Preparation of Monosilyl Acetals from Esters *via* iBu$_2$AlH Reduction and Trapping with *N*-(Trimethylsilyl)imidazole. Addition of Allyltrimethylsilane To Yield Homoallylic Alcohols or Ethers

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Received November 18, 1994⊗

Alkyl esters were reduced with iBu$_2$AlH or a 1:1 mixture of iBu$_2$AlH and iBu$_3$Al (iBu$_2$AlH·iBu$_3$Al or iBu$_5$Al$_2$H), followed by trapping of the resulting tetrahedral intermediate with TMS-imidazole to produce monosilyl acetals. Reaction of the mixed acetals with allyltrimethylsilane in the presence of Lewis acids (Hosomi–Sakurai reaction) generated homoallylic alcohols or ethers selectively, depending on the substitution of the monosilyl acetal. TMS methoxy acetals (MeO–CH–OTMS) and TMS ethoxy acetals bearing additional complexing groups such as MeO– or Ph$_2$C=N– provided alcohols with 1.5:1–9:1 threoselectivity, while simple TMS ethoxy acetals provided only ethyl ethers as products. The monosilyl acetal configuration was easily epimerized or racemized, and the configuration of the Hosomi–Sakurai product was apparently independent of the initial monosilyl acetal reactant configuration.

The electrophilic reaction of acetals with weak nucleophiles (*e.g.*, allylsilanes) is complementary to the reaction of carbonyls with strong nucleophiles (Figure 1). While the electrons of the strong nucleophile are "pushed" into the π^* orbital of the carbonyl with weak coordination by the metal, the weak nucleophile has its electrons "pulled" into the π^* orbital of an oxocarbenium ion (oxonium ion) by the positive charge. The synthesis of homoallylic ethers *via* the Lewis acid-catalyzed addition of allylsilanes to acetals (Hosomi–Sakurai reaction)[1] has proven to be quite useful.[2] Johnson has introduced chiral acetals as templates for the production of chiral homoallylic ethers with high diastereoselectivities.[3] Despite the large number of studies which have been published in this area, there are still many aspects of this reaction which bear closer examination. In an alternative scheme which does not invoke a discrete oxonium ion, the nucleophilic electrons can fill the σ^* orbital of a strongly coordinated acetal (incipient oxonium ion). Denmark and Heathcock have provided evidence for such an S$_N$2-like mechanism for certain acetals.[4]

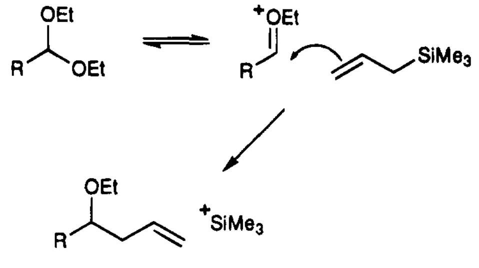

Figure 1.

Examination of the reactivity and synthetic applications of various aluminoxy acetals generated *via* iBu$_2$AlH or iBu$_2$AlH·AliBu$_3$ reduction of esters (O=COR → iBu$_2$AlOCHOR) led us to trap these reactive aluminum intermediates as their corresponding silyl ethers or monosilyl acetals.[5] Kiyooka has reported the direct reaction of similar aluminoxy acetals with silylenol ethers in the presence of Lewis acids,[6a] and has now reported the trapping of these aluminoxy acetals with silyl triflates to provide monosilyl acetals.[6b] Recently, Tietze reported an asymmetric variant of the Sakurai reaction (RCHO reactants), which may be explained by the intermediacy of such acetals.[7] In addition, the beneficial effect of Me$_3$SiOSiMe$_3$ on the yield and stereoselectivity of the TiCl$_4$-catalyzed Mukaiyama reaction of homochiral ketals may be due to the formation of acyclic monosilyl acetals *in situ*.[3b] Monosilyl acetals have been invoked by Cooke as intermediates in the reaction of esters with alkyllithiums in the presence of Me$_3$SiCl, but were not isolated, instead

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† Undergraduate participant in the National Science Foundation R.E.U. Program.

⊗ Abstract published in *Advance ACS Abstracts*, March 1, 1995.

(1) (a) Hosomi, A.; Endo, M.; Sakurai, H. *Chem. Lett.* **1976**, 941. (b) Sakurai, H.; Sasaki, K.; Hosomi, A. *Tetrahedron Lett.* **1981**, *22*, 745–8.

(2) For a review of allylsilane chemistry and references to earlier reviews, see: (a) Majetich, G. in *Organic Synthesis. Theory and Applications;* Hudlicky, T., Ed.; JAI Press: Greenwich, CT, 1989; Vol. 1, pp 173–240. For a review of acetals as synthons for carbonyl groups, see: (b) Seebach, D.; Imwinkelried, R.; Weber, T. *Modern Synth. Methods* **1986**, *4*, 125–259.

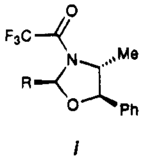
(3) (a) Johnson, W. S.; Edington, C.; Elliott, J. D.; Silverman, I. R. *J. Am. Chem. Soc.* **1984**, *106*, 7588–7591. (b) Silverman, I. R.; Edington, C.; Elliott, J. D.; Johnson, W. S. *J. Org. Chem.* **1987**, *52*, 180–183. (c) Kano, S.; Yokomatsu,T.; Iwasawa, H.; Shibuya, S. *Chem. Lett.* **1987**, 1531–1534. For useful examples of chiral allylsilane additions to achiral acetals, see: (d) Panek, J. S.; Yang, M. *J. Org. Chem.* **1991**, 5755–8 and ref 1 therein. (e) Marshall, J. A. *Chemtracts* **1992**, 75–98.

(4) (a) Denmark, S. E.; Willson, T. M. *J. Am. Chem. Soc.* **1989**, *111*, 3475–6. (b) Mori, I.; Ishihara, K.; Flippin, L. A.; Nozaki, K.; Yamamoto, H.; Bartlett, P. A.; Heathcock, C. H. *J. Org. Chem.* **1990**, *55*, 6107–6115.

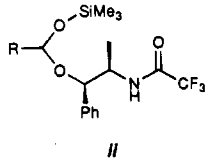
(5) Polt, R.; Peterson, M. A.; DeYoung, L. *J. Org. Chem.* **1992**, *57*, 5469–5480.

(6) (a) Kiyooka, S.: Shirouchi, M. *J. Org. Chem.* **1992**, *57*, 1–2. (b) Kiyooka, S.; Shirouchi, M.; Kaneko Y. *Tetrahedron Lett.* **1993**, *34*, 1491–4.

(7) Tietze invoked the intermediacy of *O,N*-acetals ***i*** which "interestingly" did not lead to the observed homoallylic ether products when subjected to the reaction conditions. *N,O*-Acetals ***i*** cannot therefore be the true reaction intermediates. We suggest that the monosilylacetals ***ii*** are more viable alternatives for Tietze's reaction intermediates. Tietze, L. F.; Dölle, A.; Schiemann, K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1372.

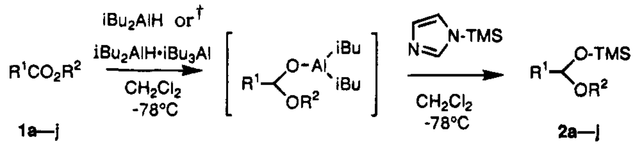


i



ii

Table 1



ester[a]	R^1	R^2	acetal	yield (%)
1a	$-[CH_2]_6CH_3$	$-CH_3$	**2a**	68
1b	$-[CH_2]_6CH_3$	$-CH_2CH_3$	**2b**	70
1c	$-CH_2CH(CH_3)_2$	$-CH_2CH_3$	**2c**	81
1d	$-CH_2CH_2CH_3$	$-CH_3$	**2d**	56[b]
1e	$\overset{S}{-}CH(CH_3)OCH_3$	$-CH_2CH_3$	**2e**	70
1f	$\overset{S}{-}CH(CH_3)OCH_2Ph$	$-CH_2CH_3$	**2f**	80
1g	$\overset{R}{-}CH(Ph)OCH_3$	$-CH_2CH_3$	**2g**	80
1h	$\overset{S}{-}CH(CH_3)N{=}CPh_2$	$-CH_2CH_3$	**2h**	71
1i	$\overset{S}{-}CH[CH_2CH(CH_3)_2]N{=}CPh_2$	$-CH_2CH_3$	**2i**	66
1j	$\overset{S}{-}CH[CH_2OSi(CH_3)_2tBu]N{=}CPh_2$	$-CH_3$	**2j**	34

