reactions of crotylstannanes with aldehydes. Based on product analysis these workers suggested the possible new reagents which, formed by metathesis, are the actual nucleophiles. Our own recently reported studies[21a] provided spectroscopic evidence that metathesis does occur with *allyl*stannanes and $SnCl_4$ independent of mixing order. Herein we describe a similar spectroscopic study with *crotyl*stannanes. In addition, this paper contains a full account of the stereochemical studies with **1** which have appeared in preliminary form.[21b]

RESULTS

A. MODEL STUDY

1. *Synthesis of 1.* The preparation of the allylstannane model **1** required only minor modification of the route previously described for the synthesis of the allylsilane **2**.[11a] From the outset we anticipated that **1** would be extremely labile due to the mutual coexistence of aldehyde and allylstannane moieties. The first attempt began with advanced intermediate **4**, Scheme 4, which was obtained in five steps from 2-cyclohexenone in 57% overall yield.[11a] The allylstannane function was installed by reductive stannylation according to Ueno[22] to provide **5** with complete regioselectivity. All attempts to reduce

Scheme 4



the ester to **1** were complicated by over-reduction and destannylation. A more efficient route involved $LiAlH_4$ reduction of **4** to alcohol **6** followed by reductive stannylation to produce allylic stannane **7**. The mild conditions of that transformation obviated the need to protect the hydroxyl function. Not surprisingly, the reactivity of the stannane function and the lability of the product combined to thwart many attempts at oxidation of **7** to **1**. A successful method was ultimately found in the method of Mukaiyama[23] using 1,1'-(azodicarbonyl)dipiperidine with bromomagnesium *t*-butoxide. The basic conditions were essential to prevent protiodestannylation or cyclization. As expected **1** was extremely labile and could not withstand silica gel column chromatography, gas chromatography or distillation. The crude oxidation product was purified by filtration through Al_2O_3 (activity V, -20°C) with pentane. Repeated integration of the methylidene signal in the ^{1}H-NMR spectrum showed <2% of **3**. As much as 10% of **3** was detected by ^{1}H-NMR analysis in samples stored at -20°C for 5 days.

2. *Cyclization of 1*. Freshly prepared samples of **1** were analyzed by ^{1}H NMR and subjected to controlled cyzlization conditions. All Lewis acid-induced cyclizations were performed in CH_2Cl_2 at 0.05 M with 1.1 equiv of the reagent. The reactions were quenched by addition of 1.0 N methanolic NaOH at -70°C to suppress acid-catalyzed skeletal rearrangements. The progress of the reactions and isomer ratios of the products were established by capillary gas chromatography using decane as an internal standard since **1** did not survive the analytical method. In all reactions >85% conversion to **3a/3b** was observed. Each Lewis acid was run in duplicate or until reproducibility of ±2% in *syn/anti* ratios was observed. Ratios were calculated on the basis of independently determined response factors vs. decane. The assignment of configuration of the products **3a/3b** was established in our earlier study.[11a]

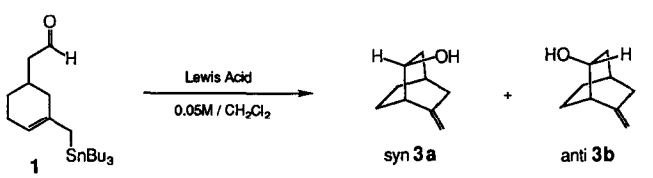


Table 1. Cyclization of **1**.[a]

reagent	time, min	temp, °C	% *syn*, **3a**[b]	% *anti*, **3b**[b]	% conversion[b]
$TiCl_4$	10	-85	82	18	84
$BF_3{\cdot}OEt_2$	15	-70	87	13	93
$AlCl_3$	10	-70	89	11	89
Et_2AlCl	5	-70	90	10	89
$ZrCl_4$	10	-70	90	10	95
$SnCl_4$	5	-70	93	7	85
$FeCl_3$	20	-70	98	2	93
CF_3COOH	10	-70	99	1	95
Δ (C_6H_6)	480	90	100[c]	0	85

[a] All reactions with Lewis acids (1.1 equiv) were performed in CH_2Cl_2 (0.05 M). At least two runs with each Lewis acid (±2%). [b] Ratios and conversions were calculated based on independently determined response factors vs. decane. [c] Only **3a** was detected in addition to 3% of a rearranged product, not **3b**.

The results of the cyclization experiments are collected in Table 1. The enhanced reactivity of **1** compared to **2** was evidenced by the greatly reduced time required for complete reaction catalyzed by CF_3CO_2H: **1**, 10 min; **2**, 720 min. All of the cyclizations were very *syn* selective and relatively insensitive to the nature of the Lewis acid (87-99% *syn*). As in the case of **2**, the $TiCl_4$-induced cyclization of **1** resulted in the formation of a secondary reaction product **A** derived from **3a**. Thus, the 82% *syn* selectivity actually corresponds to the total amount of **3a** (75%) and **A** (7%). The amount of **A** could be reduced by conducting the reaction at -85°C which then excludes it from comparison to other Lewis acids. No byproducts were observed in any other cyclization runs with Lewis acids. Interestingly, the *least* selective Lewis acid, $BF_3{\cdot}OEt_2$ is the reagent most commonly used in intermolecular reactions. The extreme *syn*-selectivity for $SiCl_4$ and CF_3CO_2H parallel the results with **2**. On the other hand, the *syn*-selective reactions with $SnCl_4$ and $FeCl_3$ are in striking contrast to the unselective cyclizations with **2** (*syn/anti* 47/53 and 68/32, respectively). It was not possible to induce reaction of **1** under nucleophilic conditions ($NaOCH_3$, $n Bu_4N^+F^-$). However, neutral thermolysis did proceed smoothly to produce exclusively **3a** along with 3% of an unidentified byproduct.

3. *Control Experiments.* The product ratios in Table 1 were shown to represent reactions under kinetic control by preparing the tri-*n*-butylstannyl ether of **3b**, **8**, and subjecting it to the reaction conditions described in Table 1. We felt it was only necessary to examine the *anti* isomer since the reactions were *syn* selective. The stannyl ether **8** was prepared by heating **3a** with $(n Bu_3Sn)_2O$,[24] followed by distillation to remove unreacted **3b**. The control experiments were performed by adding 1.05 equiv of the Lewis acid to a 0.05 M solution of **8** in CH_2Cl_2 at -70°C. The reaction mixtures were quenched with 1.0 N methanolic NaOH and the solutions were analyzed for formation of the alcohols. In all cases only the *anti* isomer **3b** was detected.

