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Supplementary Material Available: ORTEP plots of compounds **6** and **13** and HRMS and spectral data (mp, ^1H NMR, $[\alpha]_D$, and ^{13}C NMR) for compounds **7** and **9–18** (8 pages). Ordering information is given on any current masthead page.

Mechanistic and Stereochemical Divergence in the Allylsilane–Acetal Addition Reaction

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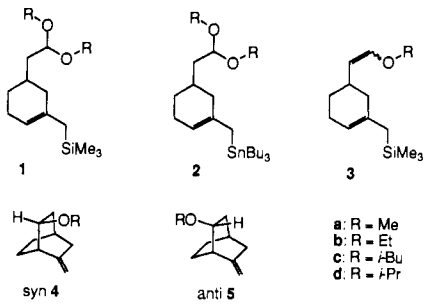
The reaction between acetals and allylic silanes is a mild and general method for formation of homoallylic ethers, Scheme I.[1] Although as first described the reaction required stoichiometric amounts of a Lewis acid, subsequent studies have shown that the reaction can be run *catalytically* using TMSOTf,[2a] TMSI,[1c] or $Ph_3C^+ClO_4^-$.[2b] The stereochemical aspects of the reaction have been slow to develop compared to the related condensations of aldehydes.[3] In the only systematic study on internal asymmetric induction with (*E*)- and (*Z*)-crotylsilanes, Sakurai reported a divergence in behavior between aliphatic and aromatic dimethyl acetals.[1d] Internal stereocontrol in additions of crotylsilanes to glycal acetates has also been studied.[4] In view of the growing interest in selective addition of silicon nucleophiles to chiral acetals[5] we have investigated the mechanism and stereochemical course of the reactions. The questions which have been the focus of our studies are as follows: (1) does the reaction proceed by an S_N1- or S_N2-like mechanism, (2) what factors (acetal structure, allylmetal, Lewis acid) affect the mechanism of the reaction, and (3) is there a mechanistically derived stereochemical preference?

We have addressed these questions by examination of the model systems **1a–d**,[6] **2a–d**,[6] and **3a,b**, and **d**.[6] These systems are related to the analogous models for allylmetal–aldehyde reactions which have been reported previously.[7] In this case, however, cyclization of **1–3** under various conditions will afford the bicyclic ethers **4**[6] and **5**.[6]



The first series of experiments addressed the Lewis acid dependence of cyclization stereochemistry with allylsilane **1a**, Table I. The wide range of selectivities from highly syn selective (TMSOTf) to unselective ($TiCl_4$) strongly suggests the involvement of the Lewis acid in the stereochemistry-determining event and argues against a common oxocarbenium ion intermediate. This idea finds additional support in the comparison of $SnCl_4$ stoichiometries (entries 8 and 9). The divergent selectivities with 1.0 and 0.5 equiv are indicative of direct Lewis acid involvement during bond formation.[8] A parallel series of experiments with the allylstannane **2a** showed similar behavior, Table II. Thus, the nature of the metal had little effect on the outcome of this reaction.[9]

We next examined the effect of acetal structure on the stereochemical course of reaction with the substrates **1a–d** and **2a,b** and **d**. To examine this feature we employed TMSOTf as the Lewis acid (Table III), and the results were surprising. For both **1** and **2** the methyl, ethyl, and isobutyl (**1** only) series were generally syn selective. However, the isopropyl cases were strikingly different showing a slight anti preference. We interpret the dramatic difference in selectivity as representing a change in mechanism rather than a steric effect related to the branching of the isopropyl group.

There are two possible limiting mechanisms for reaction, S_N2 via a complex and S_N1 via an oxocarbenium ion. The results from variations in Lewis acid and acetal structure suggested that there may be a stereochemical manifestation of the changes in mechanism. We sought to test this hypothesis by establishing the stereochemical outcome of cyclizations with the putative oxocarbenium ion, i, formed by protonation of the enol ethers, **3**, Scheme II. If the reactions of **1a–d** with TMSOTf involve prior formation of i, then the same stereochemical outcome should obtain if i is generated by TfOH protonation of the enol ethers **3**. Contrariwise, if the enol ethers cyclize to give different results, then the TMSOTf reactions cannot proceed through i.[10]