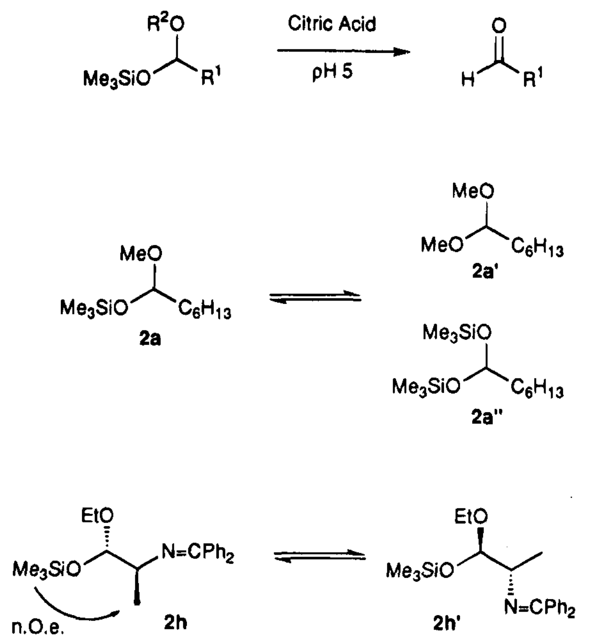
[a] iBu_2AlH for compounds **1a–g** and $iBu_2AlH{\cdot}iBu_3Al$ for **1h–j**.
[b] Compound **2d** is extremely volatile.

being hydrolyzed to the corresponding ketones.[8] Earlier, Ojima isolated monosilyl acetals as byproducts in the rhodium-catalyzed hydrosilylation of acrylic esters.[9] Since these mixed acetals show unique chemoselectivities, and may be of general synthetic utility, we would like to report our study of monosilyl acetals in the Hosomi–Sakurai reaction.

Reduction–Trapping. The results from several reduction–trapping experiments are illustrated in Table 1. Trapping did not proceed at all with TMS chloride or any of several other chlorosilanes examined, although trimethylsilyl triflate and triethylsilyl triflate were also effective in this regard. The reduction–trapping did proceed to completion in the presence of TMS-imidazole, however. Our interpretation of these results is that the imidazole moiety, and the triflate to a lesser extent, are capable of complexing with the highly Lewis-acidic alkylaluminum species,[10] thus promoting hydride attack and subsequent exchange of the proximal silicon for the aluminum (Al–O → Si–O). Essentially, one may regard the trapping reaction as the exchange of one Lewis acid (Al^+) for another (Si^+).

The conditions used for the hydride addition to the esters were adjusted to suit the substrate. For the simple aliphatic methyl and ethyl esters **1a–d** and α-alkoxy-substituted ethyl esters **1e–g**, a slight excess of iBu_2AlH was added to the ester at −78 °C in CH_2Cl_2, followed by addition of TMS-imidazole and reaction at −78 °C for several hours. Alternatively, the reaction could be allowed to warm to rt overnight with no effect on the yields. The order of addition was not important. For the esters bearing the reducible α-imino moieties, **1h–j**, the less reactive $iBu_2AlH{\cdot}iBu_3Al$ reagent was used in an analogous fashion. In all cases, the monosilyl acetal products **2a–j** were obtained as colorless oils which could be distilled *in vacuo,* or flash chromatographed, although not without some decomposition. The yields (Table 1) were generally good (66–80%) to moderate when the acetals contained additional functionality (34% for **2j**) or were volatile (56% for **1d**). Ethyl benzoate gave poor yields of the monosilyl acetal, providing good yields of benzyl alcohol under the same reaction conditions.

Scheme 1



The overall yields ($R^1CO_2R^2 \rightarrow R^1CH(OH)CH_2CH{=}CH_2$ or $R^1CH(OR^2)CH_2CH{=}CH_2$) improved when there was no purification of the intermediate monosilyl acetal. The mixed acetals were easily hydrolyzed with dilute H_3O^+, and exchange processes could be observed even in the absence of hydrolysis (Scheme 1). For example, solutions of **2a** in CH_2Cl_2 equilibrated to a mixture of the dimethylacetal **2a′**, monosilyl acetal **2a**, and bis-silyl acetal **2a″** upon standing over $MgSO_4$. Diastereomeric mixtures of monosilyl acetals initially isolated from trapping experiments were observed to equilibrate upon standing in CH_2Cl_2 solution or upon chromatography on SiO_2, presumably *via* epimerization of the mixed acetal center. An initial 7:1 mixture of **2h** and **2h′** favoring the *threo* (1*S*,2*S*) isomer was observed by NMR following reduction-trapping, presumably due to chelation-controlled hydride delivery. Assignment was made by comparison of NOE signals ($SiMe_3 \rightarrow Me$). This mixture equilibrated to ~1:1 over a period of several hours in $CDCl_3$. Generally, extraction with CH_2Cl_2, followed by washing with bicarbonate solution and drying with K_2CO_3, provided the monosilyl acetals as CH_2Cl_2 solutions which were sufficiently pure for use as electrophiles in the Hosomi–Sakurai reaction.

Hosomi–Sakurai Reaction. The experimental results obtained with the simple aliphatic monosilylacetals **2a–d** are illustrated in Table 2. In each case a 3-fold excess of $Me_3SiCH_2CH{=}CH_2$ and $SnCl_4$ was added sequentially to the monosilyl acetal in CH_2Cl_2 at −78 °C and allowed to react at −78 °C until the starting material had disappeared by TLC. At this point the reactions were quenched by the addition of MeOH followed by saturated $NaHCO_3$ and worked up in the usual fashion to provide alcohols **4**, or ethers **3**, depending on the identity of the ester moiety R^2. The reaction mixtures were very clean in all cases and were generally colorless.

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[8] Cooke, M. P. *J. Org. Chem.* **1986**, *51*, 951.

[9] Ojima, I.; Kogure, T.; Kumagai, M. *J. Organomet. Chem.* **1977**, *42*, 43–60.

[10] The role of complexation in producing a less aggregated, more active aluminum hydride species has been discussed previously in ref 5 (*cf.* the pseudo-ate complex).

Scheme 2

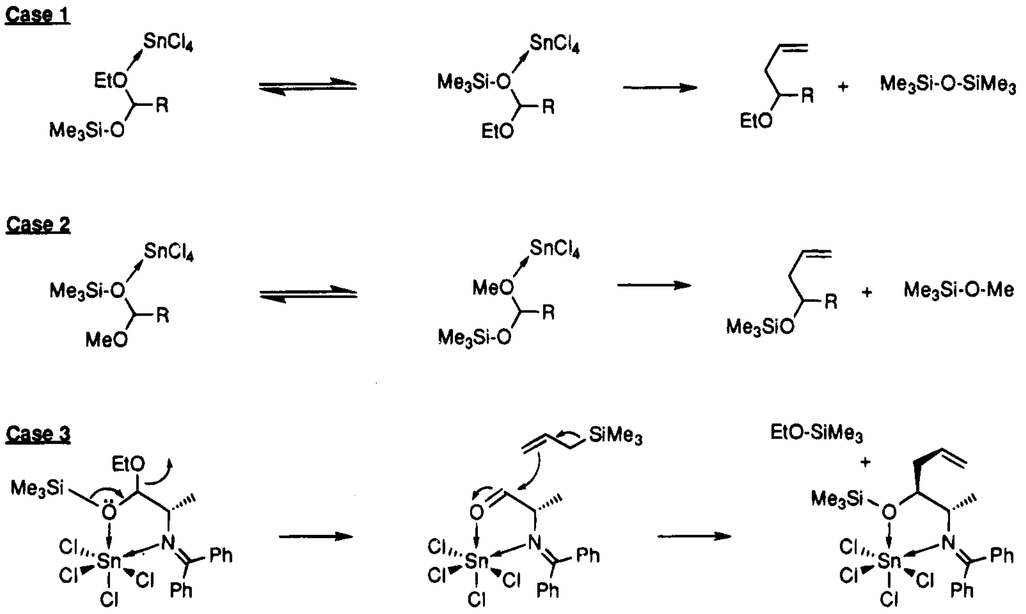
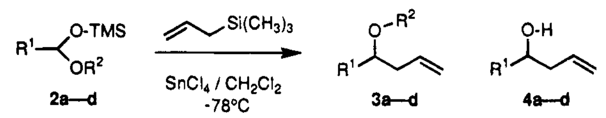