B. ^{13}C-NMR SPECTROSCOPIC STUDIES

The spectroscopic examination of reaction mixtures at low temperature required control experiments and the generation of various reference spectra. To satisfy our objectives of elucidating the nature of the reactive intermediates and clarify the origin of stereoselectivity we have investigated five reaction variables: 1) Lewis acid, 2) stoichiometry, 3) order of addition, 4) allylmetal structure and 5) aldehyde structure. For these studies two different Lewis acids, $BF_3{\cdot}OEt_2$ and $SnCl_4$, were used. In all experiments with $BF_3{\cdot}OEt_2$ we employed a 1.0:1.0:1.0 ratio of aldehyde to crotylmetal to Lewis acid. However, due to the different complexation stoichiometry of $SnCl_4$, two complete sets of experiments and control studies were conducted employing both 1.0:1.0:1.0 and 1.0:1.0:0.5 ratios of aldehyde to crotylmetal to Lewis acid. The 1-(2-butenyl)stannane ("crotyl"), **9**, utilized in these experiments was an 87:13 *E/Z* mixture obtained from the published preparation.[25] For spectroscopic simplicity the *trimethyl*stannyl moiety was selected. To identify dependence on aldehyde structure three different types of aldehyde were examined: simple aliphatic (acetaldehyde, **10**), hindered (pivaldehyde, **11**) and aromatic (4-*t*-butylbenzaldehyde, **12**).

1. *Control Experiments. Lewis Acid-Aldehyde Complexation.* 1.1. *$BF_3{\cdot}OEt_2$.* The complexation of **10-12** with $BF_3{\cdot}OEt_2$ was remarkably dependent upon the aldehyde structure, Table 2. For example, addition of $BF_3{\cdot}OEt_2$ to **10** at -80°C produced the trimer paraldehyde $(\mathbf{10})_3$ quantitatively upon mixing. The residual Et_2O remained fully complexed (69.78 and 13.12 ppm) indicating the weaker basicity of $(\mathbf{10})_3$. Warming to +20°C caused complete breakdown of the trimer to the complexed monomer $(\mathbf{10}{\cdot}BF_3)$ with a trace contamination by crotonaldehyde. The results with **11** were similar though only minor amounts of pivaldehyde trimer $(\mathbf{11})_3$ were produced. Integration of the proton signals at -80°C showed there was only about 10% trimer formation with the residual 90% of **11** remaining as uncomplexed monomer. A small quantity of uncomplexed diethyl ether (66.44 ppm and 13.72 ppm) was also seen at -80°C in the ^{13}C spectrum. Warming the solution to ambient temperature again caused the breakdown of trimer to monomer. The monomer was weakly complexed as noted by the downfield shift of the carbonyl signal from 205.88 ppm to 207.50 ppm. Aromatic aldehyde **12** did not form an oligomeric species with $BF_3{\cdot}OEt_2$. Rather, it existed at -80°C as a 1:1 mixture of free and BF_3-complexed monomers. At +20°C the complexation weakened and the signals became broadened.

1.2. *$SnCl_4$.* Reference spectra for the stable complexes of the aldehydes and $SnCl_4$ were obtained by mixing **10-12** and $SnCl_4$ in both a 1:1 and 2:1 ratio at -80°C. With a molar equivalent of $SnCl_4$ the ^{13}C-NMR spectra displayed instantaneous and quantitative complexation of the aldehyde even upon warming the probe to +20°C. The chemical shifts for **10-12** and their complexes are collected in Table 2. Most diagnostic is the downfield shift of the carbonyl carbon: **10** (17 ppm); **11** (14 ppm); **12** (6 ppm). Earlier NMR and X-ray crystallographic studies from these laboratories[15] have established the 2:1 stoichiometry of these complexes.

Table 2. Chemical shifts for aldehydes **10-12**, and their complexes.

no.	aldehyde or aldehyde complex	temp, °C	^{13}C NMR, δ								^{119}Sn NMR δ
10	CH_3CHO	+20	199.71	30.70							
		-80	201.79	31.11							
	$(CH_3CHO)_2{\cdot}SnCl_4$	+20	215.10	30.08							
		-80	218.13	30.45							-571
	$CH_3CHO{\cdot}BF_3$	+20	203.10	30.30							
	$(CH_3CHO)_3$	-80	97.93	19.95	(trimer)						
11	$(CH_3)_3CHO$	+20	205.88	42.33	23.15						
		-80	207.12	42.64	22.60						
	$[(CH_3)_3CHO]_2{\cdot}SnCl_4$	+20	218.52	43.82	23.02						
		-80	221.08	44.32	22.59						-572
	$(CH_3)_3CHO{\cdot}BF_3$	+20	207.50	42.60	23.52						
	$((CH_3)_3CHO)_3$	-80	104.40	34.47	22.60	(trimer)					
12	$(CH_3)_3CC_6H_4CHO$	+20	191.73	158.24	133.96	129.39	125.82	35.11	30.75		
		-80	192.53	158.01	132.98	129.30	125.74	34.95	30.42		
	$[(CH_3)_3CC_6H_4CHO]_2{\cdot}SnCl_4$	+20	198.77	164.19	133.19	130.25		126.72		35.72	30.34
		-80	198.84	165.26	139.20	129.19	128.75	127.22	126.51	35.85	30.11 -585
	$(CH_3)_3CC_6H_4CHO{\cdot}BF_3$	+20	195.26	165	132	131	126	35.66	30.5		
		-80	198.87	167.73	140.85	130.46	127.78	126.94	36.16	30.39	

With 0.5 equiv of $SnCl_4$ the nature of complexation was dependent upon aldehyde structure. For these purposes ^{119}Sn NMR spectroscopy proved informative.[26] The ^{119}Sn resonance for the 2:1 $(\mathbf{12})_2{\cdot}SnCl_4$ complex appeared as a single line at -585 ppm. Thus, the complex exists in solution as a single species with the same hexacoordinate geometry that was observed in the X-ray crystal structure. The 2:1 stoichiometry was confirmed by acquiring the ^{119}Sn spectrum in the absence of broadband ^{1}H decoupling. The splitting of the observed signal into a symmetrical triplet with $J_{Sn\text{-}H}$ of 65 Hz requires that two aldehydes be coordinated to the same ^{119}Sn atom.

Compared to 4-*t*-butylbenzadehyde (**12**), pivaldehyde (**11**) gave weaker complexes with $SnCl_4$. At -70°C we were able to observe both free and complexed **12** by ^{13}C NMR when less than 0.5 equiv of $SnCl_4$ were employed. However, with **11** complexation was dynamic at these temperatures. A broadening of the aldehydic carbon in the ^{13}C NMR was observed with 0.5 equiv of $SnCl_4$. With less than 0.5 equiv we were unable to observe free **11**. The weaker nature of the 2:1 complex also affected the ^{119}Sn NMR spectrum. The chemical shift at -572 ppm still corresponds to a hexacoordinate complex, but turning off the ^{1}H decoupler only led to a sharpening of the signal.

The complexes formed from acetaldehyde (**10**) with $SnCl_4$ were also of the weaker nature. In this system there arose an additional complication: mixing **10** with 0.5 equiv of $SnCl_4$ and slowly cooling the resulting solution to -70°C over ~5 min resulted in complete trimerization to paraldehyde $(\mathbf{10})_3$. We were able to partially circumvent this problem by mixing the **10** and $SnCl_4$ at r.t. and immersing the solution into a -80°C cooling bath. This technique "froze out" the $(\mathbf{10})_2{\cdot}SnCl_4$ complex, although 10-30% trimerization would often occur. The ^{119}Sn NMR spectrum showed a signal for the $(\mathbf{10})_2{\cdot}SnCl_4$ complex at -571 ppm, although no triplet was observed in the absence of ^{1}H decoupling.