Cyclization of the enol ethers was promoted with 0.95 equiv of TfOH, and the results are found in Table IV. Initially, we anticipated a difference between the *E* and *Z* isomers,[10] but the results are nearly identical in each case. The dramatic difference of the results from the methyl enol ethers (**3a**) and corresponding acetal **1a** (Table III) strongly suggests the operation of two different mechanisms of cyclization. An analogous divergence can be seen for the ethyl enol ether (**3b**) and corresponding acetal (**1b**). On the other hand, the similarity in stereochemical outcome for the isopropyl cases (**3d** vs **1d**, Table III) may be taken as a reflection of reaction via a common intermediate.[11]

We conclude that the stereochemistry of cyclization of models **1** and **2** was dependent on the mechanism of activation. Thus with

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(6) All new compounds have been fully characterized by ^1H and ^{13}C NMR, IR, MS, and microanalysis (±0.3%).

(7) (a) Denmark, S. E.; Weber, E. J. *Helv. Chim. Acta* **1983**, *66*, 1655. (b) Denmark, S. E.; Weber, E. J. *J. Am. Chem. Soc.* **1984**, *106*, 7970. (c) Denmark, S. E.; Henke, B. R.; Weber, E. J. *Ibid.* **1987**, *109*, 2512. (d) Denmark, S. E.; Weber, E. J.; Wilson, T. M.; Willson, T. M. *Tetrahedron* **1989**, *45*, 1053.

(8) Low-temperature, ^1H NMR spectroscopic examination of solutions containing **1a** with 1.0 and 0.5 equiv of $SnCl_4$ showed the exclusive existence 1:1 and 2:1 complexes, respectively.

(9) In the intermolecular additions to steroidal acetals, Yamamoto found a metal-dependent stereoselectivity and invoked a metal-based change in mechanism to explain this. Yamamoto, Y.; Nishii, S.; Yamada, J. *J. Am. Chem. Soc.* **1986**, *108*, 7116.

(10) This hypothesis presupposes that the oxocarbenium ion formed from the different precursors is of the same configuration, assumed to be *E*. Cremer, D.; Gauss, J.; Childs, R. F.; Blackburn, C. *J. Am. Chem. Soc.* **1985**, *107*, 2435.

(11) The interesting trend toward anti selectivity with increasing steric bulk of R in **3** will be discussed in a full account of this work.

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Scheme I

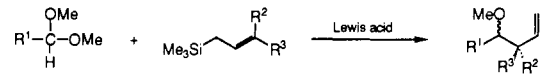


Table I. Effect of Lewis Acid in the Cyclization of **1a** → **4a/5a**[a]

entry	reagent	temp, °C	% syn (**4a**)[b]	% anti (**5a**)[b]	yield, %[b,c] (mass recovery)
1	Me_3SiOTf	−70	96	4	100
2	TfOH	−70	96	4	62 (74)
3	$Ti(OiPr)_2Cl_2$	−20	87	13	21 (91)
4	$AlCl_3$	−20	86	14	33 (78)
5	BCl_3	−70	82	18	57 (73)
6	$BF_3{\cdot}OEt_2$	−20	77	23	95 (100)
7	$TiCl_4$	−90	47	53	55 (58)
8	$SnCl_4$ (1.0 equiv)	−70	45	55	35 (60)
9	$SnCl_4$ (0.5 equiv)	−60	71	29	81 (81)

[a] All cyclizations were performed in CH_2Cl_2 (0.05 M) with 1.0 equiv of Lewis acid (except entry 9). At least 3 runs with each Lewis acid (±3%). [b] Ratios and yields were calculated based on independently determined response factors vs cyclododecane. [c] Yield is based on **4a** + **5a** vs cyclododecane; mass recovery is total integrated area including products of protiodesilylation.

Table II. Effect of Lewis Acid in the Cyclization of **2a** → **4a/5a**[a]

entry	reagent	temp, °C	% syn (**4a**)	% anti (**5a**)	yield, % (mass recovery)
1	Me_3SiOTf	−70	93	7	100
2	$BF_3{\cdot}OEt_2$	−60	94	6	63 (85)
3	$TiCl_4$	−70	41	59	44 (49)
4	$SnCl_4$	−30	38	62	25 (25)

[a] See footnotes Table I.