Table 2

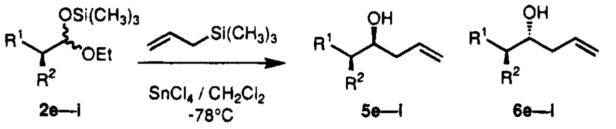


acetal	R^1	R^2	ether	yield (%)	alcohol	yield (%)
2a	$-[CH_2]_6CH_3$	$-CH_3$	**3a**	2	**4a**	82
					‖	
2b	$-[CH_2]_6CH_3$	$-CH_2CH_3$	**3b**	73	**4b**	3
2c	$-CH_2CH(CH_3)_2$	$-CH_2CH_3$	**3c**	70	**4c**	
2d	$-CH_2CH_2CH_3$	$-CH_3$	**3d**		**4d**	78

The chemical selectivity shown by these reactions is remarkable. In no case did we obtain significant amounts of ether products **3** from methyl esters or alcohol products **4** from simple ethyl esters. An attempt to optimize the reaction conditions was made using octaldehyde derivative **2b**. The reaction was run in tandem with several Lewis acids to provide the following results (Lewis acid/yield of **3b**): $Ti(OPr^i)_4$/0%, $Me_3SiOTfl$/40%, $TiCl_4$/70%, $SnCl_4$/73%, $AlCl_3$/82%, and $ZnCl_2$/90%. Although $ZnCl_2$ and $AlCl_3$ both gave better results than $SnCl_4$, for our purposes the ease of handling this liquid reagent outweighed the moderate decrease in yield. In fact, results showed that comparable yields could be obtained with $SnCl_4$ by increasing the reaction time. The stoichiometry did not seem to be particularly important. Reactions run with **2b** and 0.5, 1.0, 2.0, and 3.0 equiv of $SnCl_4$ (3 equiv $Me_3SiCH_2CH{=}CH_2$) showed comparable yields of **3b**.

Having found suitable conditions for the reaction, we next focused our attention on the chiral and more functionalized substrates. Johnson[11] has already demonstrated the utility of the Hosomi–Sakurai reaction for the synthesis of (3*S*,4*S*)- and (3*S*,4*R*)-statine, dipeptide isosteres. The results for the α-alkoxy monosilyl acetals **2e**–**g** and α-imino monosilyl acetals **2h** and **2i** are illustrated in Table 3. Interestingly, in none of these cases did we obtain any of the expected ether products. The diastereoselectivities for **5h** and **5i** are probably much higher than 2:1 and 9:1, and these ratios represent

Table 3



acetal	R^1	R^2	yields (%)	ratio[a] (**5**:**6**)
2e	$-CH_3$	$-OCH_3$	70 (**5e** + **6e**)	6:1[a]
2f	$-CH_3$	$-OCH_2Ph$	70 (**5f** + **6f**)	9:1[a]
2g	$-Ph$	$-OCH_3$	86 (**5g** + **6g**)	1.5:1[a]
2h	$-CH_3$	$-N{=}CPh_2$	65 (**5h**)[b]	>2:1
2i	$-CH_2CH(CH_3)_2$	$-N{=}CPh2$	89 (**5i**)[b]	>8:1

[a] Ratios determined by 250 MHz ^{1}H-NMR. [b] Isolated product.

a lower limit for the alkylation. Correlation to known derivatives of the diols[12] and amino alcohols[13] provided proof of the stereochemical configurations for all these compounds, with the exception of **5g**/**6g**. Furthermore, compound **5i** was converted to (3*S*,4*S*)-BOC-statine *via* oxidative cleavage of the olefin using published procedures[13c] (Scheme 3). Since the acetal **2g**, derived from (*S*)-mandelic acid, gave very poor (1.2:1) selectivity, and the isomers were not easily separated, no attempt was made to rigorously assign the configurations of **5g** and **6g**. The initial configuration at the acetal center did not seem to have any effect on the stereochemistry, which is not surprising, given the ease with which the monosilyl acetals underwent epimerization or scrambling (Scheme 1).

Imino alcohols **5h** and **5i** are particularly interesting due to their synthetic potential. Due to the imine–oxazolidine tautomerism,[14] the *threo*-isomers are readily separated *via* flash chromatography. The *erythro*-

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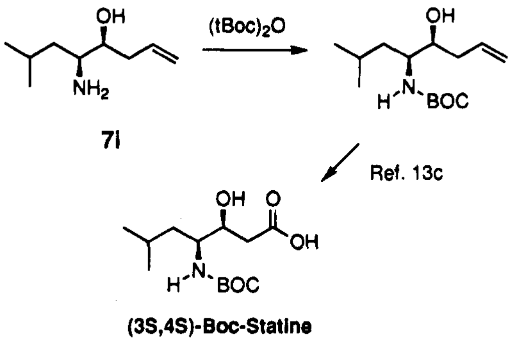
(11) Andrew, R. G.; Conrow, R. E.; Elliot, J. D.; Johnson, W. S.; Ramezani, S. *Tetrahedron Lett.* **1987**, *28*, 6535–8.

(12) For the (2*S*, 3*S*)-5-hexenediol systems: Heathcock, C. H.; Kiyooka, S.; Blumenkopf, T. A. *J. Org. Chem.* **1984**, *49*, 4214.

(13) For (2*S*, 3*S*)-2-amino-3-hydroxy-5-hexene and (5*S*,4*S*)-5-amino-4-hydroxy-7-methyl-1-octene: (a) Kano, S.; Yokomatsu, T.; Iwasawa, H.; Shibuya, S. *Chem. Lett.* **1987**, 1531–4. (b) Kiyooka, S.; Nakano, M.; Shiota, F.; Fujiyama, R. *J. Org. Chem.* **1989**, *54*, 5409–5411. The 1H-NMR spectra for the oxazolidine derivatives of both **2h** and **2i** showed vicinal coupling constants consistent with the reported structures. Compound **2i** was converted to BOC-statine via a published procedure: (c) Vara Prasad, J. V. N.; Rich, D. H. *Tetrahedron Lett.* **1990**, *31*, 1803–6.

(14) Wijayaratne, T.; Collins, N.; Li, Y.; Bruck, M.; Polt, R. *Acta Crystallogr.* **1993**, *B49*, 316–320.

Scheme 3



isomers exist mainly as the more polar imine form due to the *cis*-relationship of the substituents in the oxazolidine tautomer, resulting in vastly different R_f values for the two diastereomers. Because the yields quoted in Table 3 are for the pure isomers **5h** and **5i**, the ratios (2:1 and 8:1) represent only a lower limit for the diastereoselectivity. The same imine–oxazolidine tautomerism which facilitates separation complicates the analysis of crude NMR spectra. Traces of the ethyl ether products were observed in the reaction mixtures as well, and larger amounts (~5–10%) of the over-reduced primary alcohols were isolated as well. The over-reduced byproducts could be minimized by using the less reactive $iBu_2AlH{\cdot}iBu_3Al$ reagent in the reduction of the Schiff base esters.[5] The use of **5i** as a statine precursor has already been alluded to. A similar approach should provide taxol side chains and could be regarded as a general route to β-hydroxy γ-amino acids (GABA analogs).[15]

It is important to note that these mixed acetals combine the advantages of acetal starting materials with aldehydes. For example, like typical acetals the monosilyl acetals do not enolize, since we have seen no evidence for racemization in the derived homoallylic alcohols. On the other hand, removal of the alkyl ether is not a problem as with Johnson's homochiral acetals.[3] These very acid-labile monosilyl acetals may provide useful alternatives to the more refractory dialkyl acetals as carbonyl protecting groups.[16] The monosilylacetal **2b** was stable for prolonged periods (overnight) to PhMgBr in refluxing Et_2O.

