Communications to the Editor

Stereochemistry of Allylmetal–Aldehyde Condensations. 2. Allylstannanes[1]

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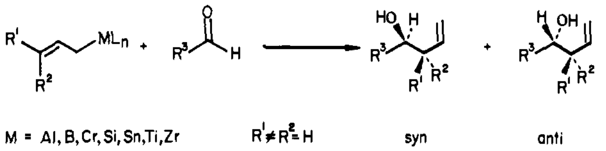
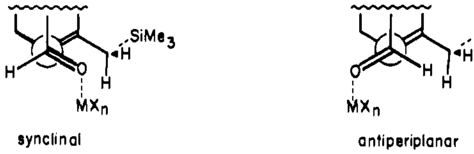
The condensation of allylic organometallic reagents with aldehydes (eq 1) is a reaction of current interest and considerable synthetic utility.[2] Due to the high stereoselectivity of the process and the synthetic potential of the homoallylic alcohols produced, the reaction serves as a useful surrogate for the aldol condensation.[3] Moreover, by judicious selection of organometallic reagent and reaction conditions, both syn(unlike)- and anti(like)-selective[4] reactions are available from the same aldehyde and allylic moiety. This remarkable dependence of diastereoselectivity on the metal has been classified into three groups[5] which relate the stereochemical outcome to the geometry of the allylic double bond. Among the various organometallic reagents that have been successfully employed, the allylsilanes and allylstannanes comprise a unique group which undergo syn(unlike)-selective reactions with aldehydes (in the presence of Lewis acid catalysts) which are independent of allyl geometry.[6] Furthermore, allylstannanes have been shown to behave quite differently in the absence of Lewis acid catalysts, wherein the allyl geometry is stereodetermining.[7] Clearly a detailed picture of the transition state(s) that explains the role of the metal atom, Lewis acid, and allyl unit is lacking.



(1)

We recently reported the results of a stereochemical study on the intramolecular condensation of allylsilane **1b** (Scheme I).[5] This model was designed to evaluate the relative importance of synclinal vs. antiperiplanar reactive geometries. A modest preference was observed for the synclinal conformation that was sensitive to the structure of the Lewis acid. We report herein an analogous study on the condensation of allylstannane **1a**.



The preparation of the substrate **1a** is shown in Scheme II. Ester, **3**,[8] prepared in four steps from 2-cyclohexenone[5] (57% yield), was converted to allylstannane **5**[8] by $LiAlH_4$ reduction to alcohol **4**[8] (91% yield) followed by hydrostannylation[9] (85% yield). After many unsuccessful attempts to oxidize **5**,[8] we found that 1,1′-(azodicarbonyl)dipiperidine under basic conditions[10] provided an excellent yield of the unstable aldehyde **1a**.[8]

As expected, **1a** is extremely labile toward cyclization.[11] Freshly prepared samples are analyzed by 200-MHz NMR[12] and subjected to controlled reaction conditions. The results of cyclization experiments are collected in Table I. The stereochemical assignment and methods are the same as those reported previously.[5,13] Control experiments with the tri-*n*-butylstannyl ether of *anti*-**2** showed that the product ratios represent kinetically controlled reactions.

All of the cyclizations in Table I are very syn selective and relatively insensitive (87–96% syn) to the nature of the Lewis acid. It is ironic that the reaction is least selective with $BF_3 \cdot OEt_2$, the Lewis acid that has been universally employed in intermolecular reactions. A striking selectivity was observed with trifluoroacetic acid (99% syn) and thermolytic cyclization was also highly syn selective (>97%).

In contrast to our experience with allylsilane **1b**, reaction of allylstannane **1a** is more facile, much more syn selective, and much less sensitive to reaction conditions. *The high syn selectivity observed necessarily implicates a preference for the synclinal over the antiperiplanar transition-state geometry.*[14] Thus, the "erythro(syn) selectivity" of allylstannane–aldehyde reactions under Lewis acid catalysis does not necessarily arise from "open-chain (antiperiplanar)" transition states as has been suggested.[6b] Indeed it is important to recognize that there are two, possibly independent, stereochemical issues here: (i) orientation of the double bonds and (ii) disposition of the tributylstannyl group (S_E' stereochemistry). The observation of a synclinal orientation of double bonds does not necessarily imply an interaction between the metal atom and the carbonyl oxygen in the transition state. In fact we suggest, on the basis of recent studies,[15] that the tin

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(1) Weber, E.; Denmark, S. "Abstracts of Papers", 187th American Chemical Society National Meeting, St. Louis, MI, April 1984; American Chemical Society: Washington, DC, 1984; ORGN 174.

(2) Reviews: (a) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 555. (b) Yamamoto, Y.; Maruyama, K. *Heterocycles* **1982**, *18*, 357. (c) Hiyama, T. *J. Synth. Org. Chem., Jpn.* **1981**, *39*, 81. See also footnote 4 of ref 5.