2. *Control Experiments - Lewis Acid-Allylmetal.* 2.1. *$BF_3{\cdot}OEt_2$.* In an earlier publication we reported that allyltrimethylstannane undergoes $BF_3{\cdot}OEt_2$-catalyzed ligand redistribution.[21a] In the current work we found no such redistribution with 1-(2-butenyl)trimethylstannane (**9**) at -80°C, but did detect an immediate isomerization of the double bond to a 52:48 *E/Z* mixture of **9**. At -40°C however, redistribution was evidenced by the appearance of Me_4Sn. The chemical shifts for various allylmetal species are collected in Table 3.

2.2. *$SnCl_4$.* Two sets of control experiments were performed with $SnCl_4$ at different stoichiometries. As in the case of allyltrimethylstannane[21a] we observed instantaneous and quantitative metathesis of **9** with an equimolar amount of $SnCl_4$

Table 3. ^{13}C-NMR Chemical shifts of stannanes.

no.	allylmetal	temp, °C	chemical shifts in ppm				
Z-9	(Z)-$CH_3CH{=}CHCH_2SnMe_3$	+20	128.60	118.20	13.68	11.82	-10.22
		-80	128.44	117.86	[a]	11.28	-10.25
***E*-9**	(*E*)-$CH_3CH{=}CHCH_2SnMe_3$	+20	129.36	120.17	17.60	15.78	-10.63
		-80	129.11	119.63	18.03	15.32	-10.65
Z-13	(Z)-$CH_3CH{=}CHCH_2SnCl_3$	+20	131.71	118.43	31.78	13.19	
		-80	132.08	117.98	32.44	13.43	
***E*-13**	(*E*)-$CH_3CH{=}CHCH_2SnCl_3$	+20	133.64	119.22	36.37	17.91	
		-80	133.80	118.79	37.35	18.29	
14	$CH_2{=}CHCH(CH_3)SnCl_3$	-80	133.39	118.73	49.36	14.49	
15	$(CH_3)_3SnCl$	+20	-0.52				
		-80	-0.63				
16	$[CH_2{=}CHCH(CH_3)]_2SnCl_2$[b]	-80	136.50	114.50	41.50	14.49	
			136.50	114.50	41.59	14.42	
17	$[CH_3CH{=}CHCH_2]_2SnCl_2$[c]	-80	126.94	120.79	26.31	18.35	
			126.94	120.94	26.02	18.35	
			127.05	121.58	30.97	13.38	
			127.05	121.72	30.93	13.48	

[a] Not determined or obscured in the spectra by other signals. [b] Mixture of meso and chiral isomers. [c] Mixture of *E,E*, *E,Z* and *Z,Z* isomers.

at -80°C. The product composed of a 55:45 *E/Z* mixture of 1-(2-butenyl)trichlorostannane (**13**) along with a trace of the allylic isomer 3-(1-butenyl)trichlorostannane (**14**) and Me_3SnCl (**15**). The isomerization of **14** to **13** was complete at -60°C.

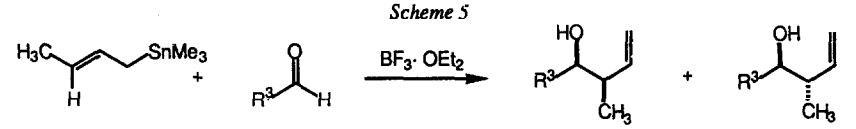
When 0.45 equiv of $SnCl_4$ were added to a solution of **9** (2:1 *E/Z*) at -80°C, most of the stannane **9** was instantly metathesized with complete allylic rearrangement to di-3-(1-butenyl)dichlorostannane **16** (both dl and meso isomers). A small amount of ***E*-9** remained unreacted. Warming the mixture to -20°C did not change the appearance of the ^{13}C NMR spectrum. The residual ***E*-9** was still present and **16** did not isomerize to the 2-butenyl isomer **17**. Adding 0.75 equiv of $SnCl_4$ to a solution of **9** (2:1 *E/Z*) at -80°C resulted in quantitative metathesis of **9** with complete allylic rearrangement to form a statistical mixture of **16** and 3-(1-butenyl)trichlorostannane **14**. After warming to -40°C half of the di-3-(1-butenyl)dichlorostannane **16** had undergone allylic rearrangement. However, **14** was stable at this temperature. After further warming to 0°C both **14** and **16** were completely rearranged. Recooling the solution to -80°C showed that **13** existed as two isomers (*E*, *Z*) and **17** existed as a mixture of all possible isomers (*E,E*, *E,Z*, *Z,Z*).

The results of the forgoing control experiments may be summarized in the following statements: 1) allylic stannanes undergo rapid metathesis with $SnCl_4$ at -80°C, 2) *Z*-2-butenylstannanes are more reactive than their *E*-isomers, 3) metathesis with $SnCl_4$ occurs with allylic inversion, 4) the metathesis products **14** and **16** are stable to allylic rearrangement at <-40°C in the absence of $SnCl_4$ and 5) the allylic isomerization appears to be an intermolecular process.

3. *Addition of 2-Butenylstannanes to Aldehydes.* 3.1. *$BF_3{\cdot}OEt_2$.* The addition of **9** (87:13 *E/Z*) to a -80°C solution containing **10** and $BF_3{\cdot}OEt_2$ showed complete formation of the acetaldehyde trimer ((**10**)$_3$) and configurational isomerization of ***E*-9** to a 1:1 *E/Z* mixture. No evidence of addition was detected. At -40°C breakdown of the trimer began and by -20°C the 2-butenylstannanes were essentially consumed to form boron ethers. Both *syn* and *anti* isomers of the homoallylic alcohols **18** were visible in the spectra, Scheme 5. No evidence of stannyl ether formation could be found. Continued warming to +20°C led to decomposition of the homoallylic products. A preparative scale reaction which had been quenched at -20°C gave an 88:12 *syn/anti* ratio of **18** by GC analysis.

The reaction of **11** in the presence of $BF_3{\cdot}OEt_2$ with **9** at -80°C was very facile. Substantial amounts of the products **19** as the boron ethers were already evident at -80°C. Continued warming to -20°C led to essentially complete consumption of isomerized **9** although **Z-9** was still present. Both *syn* and *anti* diastereomers could be seen in the spectra. The reaction appeared to be devoid of decomposition products even after 90 min at +20°C. An independent reaction quenched at +20°C yielded a 92:8, *syn/anti* ratio of diastereomeric homoallylic alcohols **19** by GC analysis.

Scheme 5



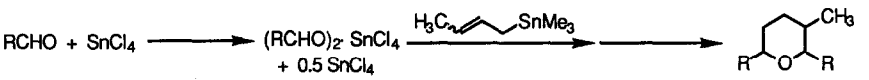
9 **10-12** *syn* **a** *anti* **b**

18: R=CH_3
19: R=*t*-Bu
20: R=4-*t*-BuC_6H_4

The reaction of precomplexed **12** with **9** at -80°C *instantaneously gave complete conversion* to boron ethers. There was no residual aldehyde or stannane. Signals for both *syn* and *anti* isomers of **20** were clearly visible in the spectrum at -40°C. Raising the temperature to 0°C had no effect on the products formed in the reaction, but continued warming to +20°C showed some decomposition. A preparative experiment quenched at 0°C gave an 86:14, *syn/anti* ratio of **20**. Furthermore, the addition of **12** to a solution of BF_3·OEt_2 and **9** (inverse order) at -80°C provided identical results (86:14, *syn/anti*), although control experiments established the ratio of (*E*/*Z*)-**9** to be 1:1.