Mechanistic Implications. Origin of the Chemoselectivity. Silyl ethers (alkoxy silanes) are generally regarded to be weaker Brønsted and Lewis bases than their corresponding alkyl ethers. Indeed, work by Keck *et al.* with $tBuSiMe_2SiO$-substituted aldehydes and allylstananes suggests that Si-Ö may *not be capable of chelation.*[17] This conclusion stems from the ability of Si to engage in π-bonding with its neighboring Ö[18] and is supported by the pioneering study done by Robert West *et al.*[19] which measured the effect ($\Delta\nu$) of various ethers and silyl ethers on the H–O stretching frequency of phenol and the H–N stretching frequency of pyrrole (Figure 2). This study showed that Et_2O had a stronger effect (larger $\Delta\nu$) than Me_3SiOEt on the H–O and H–N stretching frequencies, and concluded that dialkyl ethers were "...slightly stronger than alkoxysilanes." In a later, more quantitative study, West[19b] concluded that "Alkoxysilanes and ethers are so similar in base strength that the basicities for these classes overlap." All of these studies[18,19] support the notion that only one oxygen lone pair can engage in π-bonding with Si.

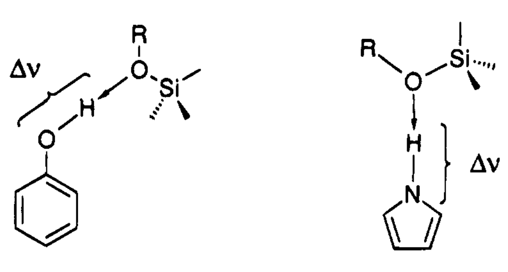


Figure 2.

Given the much longer bond length of the Si–O bond (~1.8 Å) relative to the C–O bond (~1.4 Å), and that the charge distribution in the Si–O bond is more polar (Si–O $\leftrightarrow$ Si^+ O^-), one could argue that Lewis acids might actually coordinate to silyl ethers preferentially. Any Lewis acid will have a larger steric parameter relative to H^+; thus, the longer Me_3Si–O bond length should decrease the steric interaction between the Lewis acid (metal) and the Me_3Si group, relative to Me_3C–O, known to be poor Lewis bases. In fact, for such bulky ethers this is precisely what West observed, with $Me_3SiOtBu$ showing a much larger $\Delta\nu$ than tBuOtBu. We believe that these studies overemphasize the steric interactions offered by phenol with its *ortho*-hydrogens relative to more typical Lewis acids such as $TiCl_4$ and $SnCl_4$ which may interact more strongly with the silyl ether. Thus, $Me_3SiÖ$– competes effectively for the metal against –ÖEt, but not –ÖMe, accounting for the mechanistic divergence.

Clearly, the branched acetal structures examined in this study may be regarded as "bulky" alkoxysilanes more analogous to $Me_3SiOtBu$ than to Me_3SiOEt. Furthermore, the results with the monosilylacetal alkylations support the notion (at least within this structural context) that $-OSiMe_3$ may be more basic than –OEt, and less basic than –OMe toward a variety of Lewis acids. The siloxy moiety functions as a leaving group with simple monosilylethyl acetals **2b** and **2c** (*case 1*, Scheme 2), implying that the Me_3SiO group is the most Lewis basic site in the molecule. The sterically accessible methoxy moiety functions as a leaving group with the simple

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(15) Greene, A. E.; Denis, J.; Correa, A. *J. Org.Chem.* **1991**, *56*, 6939–6942.

(16) *Protective Groups in Organic Synthesis*, 2nd ed.; Greene, T. W., Wuts, P. G. M., Eds.; John Wiley & Sons: New York, 1991; pp 178–220.

(17) Keck, G. E.; Andrus, M. B.; Romer, D. E. *J. Org. Chem.* **1991**, *56*, 417–423 and and ref 6 therein.

(18) For example, see: Shambayati, S.; Blake, J. F.; Wierschke, S. G.; Jorgensen, W. L.; Schreiber, S. L. *J. Am. Chem. Soc.* **1990**, *112*, 697–703 and references therein.

(19) (a) West, R.; Whatley, L. S.; Lake, K. J. *J. Am. Chem. Soc.* **1961**, *83*, 761–764, (b) West, R.; Wilson, L. S.; Powel, D. L. *J. Organomet. Chem.* **1979**, *178*, 5–9. The same trend was observed toward diborane (Lewis acid): (c) Sternbach, B.; MacDiarmid, A. G. *J. Am. Chem. Soc.* **1961**, *83*, 3384. West's work was also confirmed by workers who were apparently unaware of the earlier studies done in Wisconsin: (b) Stendel, V. R.; Popowski, E.; Kelling, H. *Z. Anorg. Allg. Chem.* **1983**, *506*, 195–202.

(20) (a) Sicher, J. Svoboda, M. Hrdà, M.; Rudinger, J.; Sorm, F. *Collect. Czech. Chem. Commun.* **1953**, *18*, 487–499. (b) Cram, D. J.; Kopecky, K. R. *J. Am. Chem. Soc.* **1959**, *81*, 2748. (c) Duhamel, P.; Duhamel, L.; Gralak, J. *Tetrahedron Lett.* **1972**, 2329. (d) Still, W. C.; McDonald, J. H. *Tetrahedron Lett.* **1980**, 1031. (e) Still, W. C.; Schneider, J. A. *Tetrahedron Lett.* **1980**, 1035. (f) Mulzer, J.; Angermann, A. *Tetrahedron Lett.* **1983**, *24*, 2843–6. (g) Reetz, M. T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 556. (h) Keck, G. E.; Boden, *Tetrahedron Lett.* **1984**, 265, 1879. (i) Iida, H.; Yamazaki, N.; Kibayashi, C. *J. Org. Chem.* **1986**, *51*, 3769–3771. (j) Frye, S. V.; Eliel, E. L.; Cloux, R. *J. Am. Chem. Soc.* **1987**, *109*, 1862–3. (k) Nichols, M. A.; McPhail, A. T.; Arnett, E. M. *J. Am. Chem. Soc.* **1991**, *113*, 6222–6233. (l) Reference 5.

monosilylmethylacetals **2a** and **2d** (*case 2*). With the more complex substrates **2e–j** which are capable of bidentate interaction with the Lewis acid (*case 3*), chelation with the ether moiety or the imine moiety and the Me_3SiO group explains the chemoselectivity and the stereoselectivity. This could be considered as a "cyclic Cram-like" transition state.[20] The intermediate "oxonium ion" for *case 3* may be regarded as an acetal which is simultaneously complexed by two Lewis acids[21] or may simply be Sn-catalyzed decomposition of the monosilyl acetal. Heathcock has attributed the stereocontrol of Li enolates to complexation with Me_3SiO ethers.[22]

It is impossible to determine whether these reactions display any S_N2-like character based on the information presently available, and we cannot rule out an S_N1-to-S_N2 switch as the acetal changes from EtO to MeO.[4] Jencks has presented kinetic evidence that acid-catalyzed acetal exchange can proceed *via* an S_N2 process.[23] There did not seem to be any relationship between the configuration of the monosilylacetal starting materials **2e–i** and the configuration of the homoallylic alcohols **5e–i**. Since the acetal configuration is not stable in the presence of Lewis acids, the mechanistic question is difficult to probe. Likewise, at this point it is impossible to say if transmetalation[24] of the allylsilane is involved or not. Regardless of our relative ignorance of the precise mechanistic details, we believe that this variation of the Hosomi–Sakurai reaction will prove to be useful, particularly since the starting materials are esters, since enolizable aldehydes are not generated, and since the intermediate monosilylacetals need not be isolated. Clearly, further synthetic and mechanistic studies are indicated.