(3) Reviews: (a) Heathcock, C. H. *Science (Washington, D.C.)* **1981**, *214*, 395. (b) Evans, D. A.; Nelson, J. V.; Taber, T. R. *Top. Stereochem.* **1982**, *13*, 1. (c) Mukaiyama, T. *Org. React.* **1982**, *28*, 203.

(4) For a discussion of nomenclature, see: (a) Masamune, S.; Kaiho, T.; Garvey, D. S. *J. Am. Chem. Soc.* **1982**, *104*, 5521. (b) Prelog, V.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 654.

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(6) Sn: (a) Yatagai, Y.; Yamamoto, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 4548. (b) Yamamoto, Y.; Yatagai, H.; Naruta, Y.; Maruyama, K. *Ibid.* **1980**, *102*, 7107. (c) Yamamoto, Y.; Maeda, N.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1983**, 774. (d) Maruyama, K.; Ishihara, Y.; Yamamoto, Y. *Tetrahedron Lett.* **1981**, 4235. (e) Koreeda, M.; Tanaka, Y. *Chem. Lett.* **1982**, 1297. (f) Koreeda, M.; Tanaka, Y. *Ibid.* **1982**, 1299. Si: (g) Hayashi, T.; Ito, H.; Kumada, M. *Tetrahedron Lett.* **1982**, 4605. (h) Hayashi, T.; Konishi, M.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *204*, 4963. (i) Hayashi, T.; Konishi, M.; Kumada, M. *J. Org. Chem.* **1983**, *48*, 281. (j) For recent discussions of the role of Lewis acids in reactions of allylic stannanes, see: Keck, G. E.; Abbott, D. E.; Boden, E. P.; Enholm, E. J. *Tetrahedron Lett.* **1984**, 3927 and references cited therein.

(7) (a) Servens, c.; Pereyre, M. *J. Organomet. Chem.* **1972**, *35*, C20. (b) Gambaro, A.; Marton, D.; Peruzzo, V.; Tagliavini, G. *Ibid.* **1981**, *204*, 191. (c) Pratt, A. J.; Thomas, E. J. *J. Chem. Soc., Chem. Commun.* **1982**, 1115. (d) Yamamoto, Y.; Maruyama, K.; Matsumoto, K. *Ibid.* **1983**, 489.

(8) All new compounds have been characterized by ^1H NMR (220 or 360 MHz), IR, mass spectroscopy, and combustion analysis (±0.3%).

(9) Ueno, Y.; Miyano, T.; Okawara, M. *Tetrahedron Lett.* **1982**, 443 and references cited therein.

(10) Narasaka, K.; Morikawa, A.; Saigo, K.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2773.

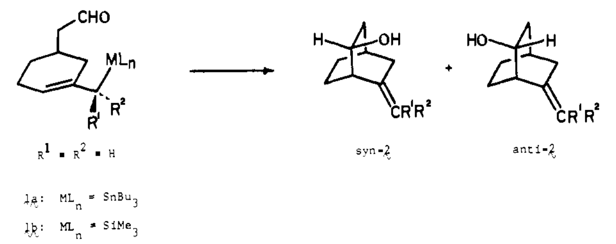
(11) **1a** does not withstand column chromatography (SiO_2, Al_2O_3), gas chromatography, or distillation (0.001 torr). The crude oxidation product is filtered through Al_2O_3 (activity V/–20 °C) with pentane and concentrated.

(12) Repeated integration of the methylidene signal showed <2% of **2**.

(13) In this case, however, an internal standard (decane) had to be used to assure high conversion to **2** (>85%) since **1a** does not survive GC.

(14) This is another manifestation of the topological rule for donor–acceptor double-bond reactions described by Seebach: Seebach, D.; Golinski, J. *Helv. Chim. Acta* **1981**, *64*, 1413.

Scheme I



Scheme II

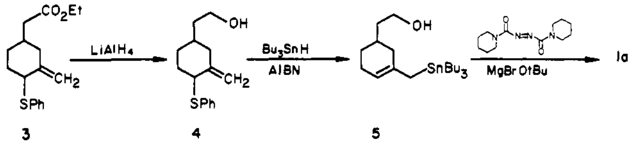
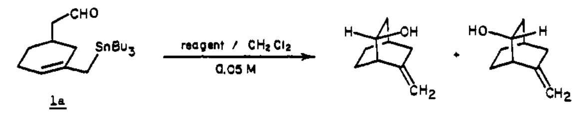


Table I.[a] Cyclization of **1a**



reagent[b]	time, min	temp, °C	% *syn*-**2**[c]	% *anti*-**2**[c]
$TiCl_4$	10	−85	82	18
BF_3·OEt_2	15	−70	87	13
$AlCl_3$	10	−70	89	11
Et_2AlCl	5	−70	90	10
$ZrCl_4$	10	−70	90	10
$SnCl_4$	5	−70	93	7
$FeCl_3$	20	−70	98	2
CF_3COOH	10	−70	99	1
Δ (C_6H_6)	480	90	97[d]	3

[a] The reactions were quenched at −70 °C ($NaOH/CH_3OH$) and analyzed by capillary GC. At least two runs with each reagent were performed to assure reproducibility, i.e., >85% conversion to **2** (vs. decane) and syn/anti ratios ±2%. [b] 1.05 equiv were used. [c] Ratios were calculated on the basis of independently determined response factors vs. decane. [d] Only *syn*-**2** was detected, in addition to 3% of a rearrangement product, thus 97% is the minimum selectivity.

group is oriented anti to the approaching aldehyde giving rise to the picture shown.