3.2. *$SnCl_4$ (1.0 equiv).* Two separate sets of experiments were run with $SnCl_4$ using 1.0 and 0.5 equiv. In all cases the stoichiometry of aldehydes to **9** was 1.0 to 1.0. The addition of **9** to a -80°C solution of **10** precomplexed with one molar equiv of $SnCl_4$ gave *complete metathesis* of the stannane to **13**. No product was visible and **10** remained as a strongly complexed species. No reaction occurred until the mixture reached -20°C. At this temperature formation of chloropyrans **21** was evident, Scheme 6. Although this would implicate the formation of the homoallylic alcohol, none was evident in the

Scheme 6



21: R=CH_3
22: R=*t*-Bu

spectrum. Increasing the temperature of the reaction did not give rise to any of the desired product. After reaching +20°C the spectrum displayed chloropyran and the complete consumption of **13**.

The addition of **9** to **11** showed similar results in that *only metathesis* of the stannane at -80°C to **13** and 3-(1-butenyl)trichlorostannane **14** was observed. Warming the solution led to isomerization of **14** to **13** and had no other effect up to -20°C. At this temperature signals for chloropyrans **22** began to emerge. Upon further warming only a minor amount of product and chloropyran signals were visible in the spectrum. There remained significant amounts of **13** and **11** at +20°C.

The addition of **9** to precomplexed **12** at -80°C again gave *only metathesis* of the allylmetal. However, in this case the sole metathesis product was **14**, still complexed to **12**. No condensation nor formation of **13** was visible. Warming to +20°C led only to isomerization of **14** to **13**. Formation of chloropyrans or homoallylic alcohols was not evident. The aldehyde was still present at the termination of this experiment.

3.3. *$SnCl_4$ (0.5 equiv).* The preceding reactions were also performed using a 1.0:1.0:0.5 ratio of reactants, so that no free $SnCl_4$ was in solution. For these experiments we employed the layer and vortex technique[27] to ensure that adventitious warming of the solution did not occur upon mixing.

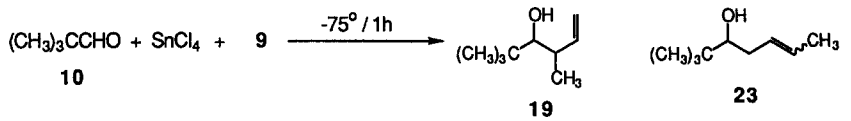
3.3.1. *Addition to Acetaldehyde (10).* Addition of 0.5 equiv of $SnCl_4$ to 1.0 equiv of **10** at r.t. followed by rapid cooling to -95°C resulted in a 1:1 mixture of complexed aldehyde (**10**)$_2$·$SnCl_4$ and paraldehyde (**10**)$_3$. To this mixture was added 1.0 equiv of **9** (2:1 *E*/*Z*) by the layer and vortex technique. The resulting ^{13}C NMR spectrum showed complete consumption of the complexed aldehyde along with a large quantity of **9** (3:1 *E*/*Z*). Some metathesis to **16** was observed and the (**10**)$_3$ remained unreacted. Upon warming to -80°C more **9** was metathesized to **16**, but no rearrangement to di-2-(1-butenyl)dichlorostannane **17** was observed. The characteristic signals for the addition products were clearly visible at -20°C.

In this system direct addition to (**10**)$_2$·$SnCl_4$ appeared to be faster than metathesis. After all the complexed aldehyde had been consumed, the remaining **9** was slowly metathesized by the [(**10**)$_3$]·$SnCl_4$ complex. Above -80°C, the stannanes added to **10** produced by the breakdown of (**10**)$_3$.

3.3.2. *Addition to Pivaldehyde (11).* The crotylstannane **9** (1.0 equiv, 2:1 *E*/*Z*) was added to a solution containing 1.0 equiv of **11** complexed to 0.49 equiv of $SnCl_4$ at -80°C by the layer and vortex technique. The resulting spectrum showed formation of Me_3SnCl **15** and consumption of most of the stannane **9**. The major metathesis product was **16** (dl and meso), the minor was **14**; both were complexed to **11**. The residual **9** was of the *E*-configuration. No addition products were observed. After warming the solution to -60°C, the remaining crotylstannane *E*-**9** was consumed and addition products

were not visible. At -40°C slow addition of the di-3-(1-butenyl)dichlorostannane **16** to the pivaldehyde without rearrangement to **17** was observed. These spectra show that metathesis occurred before direct addition to $(\mathbf{11})_2 \cdot SnCl_4$.

Two preparative experiments were run to determine the consequences of metathesis to the regiochemistry of allylation, Table 4. In separate runs using cyclododecane as an internal standard, pivaldehyde was complexed with either 0.5 equiv or 1.0 equiv of $SnCl_4$ at -75°C. To this 1.0 equiv of **9** (2:1 *E/Z*) was added and after 1 h at -75°C the reaction was quenched with 1 N NaOH/MeOH. GC analysis showed that only two products were formed. Coinjection of authentic samples showed that neither of these were the branched alcohols **19**. GC/MS revealed that they were the isomeric linear alcohols ***E,Z*-23**: their yields were estimated using the response factor for the 2-methyl-3-butenyl alcohols **19**.



10 **19** **23**

Table 4.

10, equiv	**9**, equiv	$SnCl_4$, equiv	yield, % **19** (a/b)	yield, % **23** (*E/Z*)
1.0	1.0	0.5	0	42 (25/75)
1.0	1.0	1.0	0	65 (32/68)

The spectroscopic and preparative experiments both show that a) no direct addition of **9** to the $(\mathbf{11})_2 \cdot SnCl_4$ complex occurred, b) metathesis of **9** occurred with complete allylic inversion and c) the metathesis product added to pivaldehyde with allylic inversion to yield linear alcohol **23**. It is clear from these results that *metathesis is faster than direct addition* even in the presence of excess aldehyde and the absence of uncomplexed $SnCl_4$.

3.3.3. *Addition to 4-t-Butylbenzaldehyde (12).* The crotylstannane **9** (1.0 equiv, 2:1 *E/Z*) was added to a solution of 1.0 equiv of 4-*t*-butylbenzaldehyde (**12**) and 0.49 equiv of $SnCl_4$ at -95°C by the layer and vortex technique. The resulting ^{13}C NMR spectrum showed that ***Z*-9** had been consumed but most of the *E*-isomer remained unreacted. Both metathesis to form **16** and addition to the aldehyde had occurred. Warming the solution to -80°C resulted in further addition, but no further metathesis was observed. At -60°C, slow addition to **12** was observed as both **16** and ***E*-9** reacted. At -20°C, all of the stannanes **9** and **16** had been consumed although weakly complexed aldehyde remained in solution.

In this system *metathesis and addition both occurred at a comparable rate.* However, the NMR experiment could not distinguish between direct addition of **9** or metathesis to **16** followed by addition to **12**. A series of preparative experiments are in progress to address this subtle point.