Experimental Section

CH_2Cl_2 was distilled from P_2O_5 immediately prior to use. Hexane was distilled from $K^0/Ph_2C{=}O$ under argon. iBu_2AlH and iBu_3Al were purchased (Aldrich Co.) in metal cylinders and handled neat. Preparation and use of the $iBu_2AlH{\cdot}iBu_3Al$ reagent has been previously described.[5] Esters **1a–d** were prepared from the corresponding acids by reaction with MeOH or EtOH in the presence of $SOCl_2$.[25] Alkoxy esters **1e–g** were prepared from commercial ethyl (*S*)-(−)-lactate and ethyl (*R*)-(−)-mandelate using published procedures.[26] The imino esters **1h–j** were synthesized using O'Donnell's methodology.[5,27]

Reduction with iBu_2AlH (General Procedure). Alkyl esters **1a–g**[24,25] (1.0 mmol), *N*-TMS-imidazole (3.0 mmol), and 2.5 mL of dry CH_2Cl_2 were chilled to −78 °C under argon. iBu_2AlH (1.0 mmol) in 2 mL of dry hexane was added dropwise over 25 min. with stirring. After the reaction was judged to be complete by TLC (typically 8–12 h), the reaction mixture was poured into saturated $NaHCO_3$, extracted with additional CH_2Cl_2, and dried over K_2CO_3. The resulting CH_2Cl_2/hexane solution (90–95% pure **2** by ^{1}H-NMR) was suitable for further reaction. If desired, this material could be flash[28] chromatographed on SiO_2 with hexane/EtOAc/NEt_3 (*e.g.*, 500:8:1.5 for **2b**) to provide analytically pure material (see Table 1 for yields).

Reduction with $iBu_2AlH{\cdot}iBu_3Al$ (General Procedure). Imine[26] **1h–j** (1.0 mmol) and 4 mL of dry CH_2Cl_2 were chilled to −78 °C under argon in a goose-neck flask. The reagent $iBu_2AlH{\cdot}iBu_3Al$ (2.0 mmol) in 2 mL of hexane was added *via* syringe pump over 30 min down the side of the chilled flask.[5] The resulting yellow solution was stirred at −78 °C for 3 days. After reduction *N*-TMS-imidazole (3.0 mmol) in 2 mL of dry CH_2Cl_2 was added dropwise and then allowed to come to rt, resulting in a nearly colorless solution. After being stirred for 1 h at rt, the reaction was quenched with saturated $NaHCO_3$ solution and flash[27] chromatographed on SiO_2 with hexane/EtOAc to provide pure **2h–j** (see Table 1 for yields).

Allylsilane Addition (General Procedure). Monosilyl acetal **2** (0.50 mmol) and 3.0 mL of CH_2Cl_2 were chilled to −78 °C under argon. $H_2C{=}CHCH_2Si(CH_3)_3$ (1.5 mmol) was added, followed by dropwise addition of $SnCl_4$ (1.5 mmol) in 1 mL dry CH_2Cl_2. After 2 h, 3 mL of CH_3OH was added, and the reaction mixture warmed to rt, and poured into 1 N HCl (**2a–g**) or saturated $NaHCO_3$ (**2h** and **2i**). Extraction with CH_2Cl_2 and chromatography on SiO_2 with hexane/EtOAc provided ethers **3a–c** and alcohols **4–6** (see Tables 2 and 3 for yields).

1-Methoxy-1-(trimethylsiloxy)octane (**2a**). Colorless oil.

^{1}H-NMR (250 MHz) δ: 4.61, t, 4.8 Hz, SiOCHO, 3.28, s, OCH_3, 1.59–1.47, 2H, m, β-CH_2, 1.24, 10H, br s, $-(CH_2)_5-$, 0.83, t, 6.3–6.9 Hz, CH_3, 0.13, s, $Si(CH_3)_3$.

^{13}C-NMR (62.5 MHz): 99.47, SiOCHO, 54.00, OCH_3, 37.39, $OCH\mathit{C}H_2-$, 31.77, 29.45, 29.44, 24.38, 22.63, $-(CH_2)_5-$, 14.06, $CH_2\mathit{C}H_3$, 0.42, $Si(CH_3)_3$ ppm.

IR (NaCl film): 2926, 2857, 1467, 1384, 1251, 1144, 1054, 841, 753 cm^{-1}. MS (CI-methane): *m/z* 231 (M − 1), 2 (M − CH_3), 201 (M − OCH_3) base peak, 143 (M − $OSi(CH_3)_3$), 73 ($^+Si(CH_3)_3$).

1-Undecen-4-ol[29] (**4a** = **4b**). Colorless oil.

^{1}H-NMR (250 MHz) δ: 5.87–5.73, m, $H_2C{=}C\mathit{H}CH_2-$, 5.16–5.07, m, $\mathit{H}_2C{=}CH-$, 3.62, br quint, CHO, 2.34–2.23, m, $-\mathit{H}CHCH{=}$, 2.17–2.08, m, $-HC\mathit{H}CH{=}$, 1.56, br s, OH, 1.44, br s, $CH_2C\mathit{H}_2CHO$, 1.26, br s, $-(CH_2)_5-$, 0.86, t, 7.0–6.2 Hz, CH_3.

^{13}C-NMR (62.5 MHz): 134.90, $H_2C{=}\mathit{C}HCH_2-$, 118.03, $H_2\mathit{C}{=}CHCH_2-$, 70.65, CH-OH, 41.89, $H_2C{=}CH\mathit{C}H_2-$, 36.77, 31.77, 29.59, 29.24, 25.65, 22.63, $-(CH_2)_6-$, 14.07, CH_3 ppm.

IR (NaCl film): 3400 br, 2926, 2855, 912.

MS (CI-methane): *m/z* = 171 (M + 1), 129 (M − CH_2-$CH{=}CH_2$), 111 (M − H_2O − $CH_2CH{=}CH_2$), 97 (M − CH_2 − H_2O − $CH_2CH{=}CH_2$) base peak, 83 (M − CH_2 − CH_2 − H_2O − $CH_2CH{=}CH_2$).

1-Ethoxy-1-(trimethylsiloxy)octane, (2b). Colorless oil.

^{1}H-NMR (250 MHz) δ: 4.70, dd, 5.6, 5.0 Hz, SiOCHO, 3.68, dq, 9.2, 7.0, $O\mathit{H}CHCH_3$, 3.35, dq, 9.2, 7.0, $OHC\mathit{H}CH_3$, 1.70–1.45, 2H, m, β-CH_2, 1.24, br s, $-(CH_2)_5-$, 1.17, t, 7.1 Hz, $OCH_2C\mathit{H}_3$, 0.85, t, 6.9–6.3 Hz, CH_3, 0.13, s, $Si(CH_3)_3$.

^{13}C-NMR (62.5 MHz): 98.29, SiOCHO, 62.06, OCH_2-, 37.68, $OCH\mathit{C}H_2-$, 31.77, 29.41, 29.22, 24.51, 22.60, $-(CH_2)_5-$, 15.13, OCH_2CH_3, 14.05, CH_3, 0.48, $Si(CH_3)_3$ ppm.

IR (NaCl film): 2956, 2928, 2857, 1457, 1379, 1251, 1136, 1038, 870, 840 cm^{-1}.

MS (electron impact): *m/z* 245 (M − 1), 231 (M − CH_3), 201 (M − OCH_2CH_3) 97% of base peak, 157 (M − $OSi(CH_3)_3$) base peak.

4-Ethoxy-1-undecene (3b). Colorless oil.

^{1}H-NMR (250 MHz) δ: 5.89–5.72, m, $H_2C{=}C\mathit{H}CH_2-$, 5.08–4.98, m, $\mathit{H}_2C{=}CH-$, 3.60–3.36, 2H, m, $OC\mathit{H}_2CH_3$, 3.25, quintuplet, 5.8 Hz, 2.22, 2H, t, 7.0–5.9 Hz, $OCHC\mathit{H}_2CH{=}$, 1.42, br s, $CH_2C\mathit{H}_2CHO$, 1.25, br s, $-(CH_2)_5-$, 1.16, t, 7.0 Hz, $OCH_2C\mathit{H}_3$, 0.86, t, 6.7–6.3 Hz, CH_3.

^{13}C-NMR (62.5 MHz): 135.28, $H_2C{=}\mathit{C}HCH_2-$, 116.55, $H_2\mathit{C}{=}CHCH_2-$, 78,90, OCH, 64.24, OCH_2, 38.51, $H_2C{=}CH\mathit{C}H_2-$, 34.01, 31.84, 29.71, 29.30, 25.46, 22.66, $-(CH_2)_6-$, 15.60, $OCH_2\mathit{C}H_3$, 14.10, CH_3 ppm.

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(21) For evidence of simultaneous coordination of a carbonyl by two main-group Lewis acids, see: Sharma, V.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **1992**, *114*, 7931–3.