The origins of the strong preference for the synclinal geometry are as yet unclear. Inspection of Dreiding molecular models of the complexes of **1a** in which the Lewis acid is *E* complexed[16] is informative. In the analogous silanes we observed a significant steric contribution from the Lewis acid which favored the antiperiplanar orientation with increasing bulk.[5] The insensitivity to Lewis acid size in the case at hand indicates the lack of a steric component, which, in view of the facility of reaction, suggests an earlier transition state. The extremely selective cyclization induced by a proton (the sterically least demanding initiator) supports the contention that steric effects are not important contributors to the preference for synclinal geometry.

These results provide the first unambiguous picture of the double-bond orientation in reactions of allylstannanes and have important implications in the interpretation of intermolecular reaction pathways.

Work is in progress on a system that unambiguously defines the orientation of the metal atom in **1a** and **1b**. These results as well as investigations with other allyl metalloids will be the subject of future reports.

Acknowledgment. Financial support was provided by the National Science Foundation (CHE-8208565) to whom we are grateful. This work was supported in part by the University of Illinois Regional Instrumentation Facility (NSF-CHE 79-16100) and Mass Spectrometry Laboratory (NIH GM 27029).

Registry No. 1a, 92937-61-6; **1b**, 88354-72-7; *syn*-**2**, 87422-06-8; *anti*-**2**, 87422-07-9; **3**, 88354-75-0; **4**, 92937-62-7; **5**, 92937-63-8; AIBN, 78-67-1; $TiCl_4$, 7550-45-0; BF_3·OEt_2, 109-63-7; $AlCl_3$, 7446-70-0; Et_2AlCl, 96-10-6; $ZrCl_4$, 10026-11-6; $SnCl_4$, 7646-78-8; $FeCl_3$, 7705-08-0; CF_3CO_2H, 76-05-1; Bu_3SnH, 688-73-3; $LiAlH_4$, 16853-85-3; MgBrO-*t*-Bu, 19065-60-2; 1,1′-(azodicarbonyl)bispiperidine, 10465-81-3.

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(16) The precise structure of Lewis acid–aldehyde complexes has yet to be firmly established. Our assumption of an *E* configuration (Lewis acid cis to hydrogen) finds precedence in the BF_3 adducts of unsymmetrical ketones[17a] and enones[17b] wherein the preferred mode of complexation places the boron cis to the smaller group. Further support is found in the considerable body of structural information for protonated aldehydes[17c] in which the two hydrogens are nearly exclusively cis. Molecular orbital calculations for benzaldehyde–BF_3[17d] and acetaldehyde–H^+[11e] indicate a preferred *Z* configuration.

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Formation of the Long-Lived H_2O^-· Ion in the Gas Phase

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Recently the observation of long-lived H_3O^-[1] and NH_4^-[2] ions in our Fourier transform ion cyclotron resonance (FTICR) spectrometer[3,4] has been reported. The H_3O^- ions were generated by reaction of OH^- with formaldehyde through a successive proton and hydride transfer in the corresponding collision complex as summarized in eq 1. The NH_4^- ions could be formed by reaction

$$OH^- + CH_2O \rightleftarrows [OH^-{\cdot}CH_2O]^* \rightleftarrows [H_2O{\cdot}HCO^-]^* \rightarrow H^-{\cdot}H_2O + CO \qquad (1)$$

of NH_2^- with formaldehyde as well. In this case, however, the successive proton and hydride transfer do not occur in the same collision complex. This is due to the fact that the gas-phase acidity of formaldehyde lies in between that of water and ammonia,[5] so that NH_2^- can abstract a proton from formaldehyde in an exothermic reaction channel resulting in the formation of the product ion HCO^-. This then transfers a hydride to ammonia in a subsequent ion/molecule reaction. Equation 2 summarizes the

$$NH_2^- + CH_2O \rightarrow NH_3 + HCO^- \qquad (2a)$$

$$HCO^- + NH_3 \rightarrow H^-{\cdot}NH_3 + CO \qquad (2b)$$

formation of NH_4^-. Thus, the final step in the formation of both H_3O^- and NH_4^- is the transfer of a hydride to water and ammonia, respectively. This is consistent with the results of stable-isotopic

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(2) Kleingeld, J. C.; Ingemann, S.; Jalonen, J. E.; Nibbering N. M. M. *J. Am. Chem. Soc.* **1983**, *105*, 2474-2475.

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