DISCUSSION

A. MODEL STUDY

The consistently high *syn*-selectivity in reactions of **1** clearly implicates a significant preference for the synclinal orientation of double bonds in the transition state (**i**, Scheme 2). This tendency is not strongly related to the nature of the Lewis acid in contrast to our experience with the silane model **2**. Previous studies from these laboratories have demonstrated the stereochemical significance of the bulk of the Lewis acid-aldehyde complex in these reactions. The insensitivity to Lewis acid size in this case, together with the facility of reaction, argue for an early transition state. What, then, is the origin of the preference?

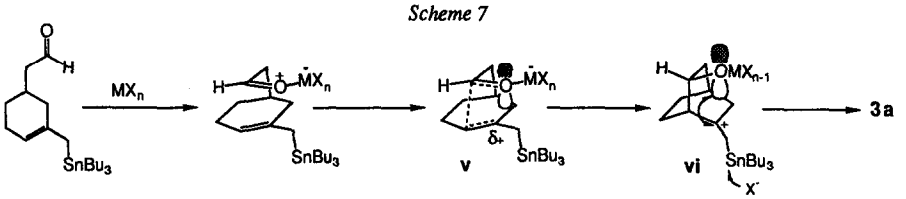
At the outset we discount the argument that the model is intrinsically biased to form the *syn* isomer **3a** for two reasons. First, **3b** is the major product (**3a/3b** 5:95) in the reaction of **2** with *n*-$Bu_4N^+F^-$. Second, calculated strain energies (MM2) for **i** and **ii** (not complexed, ML_n=$SiMe_3$) fixing the reacting centers at 2.10Å weakly *favor* **i** (0.7 kcal/mol). Further, strain energies calculated by fixing the reacting centers of **iii** and **iv** at 1.60 to 2.30Å (0.10Å intervals) always favor **iv** by 0.3 to 0.7 kcal/mol. Finally, strain energies calculated for **3a** and **3b** and their Me and *t*Bu ethers are all within 0.2 kcal/mol, favoring **3a**.

iii iv

To discuss possible origins for the synclinal preference we first note that the gauche relationship of the donor and acceptor π-systems is an example of the general topological rule for reactions of this type. Seebach[28] has delineated the conditions under which the preferred approach of two sp^2 centers in a variety of reactions will follow this rule and has compiled an impressive list of effects which have been forwarded to explain the preference in different reactions. Of these factors, we feel two may have relevance here: 1) Coulomb attraction and 2) secondary orbital interactions.

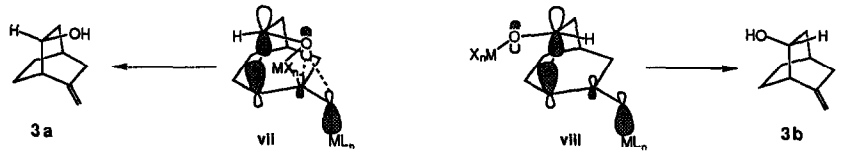
The first effect (Coulomb attraction, Scheme 7) focuses on the charge accumulation in an unsymmetrical transition state, v, represented in the limit by intermediate vi[29]. Since these reactions are conducted in non-polar solvents, charge

Scheme 7



separation (to 3b) is expected to be energetically disfavored. A similar effect has been invoked by Huisgen[30] to explain retention of configuration in [2+2]-cycloadditions of electronically complementary olefins. The second effect is related to the first but focuses on the HOMO of the allylmetal and LUMO of the complexed aldehyde, Scheme 8. In structure vii, leading

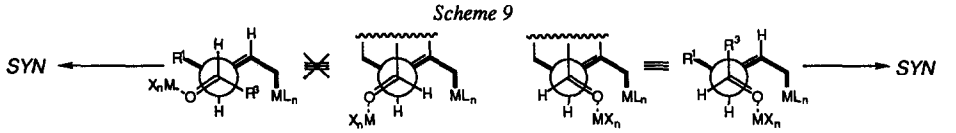
Scheme 8



to 3a, there is an in-phase overlap between the oxygen and the metal-bearing carbon which is absent in the antiperiplanar orientation, viii, leading to 3b. This "cycloaddition-like" transition state was first proposed by Mulzer[31] to explain the stereochemical course of aldol reactions with acid dianions[32]. It may be possible to distinguish these proposals by studying the effect of solvent, although the range will be limited.

Whatever the reason, the fact remains that synclinal arrangements are possible and can be significantly preferred. However, it should be stressed that this fact *does not necessarily negate* the Yamamoto[6] hypothesis of an open-chain transition state for Type 2 additions because antiperiplanar transition state ii does not precisely model it, Scheme 9.

Scheme 9



Nevertheless, we feel that the factors which influence the decision between i and ii are pervasive and must be taken into account in the evaluation of reactions between acyclic partners. Thus, taken together with our earlier studies we propose that for Type 2 reactions which proceed by direct addition (not metathesis): 1) there exists a preference for the synclinal orientation of double bonds and 2) the bulk of the Lewis acid-aldehyde complex and the stoichiometry of complexation are stereochemically significant.

B. SPECTROSCOPIC STUDIES

The complexation and metathesis experiments constitute a major portion of this work. However, due to space limitations an independent discussion of these studies will be presented elsewhere. The issue at hand is to understand how the interplay of Lewis acid, aldehyde, allylstannane, stoichiometry, addition order, etc. influence the course of the addition and thereby the structure of the products.

With $BF_3{\cdot}OEt_2$ as the Lewis acid there is no evidence for metathesis. However, the nature of the aldehyde does have an effect. Unbranched aliphatic aldehydes may trimerize at low temperature permitting a $BF_3{\cdot}OEt_2$-catalyzed olefin

isomerization followed by ligand redistribution of the stannane. The nature of the species responsible for redistribution is unclear. Branched or aromatic aldehydes undergo direct addition with no evidence of intermediates. Interestingly, Tagliavini[16b] has suggested the formation of new allylmetal substrates in the presence of $BF_3{\cdot}OEt_2$ based on product analysis. We believe these to be allylically rearranged stannanes rather than new boron reagents.

The stiuation with $SnCl_4$ as the Lewis acid is both simpler and more complex! With a molar equiv of $SnCl_4$ per aldehyde metathesis is the preferred pathway for all aldehydes. The rate of isomerization of the metathesis products, **13** and **14**, depends upon the Lewis basicity of the aldehyde and the presence of $SnCl_4$. Further, depending upon the reactivity of the aldehyde either trichlorostannyl species, **13** or **14**, may react. Thus, in this case, order of addition will be important. Combining **9** with $SnCl_4$ first will give only **13** which leads to branched homoallylic alcohols. Although metathesis will also occur in the presence of aldehydes the regiochemistry and stereochemistry of the products is controlled by the rate of isomerization of the intermediates.

When one-half a molar equivalent of $SnCl_4$ per aldehyde is used, the reaction pathway and product distribution become very sensitive to aldehyde structure and addition order. We have spectroscopically documented a spectrum of mechanistic pathways ranging from direct addition (acetaldehyde) to complete metathesis (pivaldehyde) to a competitive addition and metathesis (4-*t*-butylbenzaldehyde).