(22) Heathcock, C. H.; Pirrung, M. C.; Lampe, J.; Buse, C. T.; Young, S. D. *J. Org. Chem.* **1981**, *46*, 2290–2300, *inter alia*.

(23) (a) Amyes, T. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1989**, *111*, 7888–7890. (b) Amyes, T. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1989**, *111*, 7900–7909.

(24) Keck, G. E.; Andrus, M. B.; Castellino, S. *J. Am. Chem. Soc.*, **1989**, *111*, 8136–8141.

(25) Brenner, M.; Huber, W. *Helv. Chim. Acta.* **1953**, *36*, 1109–15.

(26) Brouillette, W. J.; Grunewald, G. L. *J. Med. Chem.* **1984**, *27*, 202–206.

(27) O'Donnell, M. J.; Polt, R. L. *J. Org. Chem.* **1982**, *47*, 2663–2666.

(28) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

(29) (a) Boldini, G. P.; Savoia, D.; Tagliavini, E.; Trombini, C.; Umani-Rouchini, A. *J. Organomet. Chem.* **1985**, *280*, 307. (b) Cazes, B.; Verniere, C.; Gorè, J. *Synth. Commun.* **1983**, *13*, 73.

IR (NaCl film): 2956, 2928, 2857, 1641, 1458, 1442, 1344, 1248, 1112, 911 cm^{-1}.

MS (CI-methane): *m/z* 199 (M + 1), 157 (M − CH$_2$-CH=CH$_2$).

1-Ethoxy-1-(trimethylsiloxy)-3-methylbutane (**2c**). Colorless oil.

^{1}H-NMR (250 MHz) δ: 4.77, dd, 6.3, 4.8 Hz, SiOCHO, 3.71−3.61, m, O*H*CHCH$_3$, 3.42−3.29, m, OHC*H*CH$_3$, 1.80−1.62, m, (CH$_3$)$_2$C*H*CH$_2$, 1.57−1.47, m, (CH$_3$)$_2$CH*H*CH−, 1.41−1.30, m, (CH$_3$)$_2$CHHC*H*−, 1.17, t, 7.1 Hz, OCH$_2$C*H*$_3$, 0.87, d, 6.7 Hz, (C*H*$_3$)$_2$CH−, 0.13, s, Si(CH$_3$)$_3$.

^{13}C-NMR (62.5 MHz): 97.09, SiOCHO, 62.03, O*C*H$_2$CH$_3$, 46.60, (CH$_3$)$_2$CH*C*H$_2$, 24.21, (CH$_3$)$_2$*C*HCH$_2$, 22.92, 22.63, (*C*H$_3$)$_2$-CH−,15.16, OCH$_2$*C*H$_3$, 0.52, Si(CH$_3$)$_3$ ppm.

IR (NaCl film): 2958, 1252, 1138, 1063, 1037, 842 cm^{-1}.

MS (CI-methane): *m/z* 203 (M − 1), 189 (M − CH$_3$), 159 (M − OCH$_2$CH$_3$) base peak.

4-Ethoxy-6-methylhept-1-ene (**3c**). ^{1}H-NMR (250 MHz) δ: 5.89−5.72, m, H$_2$C=C*H*CH$_2$−, 5.08−5.00, m, *H*$_2$C=CH−, 3.57, 1H, dq, 9.1, 6.9 Hz, O*H*CHCH$_3$, 3.46−3.29, 2H, m, O*H*CHCH$_3$ + CHO, 2.22, 2H, t, 6.6−6.0 Hz, OCHC*H*$_2$CH=, 1.72, 1H, octet, 6.9 Hz, (CH$_3$)$_2$C*H*CH$_2$, 1.47−1.34, 1H, m, (CH$_3$)$_2$CH*H*CH, 1.24−1.07, 1H, m, (CH$_3$)$_2$CHHC*H*, 1.16, t, 6.9 Hz, OCH$_2$C*H*$_3$, 0.88, d, 6.7 Hz, (C*H*$_3$)CH(CH$_3$), 0.87, d, 6.6 Hz, (CH$_3$)CH(C*H*$_3$).

^{13}C-NMR (62.5 MHz APT): 135.17, H$_2$C=*C*HCH$_2$−, 116.70, H$_2$*C*=CHCH$_2$−, 76.97, CHO, 64.18, CH$_2$O, 43.60, (CH$_3$)$_2$-CH*C*H$_2$, 38.80, H$_2$C=CH*C*H$_2$−, 24.51, (CH$_3$)$_2$*C*HCH$_2$, 23.31, 22.36, (*C*H$_3$)$_2$CH−, 15.63, OCH$_2$*C*H$_3$.

IR (NaCl film): 2956, (2360), 1369, 1248, 1113, 911, 837 cm^{-1} (CDCl$_3$ impurity).

1-Methoxy-1-(trimethylsiloxy)butane (**2d**). Colorless oil.

^{1}H-NMR (250 MHz) δ: 4.61, t, 5.2 Hz, OCHO, 3.27, s, OCH$_3$, 1.55−1.46, 2H, m, β-CH$_2$, 1.37−1.28, 2H, m, γ-CH$_2$, 0.87, t, 7.4 Hz, CCH$_3$, 0.10, s, −Si(CH$_3$)$_3$.

^{13}C-NMR (62.5 MHz): 99.20, OCHO, 53.89, OCH$_3$, 39.42, OCH*C*H$_2$−, 17.63, −*C*H$_2$CH$_3$, 13.86, C*C*H$_3$, 0.34, −Si(CH$_3$)$_3$ ppm.

IR (NaCl film): 2957, 2873, 2826, 1465, 1383, 1251, 1196, 1150, 1124, 1059, 1031, 990, 911, 842, 753 cm^{-1}.

MS (CI-methane): *m/z* 175 (M − 1), 161 (M − CH$_3$), 145 (M − OCH$_3$) base peak.

1-Hepten-4-ol[29,30] (**4d**). Colorless oil.

^{1}H-NMR (250 MHz) δ: 5.89−5.73, sym. m, H$_2$C=C*H*CH$_2$−, 5.16−5.08, m, *H*$_2$C=CH−, 3.64, 1H, sym m, CHO, 2.34−2.23, 1H, m, H$_2$C=CH*H*CH−, 2.17−2.05, 1H, m, H$_2$C=CHHC*H*−, 1.59, br s, −OH + H$_2$O, 1.50−1.30, m, −(CH$_2$)$_2$−, 0.91, t, 7.0 Hz, −CH$_3$.

^{13}C-NMR (62.5 MHz): 134.90, −CH=, 118.08, =CH$_2$, 70.35, CHOH, 41.92, −*C*H$_2$CH=, 38.92, HOCH*C*H$_2$CH$_2$−, 18.83, −*C*H$_2$CH$_3$, 14.04, −CH$_3$ ppm.

IR (NaCl film): 3347 br, 2905, 1632, 1472, 1451, 1365, 1323, 1269, 1152, 1040, 1004, 929 cm^{-1}.

MS (CI-methane): *m/z* 116 (M + 1), 114 (M − 1), 97 (M + 1 − H$_2$O) base peak, 73 (M − CH$_2$CH=CH$_2$).

(2*S*)-1-Ethoxy-2-methoxy-1-(trimethylsiloxy)propane (**2e**). Colorless oil.

^{1}H-NMR (250 MHz) δ: 4.55, d, 4.8 Hz, OCHO, 3.70, dq, 9.2, 7.2 Hz, CH$_3$HC*H*O, 3.37, dq, 9.2, 7.2 Hz, CH$_3$*H*CHO, 3.34, s, −OCH$_3$, 3.13, dq, 4.8, 6.2 Hz, CH$_3$C*H*CH−, 1.17 δ, t, 7.2 Hz, −CH$_2$C*H*$_3$, 1.10, d, C*H*$_3$CH−, 0.13, s, −Si(CH$_3$)$_3$.

(2*S*,3*S*)-2-Methoxy-5-hexen-3-ol (**5e**). Colorless oil.

^{1}H-NMR (250 MHz) δ: 5.94−5.76, sym m, H$_2$C=C*H*CH$_2$−, 5.14−5.04, m, *H*$_2$C=CH−, 3.48−3.41, m, C*H*OH, 3.35, s, −OCH$_3$, 3.16, quint, CH$_3$C*H*CH−, 2.67, br s, −OH, 2.37−2.08, m, CHC*H*$_2$CH=, 1.10, d, 6.2 Hz, −CHC*H*$_3$.