Table III. Effect of Acetal Structure in the Cyclization of **1** and **2** → **4/5** with TMSOTf[a]

substrate	ML'_3	R	% syn (**4**)[b]	% anti (**5**)[b]
1a	$SiMe_3$	Me	96	4
1b	$SiMe_3$	Et	92	8
1c	$SiMe_3$	*i*Bu	90	10
1d	$SiMe_3$	*i*Pr	38	62
2a	$SnBu_3$	Me	93	7
2b	$SnBu_3$	Et	92	8
2d	$SnBu_3$	*i*Pr	43	57

[a] All cyclizations were performed in CH_2Cl_2 (0.05 M) with 1.0 equiv of TMSOTf for **1** and 2.0 equiv for **2**. At least 3 runs with each substrate (±3%). [b] Ratios were calculated on independently determined response factors vs cyclododecane. All yields were >95%.

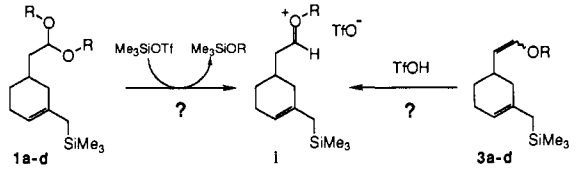
Table IV. Effect of Enol Ether Structure in the Cyclization of **3** → **4/5**[a]

substrate	R	*E*/*Z*[b]	temp, °C	% syn (**4**)[c]	% anti (**5**)[c]	yield, %[c]
(*E*)-**3a**	Me	96/4	−50	60	40	25[d]
(*Z*)-**3a**	Me	0/100	−70	53	47	79
(*E*)-**3b**	Et	100/0	−70	31	69	76
(*Z*)-**3b**	Et	23/77	−70	38	62	74
(*E*)-**3d**	*i*Pr	100/0	−70	25	75	84
(*Z*)-**3d**	*i*Pr	0/100	−70	27	73	76

[a] All cyclizations were performed in CH_2Cl_2 (0.05 M) with 0.95 equiv of TfOH. At least 3 runs with each substrate (±3%). [b] Established by capillary GC analysis. [c] Ratios and yields determined by independently determined response factors vs cyclododecane. [d] The major product resulted from protiodesilylation.

TMSOTf these methyl, ethyl, and probably isobutyl acetals react via an S_N2-type mechanism, while the isopropyl acetals react via prior ionization to an oxocarbenium ion (i). Accordingly, these conclusions are supported by the observed Lewis acid dependences wherein the nature of the Lewis acid acetal complex is expected to influence the S_N2-type reaction. Furthermore, the inherent strain in diisopropyl acetals should favor ready ionization compared to ethyl and methyl analogues.

Scheme II



Studies are in progress on the structure of Lewis acid acetal complexes and the stereochemical course of reactions with cyclic acetals.

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Supplementary Material Available: Full characterization for the models **1**, **2**, and **3** are provided along with representative cyclization procedures (8 pages). Ordering information is given on any current masthead page.

Metal-Promoted Carbon–Carbon Bond Formation in the Gas Phase: Reaction of Iron Carbonyl Cations with Allyl Chloride

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Gaseous transition-metal ions, bare[1] or bearing ligands,[2] have been shown to be extremely reactive with various organic compounds; for example, group 8 metal cations are able to cleave C–H and C–C bonds of alkanes.[3] However, contrary to solution organometallic chemistry, gas-phase organometallic chemistry includes relatively few examples of carbon–carbon bond formation.[4] We report here our first results concerning the $Fe(CO)_n^+$-allyl chloride (3-chloro-1-propene) system, in which a new type of C–C bond formation is encountered.

The reactivity of each $Fe(CO)_n^+$ ion (n = 0–5) with allyl chloride was studied by using a MS/MS/MS multiquadrupole spectrometer, described elsewhere,[5] with the following configuration: (i) source, electron impact on $Fe(CO)_5$; (ii) first quadrupolar analyzer, selection of $Fe(CO)_n^+$ reagent ion; (iii) first collision cell, reaction with allyl chloride (ca. 1 mTorr); (iv) second quadrupolar analyzer, selection of a reaction product; (v) second collision cell, CAD of this product (collision gas; Argon, ca. 0.7 mTorr, collision energy 15–25 eV); (vi) third quadrupolar analyzer, scanning. The relatively high pressure in the first collision cell allows successive reactions.

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