From a preparative standpoint and for understanding the outcome of experiments in the literature, the studies with 1.0 equiv of $BF_3{\cdot}OEt_2$ or $SnCl_4$ are of interest. The results with 0.5 equiv of $SnCl_4$ are of mechanistic interest only. Further preparative and spectroscopic studies of allylic stannanes with other Lewis acids are in progress.

EXPERIMENTAL SECTION

General Methods. - Bulb-to-bulb distillations were performed on a Büchi GKR-50 Kugelrohr; boiling points (bp) refer to air-bath temperature and are uncorrected. Melting points (mp) were determined on a Thomas-Hoover capillary melting point apparatus and are corrected. Analytical TLC was performed on Merck silica gel plates with QF-254 indicator. Analytical gas chromatography was performed on a Varian 3700 chromatograph fitted with a flame ionization detector. (N_2 carrier gas for packed columns, 30 mL/min; H_2 for capillary columns, 1 mL/min). Columns: A) 23 m OV-101 WCOT, split ratio 30:1, B) 3% OV-17 on chromosorb W (6 ft x 1/8 in). Retention times (t_R) and integrals were obtained from a Hewlett Packard 3390 recorder. All reactions were performed in oven (140°C) or flame-dried glassware under an inert atmosphere of dry N_2. Infrared spectra (IR) were obtained on either a Nicolet 7199C FT-IR or Perkin-Elmer 1320 IR spectrophotometer in chloroform solutions unless otherwise stated. Peaks are reported in cm^{-1} with the following relative intensities: s (strong, 67-100%), m (medium, 34-66%), weak, 0-33%). ^{1}H-NMR spectra were recorded on either Varian HR-220 (220 MHz), XL-200 (200 MHz) or Nicolet NTC-360 (360 MHz) spectrometers in deuterochloroform or carbon tetrachloride with chloroform as an internal standard δ=7.26) unless otherwise stated. Chemical shifts are given in ppm (δ): multiplicities are indicated by s (singlet), d (doublet), t (triplet), qa (quadruplet), q (quintet), m (multiplet) or br (broadened). Coupling constants, *J*, are reported in Hz. Mass spectra were obtained on a Varian MAT CH-5 spectrometer with ionization voltages of 10 and 70 eV. Data are reported in the form *m/z* (intensity relative to base = 100). High resolution mass spectra were obtained on a Varian MAT-731 spectrometer. Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory.

The VT-NMR experiments were performed in 1:1 $CD_2Cl_2/CDCl_3$ on a General Electric GN-300NB broadband spectrometer (10 mm tubes) operating at 75.46 MHz (^{13}C) or 111.85 MHz (^{119}Sn) or a General Electric QE-300 spectrometer (75.46 MHz, ^{13}C, 5 mm tubes). The variable temperature units were calibrated over the range -95 to -20°C against a methanol sample. ^{13}C-NMR spectra were acquired with broadband ^{1}H decoupling using a 25.0 ms pulse with a 1 s delay. A block size of 32 K data points and a sweep width of 10,000 Hz were used giving an acquisition time of ~7.5 min for 256 scans. ^{13}C spectra were internally referenced to $CDCl_3$ (δ 77.06 ppm). ^{119}Sn-NMR spectra were acquired with broadband ^{1}H decoupling using a 21.5 ms pulse with a 2 s delay. A block size of 32 K data points and a sweep width of 45,000 Hz were used giving an acquisition time of ~15 min for 256 scans. ^{119}Sn spectra were externally referencd to $SnMe_4$ (δ 0.0 ppm).

A. MODEL **1**

Preparation of 2,3'-(Tributylstanniomethyl)-3'-cyclohexenyl-1-ethanal (1). *2,3'-Methylidene-4'-(phenylthio)cyclohexyl-1-ethanol* (**6**). To a solution of 2.18 g (7.29 mmol) of **4** in 30 mL of Et_2O at 0°C was added 2.30 g (6.08 mmol) of $LiAlH_4$. The reaction mixture was stirred at 0°C for 1 h and quenched with H_2O (0.23 mL) followed by 1N NaOH (0.23 mL) and H_2O (0.69 mL). The resulting mixture was filtered and the filtrate was extracted with Et_2O (3x30 mL). The organic extracts were washed individually in series with H_2O (1x15 mL) and brine (1x15 mL). The combined organic extracts were dried (Na_2SO_4) and evaporated. The oily residue was column chromatographed on silica gel (hexane/EtOAc 7:3) to give 1.55 g (91% yield) of **6** as a white solid: Mp 60-62°C. R_f 0.28 (hexane/Et_2O 7:3). IR: 3220m, 3015w, 2915s, 2885w, 2860w, 1645w, 1585m, 1480m, 1445w, 1440m, 1230m, 1215s, 1090w, 1050w, 1025s, 1005w, 975w, 905m. ^{1}H NMR (220 MHz, CCl_4): 1.09-2.11 (m, 10H), 2.63 (d, *J* = 10, 1H, H-C(4')), 3.59 (t, *J* = 6, 2H, 2H-C(1)), 4.92 and 4.75 (2s, 2H, $=CH_2$), 7.08-7.27 (m, 5H, arom. H). MS (70 eV): (M^++1, 15), 248 (100), 139 (21), 138 (42), 121 (39), 120 (16), 110 (33), 95 (44), 94 (36), 93 (33), 92 (34). Anal. calc. for $C_{15}H_{20}OS$: C 72.54, H 8.12; S 12.91; found: C 72.68; H, 8.26; S 13.15.

2,3'-(Tri-n-butylstanniomethyl)-3'-cyclohexenyl-1-ethanol (**7**). To a solution of 1.23 g (4.97 mmol) of **6** in 12 mL of benzene was added 4.34 g (14.91 mmol) of tri-*n*-butyltin hydride and a catalytic amount of AIBN. After heating to reflux for 2 h, the volatiles were evaporated. The residue was chromatographed on Al_2O_3 (neutral, activity I) with hexane/EtOAc

mixtures of increasing polarity as eluent. Distillation afforded 1.67 g (78% yield) of **7** as a clear colorless oil: Bp 150°C /0.02 Torr. GC: t_R = 8.16 min, column B: 70°C (2 min), 40°C, 250°C. IR: 3620w, 3010m, 2955s, 2920s, 2850s, 1650w, 1464m, 1455m, 1417w, 1375w, 1353w, 1337w, 1290w, 1220s, 1210s, 1158w, 1069m, 1046m, 1029m, 999w, 909w, 884w. ^{1}H NMR (220 MHz, CCl_4): 0.77-0.93 (m, 16H), 1.24-1.62 (m, 23H), 3.62 (dd, J = 12 and 6, 2H, 2H-C(1)), 5.14 (s, 1H, H-C(4')). MS (70 eV): (no M^+ ion), 240 (3), 239 (16), 237 (12), 235 (97), 234 (97), 233 (72), 232 (38), 231 (33), 183 (13), 181 (11), 179 (100), 178 (27), 177 (82), 176 (27), 175 (43), 151 (14), 123 (12), 94 (15), 93 (15), 92 (20), 91 (12), 58 (14), 57 (20), 56 (11), 43 (31). Anal. calc. for $C_{12}H_{42}OSn$: C 58.76, H 9.86; found: C 58.96, H 9.90.