(2*S*)-1-Ethoxy-2-(phenylmethoxy)-1-(trimethylsiloxy)-propane (**2f**). Colorless oil.

^{1}H-NMR (250 MHz) δ: 7.40−7.26, m, 5H, Ph−, 4.64−4.60, dd, PhCH$_2$O−, 4.63, d, 4.8 Hz, OCHO, 3.74−3.37, m, −OC*H*$_2$-CH$_3$ + CC*H*OCH$_2$Ph, 1.24, d, 5.6 Hz, −CHC*H*$_3$, 1.20, t, 5.8 Hz, −OCH$_2$C*H*$_3$, 0.14, s, −Si(CH$_3$)$_3$.

(2*S*,3*S*)-2-(Phenylmethoxy)-5-hexen-3-ol[12] (**5f**). Colorless oil.

^{1}H-NMR (250 MHz) δ: 7.40−7.25, m, 5H, Ph−, 5.97−5.80, m, H$_2$C=C*H*CH$_2$−, 5.18−5.06, m, *H*$_2$C=CH−, 4.66, d, 11 Hz, −OHC*H*Ph, 4.44, d, −O*H*CHPh, 3.58−3.50, m, HOC*H*−, 3.45, quint, CH$_3$C*H*CH−, 2.58, br s, −OH, 2.39−2.15, m, CHC*H*$_2$-CH=, 1.21, d, 6.1 Hz, CHC*H*$_3$.

(2*R*)-1-Ethoxy-2-methoxy-2-phenyl-1-(trimethylsiloxy)-ethane (**2g**). Colorless oil. Note: 2:3 mixture of diastereomers.

^{1}H-NMR (250 MHz) δ: 7.30, br s, 5H, Ph−, 4.75, 0.4H, d, 6.1 Hz, OCHO, 4.67, 0.6H, d, 5.6 Hz, OCHO, 4.07, 0.4H, d, 6.1 Hz, OCHPh, 3.99, 0.6 H, d, 5.6 Hz, OCHPh, 3.78−3.42, m, 3H, OC*H*$_2$CH$_3$, 3.25, s, 1.2H, OCH$_3$, 3.24, s, 1.8H, OCH$_3$, 3.27−3.13, m, 1H, OC*H*$_2$CH$_3$, 1.23, 1.2H, t, 7.0 Hz, −OCH$_2$C*H*$_3$, 0.99, 1.8H, t, 7.0 Hz, −OCH$_2$C*H*$_3$, 0.13, 5.4H, s, Si(CH$_3$)$_3$, −0.16, 3.6H, s, Si(CH$_3$)$_3$.

(1*R*)-1-Methoxy-1-phenyl-4-penten-2-ol (5g + 6g mixture). Colorless oil. Note: 2:3 mixture of diastereomers.

^{1}H-NMR (250 MHz) δ: 7.39−7.24 , 5H, Ph, 5.88−5.73, m, H$_2$C=C*H*CH$_2$−, 5.12−4.96, m, *H*$_2$C=CH−, 4.13, 0.4H, d, 5.2 Hz, PhC*H*OCH$_3$, 3.95, 0.6H, d, 7.8 Hz, PhC*H*OCH$_3$, 3.79, 3.74, two ddd, 1H, HOC*H*, 3.25, s, 1.2H, OCH$_3$, 3.21, s, 1.8H, OCH$_3$, 2.48, br s, OH, 2.27−1.92, m, CHC*H*$_2$CH=.

^{13}C-NMR (62.5 MHz): 138.16, 1.37.96, quat Ph, 134.96, 134.52, 128.44, 128.34, 128.26, 127.98, 127.7, Ph and −CH=, 117.49, 117.18, =CH$_2$, 87.09, 86.14, PhCHO, 74.38, 73.77, −CHOH, 57.03, 56.68, OCH$_3$, 36.65, 36.54, −CH$_2$− ppm.

IR: ~3500 br, 3072, 2970, 2931, 2908, 1637, 1442, 1099, 904 cm^{-1}.

MS (CI-methane): *m/z* 175 (M + 1 − H$_2$O).

(2*S*)-1-Ethoxy-2-[*N*-(diphenylmethylene)amino]-1-(trimethylsiloxy)propane (**2h**). Colorless oil. Note: 6:1 mixture of diastereomers.

^{1}H-NMR (250 MHz) δ: 7.65−7.12 δ, m, Ph$_2$C, 4.81, d, 6.4 Hz, OCHO, 3.80−3.59, 1H, m, O*H*CHCH$_3$, 3.53−3.40, 2H, m, OHC*H*CH$_3$ + =NC*H*, 1.14, t, 7.0 Hz, OCH$_2$C*H*$_3$, 1.12, d, 6.4 Hz, CH-CH$_3$, 0.15, 6H, s, CH$_3$Si(C*H*$_3$)$_2$, 0.09, 3H, s, C*H*$_3$Si-(CH$_3$)$_2$.

^{13}C-NMR (62.5 MHz): 137.20, quat Ph, 129.67, 128.43, 128.35, 127.96, Ph, 101.48, SiOCHO, 63.00, O*C*H$_2$CH$_3$, 62.66, CHN=, 17.96, OCH$_2$*C*H$_3$, 15.38, CH$_3$CH, 0.65, Si(CH$_3$)$_3$ ppm.

$[\alpha]_D = +33.6°$ ($c = 1.00$, CHCl$_3$).

HRMS (CI − isobutane): 356.2035 obsd (356.2046 calcd for $C_{21}H_{30}NSiO_2^+$).

(2*S*,3*S*)-2-[*N*-(Diphenylmethylene)amino]-5-hexen-3-ol (**5h**). Note: 4:1 mixture of tautomers oxazolidine:Schiff base.

^{1}H-NMR (250 MHz) δ: 7.83−7.15, m, Ph$_2$C, 5.94−5.78, m, H$_2$C=C*H*CH$_2$−, 5.12−4.99, m, *H*$_2$C=CH−, 3.58, ddd, 7.9, 6.8, 5.4 Hz, CHO, 2.98, dq, 7.9, 6.4 Hz, CHN, 2.36−2.12, m, C*H*$_2$-CH= + OH/NH, 1.20, 2.46H, d, 6.3 Hz, CH$_3$ oxazolidine tautomer, 1.15, 0.54H, d, 6.5 Hz, CH$_3$ imine tautomer.

^{13}C-NMR (62.5 MHz): 137.54, Ph$_2$*C*, 132.35, −CH=, 129.99, 128.22, 127.88, 127.33, 127.02, 126.24, 125.50, Ph, 116.67, =CH$_2$, 84.34, CHO, 59.10, CHN, 38.27, CH$_2$, 17.35, CH$_3$ ppm.

IR (NaCl film): 3297 weak, 3061, 3026, 2975, 2927, (2359), 1661, C=N str, 1489, 1449, 1318, 1277, 1232, 1091, 959 cm^{-1} (CDCl$_3$ imp).

$[\alpha]_D = +70.5°$ ($c = 1.80$, CHCl$_3$).

MS (CI-methane): *m/z* 280 (M + 1).

(2*S*,3*S*)-2-Amino-5-hexen-3-ol[13a,b] **(7h).** Waxy solid, mp 40.5−43.0 °C.

^{1}H-NMR (250 MHz) δ: 5.97−5.81, m, H$_2$C=C*H*CH$_2$−, 5.17−5.07, m, *H*$_2$C=CH−, 3.28, ddd, 6.3, 6.5, 7.7 Hz, C*H*OH, 2.79, quintuplet, 6.4 Hz, C*H*NH$_2$, 2.39−2.29, 1H, m, −*H*CHCH=, 2.21−2.09, 1H, m, −HC*H*CH=, 1.96, 3H, br s, OH + NH$_2$, 1.11, d, 6.5 Hz, CH$_3$.

^{13}C-NMR (62.5 MHz): 134.73, −CH=, 117.22, =CH$_2$, 74.35, CHOH, 50.71, CHNH$_2$, 38.46, CH$_2$, 19.53, CH$_3$ ppm.

IR (NaCl plate): 3353, br, 1641, 1574, 1446, 1372, 1067, 991, 913 cm^{-1}.

$[\alpha]_D = +10.4°$ ($c = 1.02$, CHCl$_3$).

HRMS (CI − methane): *m/z* 116.1066 obsd (116.1075 calcd for $C_6H_{14}NO^+$).

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(30) Herold, T.; Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 768.

(2*S*)-1-Ethoxy-2-[*N*-(diphenylmethylene)amino]-4-methyl-1-(trimethylsiloxy)pentane (2i). Colorless oil. Note: 3:1 mixture of diastereomers.

^{1}H-NMR (250 MHz) δ: 7.62−7.22, m, 10H, Ph, 4.84, 0.25H, d, 6.6 Hz, OCHOSi, 4.81, 0.75H, d, 6.4 Hz, OCHOSi, 3.75−3.50, m, 2H, $\mathrm{O}\mathit{H}\mathrm{CHCH_3}$ + $=\mathrm{NC}\mathit{H}-$, 3.45−3.30, m, 1H, $\mathrm{OHC}\mathit{H}\mathrm{CH_3}$, 1.60−1.30, m, 3H, $\mathrm{(CH_3)_2}$-CHCH_2-, 1.16, t, 7.0 Hz, $\mathrm{OCH_2}\mathit{CH}_3$, 0.78, d, 6.5H, $\mathit{CH}_3\mathrm{CHCH_3}$, 0.38, d, 6.5H, $\mathrm{CH_3CHC}\mathit{H}_3$, 0.14, 6H, s, $\mathrm{CH_3Si(C}\mathit{H}_3)_2$, 0.04, 3H, s, $\mathrm{C}\mathit{H}_3\mathrm{Si(CH_3)_2}$.

^{13}C-NMR (62.5 MHz): 167.72, C=N, 140.72, 137.02, quat Ph, 129.4, 128.82, 128.44, 127.95, 127.85, 127.74, Ph, 101.43/100.69, OCHO, 65.47/64.66, $=\mathrm{N}\mathit{C}\mathrm{H}-$, 63.97/62.71, $\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$, 41.36/41.22 $\mathrm{(CH_3)_2CH}\mathit{C}\mathrm{H_2}-$, 24.62/24.27, 24.12, 22.10/21.78, $(\mathit{C}\mathrm{H_3})_2\mathrm{CH}-$ + $\mathrm{(CH_3)_2}\mathit{C}\mathrm{H}-$, 15.30/15.10, $\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$, 0.86/0.48, $\mathrm{Si(CH_3)_3}$.

(4*S*,5*S*)-5-[*N*-(Diphenylmethylene)amino]-7-methyl-1-octen-4-ol (5i). Colorless oil. Note: almost exclusively oxazolidine tautomer.[5]

^{1}H-NMR (250 MHz) δ: 7.72−7.19, m, 10H, Ph, 5.99−5.80, m, $\mathrm{H_2C{=}C}\mathit{H}\mathrm{CH_2}-$, 5.13−5.01, m, $\mathit{H}_2\mathrm{C{=}CH}-$, 3.57, dt, 6.0, 5.7 Hz, $\mathrm{CH_2C}\mathit{H}\mathrm{O}-$, 2.94, dt, 7.7, 7.4 Hz, $\mathrm{CH_2C}\mathit{H}\mathrm{NH}-$, 2.19, 2H, dd, 6.0, 6.9 Hz, $\mathrm{OCHC}\mathit{H}_2\mathrm{CH}{=}$, 1.85, 1H, apparent septet, 6.7 Hz, $\mathrm{CH_2C}\mathit{H}\mathrm{(CH_3)_2}$, 1.27, 2H, dd, 7.1, 7.0, $\mathrm{NCHC}\mathit{H}_2\mathrm{CH(CH_3)_2}$, 0.91, d, 6.6 Hz, $\mathrm{C}\mathit{H}_3\mathrm{CHCH_3}$, 0.89, d, 6.6 Hz, $\mathrm{CH_3CHC}\mathit{H}_3$, 0.12, 6H, s, $\mathrm{CH_3Si(C}\mathit{H}_3)_2$, 0.03, 3H, s, $\mathrm{C}\mathit{H}_3\mathrm{Si(CH_3)_2}$.

(4*S*,5*S*)-5-Amino-7-methyl-1-octen-4-ol[13a,b,31] **(7i)**. Colorless oil. ^{1}H-NMR (250 MHz) δ: 5.87−5.76, m, $\mathrm{H_2C{=}C}\mathit{H}\mathrm{CH_2}-$, 5.09−5.02, m, $\mathit{H}_2\mathrm{C{=}CH}-$, 3.25, dt, 5.1, 7.3 Hz, $\mathrm{CH_2C}\mathit{H}\mathrm{O}-$, 2.61, apparent quint, 4.5−5.1 Hz, $\mathrm{CH_2C}\mathit{H}\mathrm{NH}-$, 2.29−2.08, 2H, m, $\mathrm{OCHC}\mathit{H}_2\mathrm{CH}{=}$, 1.87, 3H, br s, OH + $\mathrm{NH_2}$, 1.66, 1H, m, $\mathrm{CH_2C}\mathit{H}\mathrm{(CH_3)_2}$, 1.29−1.06, m, $\mathrm{CHC}\mathit{H}_2\mathrm{CH(CH_3)_2}$, 0.87, d, 6.6 Hz, $\mathrm{C}\mathit{H}_3\mathrm{CHCH_3}$, 0.82, d, 6.5 Hz, $\mathrm{CH_3CHC}\mathit{H}_3$.

^{13}C-NMR (62.5 MHz APT): 135.05, −CH=, 117.26, $=\mathrm{CH_2}$, 73.34, CHOH, 52.50, $\mathrm{CHNH_2}$, 43.63, $\mathit{C}\mathrm{H_2CH}{=}$, 38.83, $\mathit{C}\mathrm{H_2CH(CH_3)_2}$, 24.71, $\mathrm{CH_3}\mathit{C}\mathrm{HCH_3}$, 23.72, $\mathit{C}\mathrm{H_3CHCH_3}$, 21.58, $\mathrm{CH_3CH}\mathit{C}\mathrm{H_3}$ ppm.

(2S)-3-(*tert*-Butyldimethylsiloxy)-2-[*N*-(diphenylmethylene)amino]-1-methoxy-1-(trimethylsiloxy)propane (2j). Colorless oil. Note: data provided for one diastereomer (ratio highly variable (4:1−1:10) in various runs).

^{1}H-NMR (250 MHz) δ: 7.65−7.23, m, $\mathrm{Ph_2C}$, 4.79, d, 6.1 Hz, SiOCHO, 3.86−3.82, 2H, m, $\mathrm{SiOCH_2}$, 3.71−3.66, 1H, m, NCH, 3.33, s, $\mathrm{OCH_3}$, 0.84, s, $\mathrm{C(CH_3)_3}$, 0.07, $\mathrm{Si(CH_3)_2}$, 0.04, $\mathrm{SiCH_3}$, 0.00, $\mathrm{SiCH_3}$, −0.04, $\mathrm{SiCH_3}$.

^{13}C-NMR (62.5 MHz APT): 168.80, C=N, 140.24, 137.02, quat Ph, 129.66, 129.55, 128.76, 128.64, 128.52, 128.43, 127.99, 127.95, 127.83, 127.69, Ph, 99.50, OCHO, 68.71, $\mathrm{OCH_2}$, 64.15, CHN, 54.83, $\mathrm{OCH_3}$, 25.95, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$, 18.37, $\mathrm{Si}\mathit{C}\mathrm{(CH_3)_3}$, 0.43, −0.20, −5.00, $\mathrm{SiCH_3}$ ppm.

Acknowledgment. We would like to thank Dr. Peter G. M. Wuts of the Upjohn Co. for useful scientific discussions and gratefully acknowledge the National Science Foundation for financial support of this work (CHE-9201112).

Supplementary Material Available: ^{1}H- and/or ^{13}C-NMR spectra are available for all the acetals **2a−j**, ethers **3b** and **3c**, alcohols **4a,b**, **d**, **5e−5i**, **6e−6g**, and amino alcohols **7h** and **7i** (34 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.

JO941962P

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(31) Luly, J. R.; Dellaria, J. F.; Plattner, J. J. *Eur. Pat. Appl.* E. P. 172,346 (C. I. C07K5/00), 26 Feb 1986.