2,3'-(Tri-n-butylstanniomethyl)-3'-cyclohexenyl-1-ethanal (**1**). A solution of *t*-butoxymagnesium bromide was prepared by adding 0.038 mL (0.400 mmol) of *t*-butanol to 0.138 mL (0.400 mmol) of methylmagnesium bromide in 2.0 mL of THF. To this solution was added 0.140 g (0.326 mmol) of **7** in 1.5 mL of THF. After stirring at r.t. for 5 min, the reaction mixture was treated with 0.103 g (0.408 mmol) of 1,1'-(azodicarbonyl)dipiperidine. The resulting dark red solution was stirred at r.t. for 1 h. During this time the color faded and the formation of a precipitate was observed. The reaction mixture was quenched with 5 mL of H_2O and extracted with Et_2O (3x20 mL). The Et_2O extracts were individually washed in series with one, 5-mL portion of water and 15 mL of brine. The Et_2O extracts were combined, dried (K_2CO_3) and evaporated. The residue was filtered through Al_2O_3 (activity V/-20°C) with pentane as eluent. Evaporation afforded 0.110 g (82% yield) of **1** as a clear, colorless oil. IR: 3021s, 2950s, 2925s, 2871m, 2854m, 2724w, 2400w, 1717s, 1650w, 1519w, 1463m, 1455m, 1440m, 1418m, 1375m, 1355w, 1338w, 1217s, 1159w, 1070w, 1046m, 959w, 928m, 874w, 849w, 750s. ^{1}H NMR (220 MHz, $CDCl_3$): 0.70-2.15 (m, 36H), 2.40 (dd, J = 6.6 and 2.2, 2H, 2H-C(2)), 5.24 (s, 1H, H-C(4')), 9.81 (t, J = 2.2, 1H, H-C(1)). ^{13}C NMR (50 MHz, $CDCl_3$): 10.33, 14.43, 20.43, 25.45, 28.09, 29.25, 29.83, 37.92, 51.12 C(2), 116.95 C(4'), 137.01 C(3'), 203.29 C(1). MS (10 eV): 371 (7), 369 (7), 291 (11), 289 (9), 235 (18), 234 (6), 233 (13), 231 (8), 179 (14), 177 (13), 175 (9), 138 (7), 105 (10), 95 (14), 94 (100), 93 (24), 92 (21), 91 (9), 83 (6), 79 (50), 77 (6), 67 (6), 43 (6). MS (FI): 433, 432, 431, 430, 429, 428 (M+), 426, 425, 424. Anal. calc. for $C_{21}H_{40}OSn$: C 59.04, H 9.44, Sn 27.78; found: C 59.01, H 9.51, Sn 27.80.

Preparation and Assignment of Stereochemistry of Bicyclic[2.2.2]octan-2-ols (3a) and (3b). *rel-(1R,2R,4S)-6-Methylidenebicyclo[2.2.2]octan-2-ol* (**3a**) *and* rel-*(1R,2S,4S)-6-Methylidenebicyclo[2.2.2]-octan-2-ol* (**3b**). To a solution of 0.894 g (6.57 mmol) of 6-methylenebicyclo[2.2.2]octan-2-one[33] in absolute ethanol at 0°C was added 0.248 g (6.57 mmol) of $NaBH_4$. The reaction mixture was warmed to r.t. and stirred for 3 h. The reaction was quenched by the addition of 10 mL of H_2O and extracted with Et_2O (3x25 mL). The Et_2O extracts were individually washed in series with brine (2x10 mL), dried ($MgSO_4$) and evaporated to give 0.863 g (95% yield) of a viscous oil. GC analysis: column A: 70°C (8 min), 10°C/min to 140°C, two components: t_R = 9.24 min (70%) and 10.31 min (30%). These components were separated by multiple column chromatography with hexanes/EtOAc as eluent. Component one (**3a**): white solid, mp 60-62°C. R_f 0.30 (hexane/EtOAc 3:1). GC: t_R = 9.24 min. IR: 3600w, 3560w, 3070w, 3010s, 2940s, 2875s, 2830w, 1652m, 1470w, 1450m, 1431m, 1395m, 1299s, 1234m, 1220m, 1210m, 1108w, 1094w, 1086s, 1074w, 944w, 936w, 895s, 880m, 869w, 838w. ^{1}H NMR (220 MHz, CCl_4): 1.19-2.24 (br m, 11H), 3.75-3.79 (m, 1H, H-C(2)), 4.80 (t, J = 2, 2H-C(6)). MS (70 eV): 138 (M^+, 6), 105 (13), 95 (14), 94 (100), 93 (29), 91 (21), 79 (77), 77 (19), 67 (10), 53 (13), 41 (22), 39 (24). Anal. calc. for $C_9H_{14}O$: C 78.21, H 10.21; found: C 78.19, H 10.22. Component two (**3b**): white solid, mp 54-56°C. R_f 0.30 (hexane/EtOAc 3:1). GC: t_R = 10.31 min. IR: 3610m, 3070w, 3010m, 2940s, 2875m, 1650m, 1468w, 1449w, 1430w, 1225m, 1207m, 1131w, 1090w, 1061m, 1012m, 920m, 901w, 885m. ^{1}H NMR (220 MHz, CCl_4): 1.29-2.15 (m, 11H), 3.88-3.94 (m, 1H, H-C(2)), 4.66 and 4.79 (2d, J = 2, 2H, 2H-C(9)). MS (70 eV): 138 (M^+, 8), 105 (15), 95 (12), 94 (100), 93 (31), 92 (35), 91 (24), 79 (78), 77 (19), 53 (13), 41 (22), 39 (24). Anal. calc. for $C_9H_{14}O$: C 78.21, H 10.21; found: C 78.49, H 10.11.

Lanthanide Shift Study of (3a) and (3b).- To separate solutions of **3a** and **3b** (0.39 M) in CCl_4 was added Resolve-Al Eu(fod)$_3$ in increments of 0.10 equiv ranging from 0.10 equiv to 0.50 equiv. Between the addition of each increment the ^{1}H-NMR spectrum of the solutions was recorded. The average methylidene signals, relative to TMS, were measured for each of the NMR spectrum. The slope of the LIS for each isomer was calculated: **3a**, 6.61 ppm/equiv; **3b**, 2.81 ppm/equiv.

Cyclization of 1. General Procedure. - 1. *$SnCl_4$, Et_2AlCl, $BF_3{\cdot}OEt_2$, $SiCl_4$ and CF_3CO_2H.* To a solution of **1** (1.0 equiv, 0.05 M) in CH_2Cl_2 at -70°C was added 1.1 equiv of a 1.0 M solution of the Lewis acid in CH_2Cl_2. The reaction mixture was stirred at -70°C until complete reaction of **1** was observed (see Table 1 for reaction times). The reaction mixture was quenched with 1.0 N NaOH in MeOH and allowed to warm to r.t. A 0.5-mL aliquot was removed, treated with excess tetrabutylammonium fluoride in THF and washed with 0.5 mL of water. The organic layer was analyzed by capillary GC (column A).

2. *$FeCl_3$, $AlCl_3$ and $ZrCl_4$.* To a suspension of Lewis acid (1.1 equiv) in CH_2Cl_2 at -70°C was added a solution of **3** (1.0 equiv) in CH_2Cl_2. The amounts of CH_2Cl_2 used were adjusted to insure that the reaction mixture was 0.05 M in **1** after the addition was complete. The reaction mixture was stirred at -70°C until complete reaction of **3a** was observed. The reaction mixture was quenched with excess 1.0 N NaOH in MeOH. See procedure 1. for workup and analysis.

3. *Thermolysis of 1.* A 0.05 M solution of **1** in benzene was heated to 90°C for 8 h in a sealed reaction vial. After cooling to r.t., a 0.50-mL aliquot was removed and treated with 0.50 mL of 1.0 N NaOH in MeOH. The solution was washed with 0.50 mL of water and the organic phase was analyzed by capillary GC (column A).

B. NMR STUDIES

General Procedure for the Formation of Lewis Acid-Aldehyde Complexes. - A 10-mm NMR tube was flame dried in a stream of dry nitrogen and then sealed with a septum. The aldehyde (~1.0 mmol) was weighed into the tube using a syringe. The tube was charged with $CDCl_3$ (1.0 mL) and CD_2Cl_2 (1.0 mL). The resulting 0.5 M solution was cooled to -80°C in a dry ice/Et_2O cooling bath and equilibrated for 10 min. Freshly distilled, neat Lewis acid was added to the solution and the tube was swirled and gently shaken in the cooling bath to effect mixing. The probe of the NMR spectrometer was cooled to -80°C and the sample was inserted. The ^{13}C (and ^{119}Sn) spectra were recorded. After accumulation of the FID was complete, the probe was warmed to -60°C and allowed to equilibrate for 10-15 min. A spectrum was again acquired. This process was repeated at 20° intervals over the range of -80° to +20°C.

General Procedure for the Reactions of Lewis Acids and 9. - A 5 or 10 mm NMR tube was flame dried in a stream of dry nitrogen and quickly sealed with a septum. Into the tube was carefully measured the allylmetal (0.50 or 1.0 mmol) using a syringe. The tube was then charged with 0.50 or 1.0 mL $CDCl_3$ and 0.50 or 1.0 mL CD_2Cl_2. The sample was placed in the NMR at ambient temperature and shimmed to obtain maximum lock signal. The probe was then cooled to

-80°C and allowed to equilibrate at this temperature for 20 min after which the NMR was reshimmed on the sample. The sample was removed from the probe and placed in a dry ice/Et_2O bath at -80°C. The freshly distilled Lewis acid (0.50 or 1.0 mmol) was syringed onto the inside of the cooled NMR tube below the level of the cooling bath but above the level of the reaction. The reaction was then vigorously shaken for approximately 2 seconds and returned to the cooled probe. (The overall time lapse between removal and reinsertion of the sample was less than 2 min). A spectrum was immediately acquired at -80°C (typically 100 to 200 pulses were required for a good signal-to-noise ratio). After the accumulation of the FID was complete, the probe was warmed to -60°C and allowed to equilibrate for 10 to 15 min. A spectrum was again acquired. This process was repeated at 20° intervals over the range of -80° to +20°C.

1. *Metathesis of 9 with 0.5 equiv of $SnCl_4$.* Into a flame-dried NMR tube was weighed **9** (2:1 *E/Z*, 105.5 mg, 0.48 mmol). $CDCl_3$ (1.0 mL) and CD_2Cl_2 (1.0 mL) were added. The solution was cooled to -80°C and equilibrated for 10 min. Freshly distilled, neat $SnCl_4$ (28.2 μL, 0.24 mmol) was added and the tube was swirled and gently shaken in the cooling bath to effect mixing. The sample was placed into the precooled spectrometer probe and the ^{13}C-NMR spectra recorded at 20° intervals over the range -80° to 0°C.

2. *Metathesis of 9 with 0.75 equiv of $SnCl_4$.* The procedure above was employed using **9** (2:1 *E/Z*, 88.0 mg, 0.40 mmol) and $SnCl_4$ (35.3 μL, 0.30 mmol). ^{13}C-NMR spectra were recorded at 20° intervals over the range -80° to 0°C. The final solution was recooled to -80°C and the ^{13}C-NMR spectrum recorded.

General Procedure for the Reactions of Aldehydes, Lewis Acids and Allylmetals. - 1. *BF_3·OEt and $SnCl_4$ (1.0 equiv).* A 5-mm NMR tube was flame dried in a stream of dry nitrogen and quickly sealed with a septum. Into the tube was carefully measured the aldehyde (0.50 mmol) using a syringe. The tube was then charged with 0.50 mL $CDCl_3$ and 0.50 mL CD_2Cl_2. The sample was placed in the NMR at ambient temperature and shimmed to obtain maximum lock signal. The probe was then cooled to -80°C and allowed to equilibrate at this temperature for 20 min after which the NMR was reshimmed on the sample. The sample was removed from the probe and placed in a dry ice/Et_2O bath at -80°C. The freshly distilled Lewis acid (0.50 mmol) was syringed onto the inside of the cooled NMR tube below the level of the cooling bath but above the level of the reaction. The reaction was then vigorously shaken for approximately 2 seconds and returned to the cooled probe. (The overall time lapse between removal and reinsertion of the sample was less than 2 min.) The probe was reshimmed and spectrum of the complexed aldehyde was obtained and compared to the reference spectra. The allylmetal (0.50 mmol) was syringed into the NMR tube as before and a spectrum was immediately acquired at -80°C (typically 100 to 200 pulses were required for a good signal-to-noise ratio). After the accumulation of the FID was complete, the probe was warmed to -60°C and allowed to equilibrate for 10 to 15 min. A spectrum was again acquired. This process was repeated at 20° intervals over the range of -80° to +20°C.

2. *$SnCl_4$ (0.5 equiv).* A 0.5 M or 0.2 M solution of the Lewis acid-aldehyde complex was prepared as described in 1. Its ^{13}C and/or ^{119}Sn NMR was checked with the probe of the spectrometer cooled to the requisite temperture (-95°C or -80°C). The spinner air supply was turned off and the sample ejected from the probe. The sample was placed in a -80°C cooling bath with the coolant just covering the level of the solution. Holding the tube vertically, neat **9** was added by syringe, running the liquid down the side of the tube so that it formed a layer on top of the solution. The NMR tube was carefully reinserted into the probe, being careful not to mix the biphase solution. The sample was equilibrated at the desired temperature *without* spinning for at least 10 min. A ^{13}C-NMR spectrum acquired during this period showed only the Lewis acid-aldehyde complex. Next, the spinner air supply was turned on and the NMR tube was vortexed at 40-50 rps for 2-6 min to effect complete mixing of the sample. A ^{13}C-NMR spectrum was immediately acquired with the minimum number of acquisitions to generate an acceptable signal-to-noise ratio (NA = 32 or 64). Additional ^{13}C-NMR spectra were recorded at this temperature and at 20° intervals up to 0°C.

Acknowledgement. - We gratefully acknowledge financial support by grants from the National Science Foundation (NSF CHE-8208565, 85-15371). S.E.D. also acknowledges support from the NSF (Presidential Young Investigator Award (1985-1990) and the Alfred P. Sloan Foundation (1985-1989).

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