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STEREOSELECTIVE INTRAMOLECULAR ALLYLSILANE ADDITIONS TO CHIRAL ALDEHYDES

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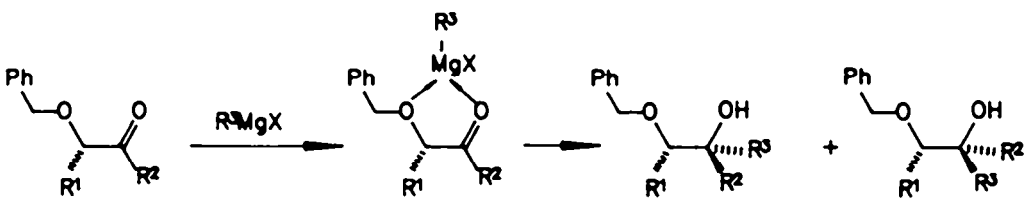
Abstract

The sense of 1,3-asymmetric induction in the $TiCl_4$ mediated allylsilane addition of O-(allyl)silyl protected aldehydes 14 is opposite (>90% syn selectivity) to that of the previously reported reaction of the O-benzyl protected analogs 7 with allyltrimethylsilane (>90% anti selectivity). Crossover experiments show that strict intramolecularity pertains, suggesting an intramolecular allylsilane addition as depicted in 15. Surprisingly, the switch from $TiCl_4$ to $SnCl_4$ results in the reversal of diastereofacial selectivity and in an intermolecular allyl transfer mechanism. α-Chiral β-silyloxy aldehydes of the type 35 are not very well suited for stereoselective allylations.

INTRODUCTION

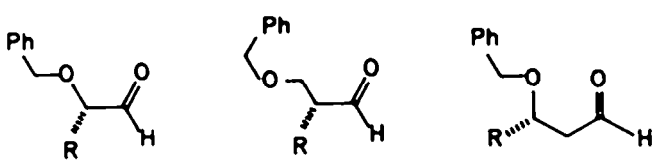
The problem of 1,2- and 1,3-asymmetric induction in Grignard reactions of α- and β-alkoxy carbonyl compounds was first studied by Cram[1]. α-Alkoxy ketones 1 were shown to react with chelation-control to produce the adducts 3 preferentially, a process that was later optimized by Still[2] (3:4 ≥ 99:1). Chelates of the type 2 were postulated to be the reactive intermediates which are attacked from the sterically less hindered side[1]. Here, as in the rest of the publication, only one enantiomer is shown, although racemic materials were used.



1 2 3 4

99 : 1

With a few exceptions, this method does not extend to the analogous α-alkoxy aldehydes 5[2,3]. In the case of α-chiral β-alkoxy aldehydes[4], cuprates allow for chelation controlled Grignard-type additions, but β-chiral β-alkoxy aldehydes react stereorandomly[4]. Until 1983 no general method for chelation-controlled aldol additions in any of these cases was available. The same applies to the reversal of diastereofacial selectivity (non-chelation controlled Grignard and aldol additions).

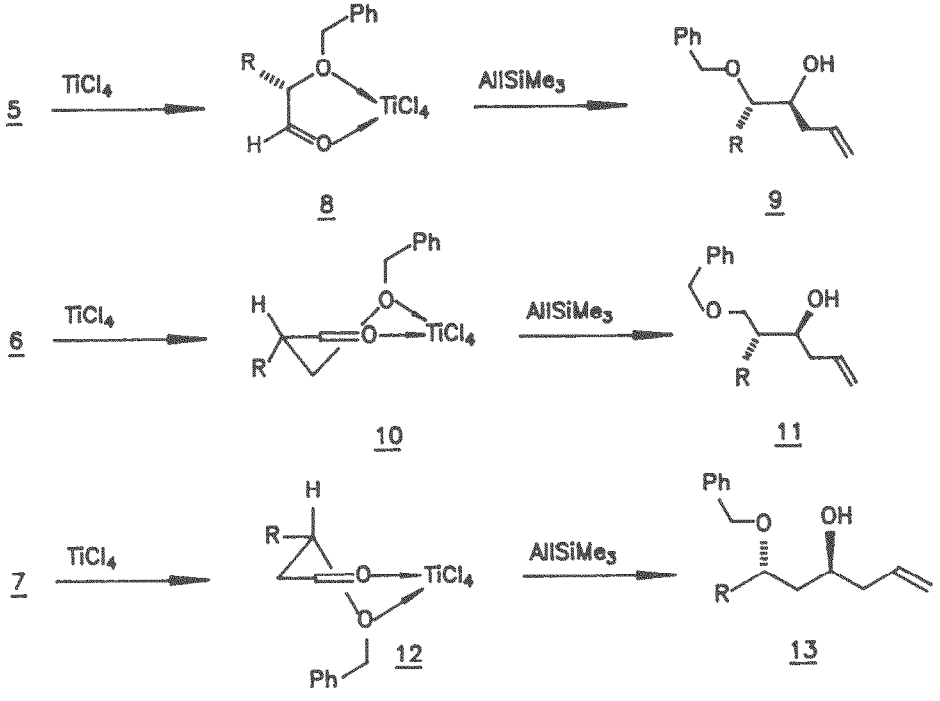


5 6 7

We have previously offered solutions to some of these problems on the basis of the following strategies[5]:

1) Use of the Lewis acidic reagents such as CH_3TiCl_3 which react with 5-7 to form chelation controlled adducts[6-8].

2) Use of a Lewis acid of the type $TiCl_4$, $SnCl_4$ or $MgBr_2$ to form stable chelates such as 8, 10, or 12 followed by the addition of such C-nucleophiles as dialkylzinc, allylsilanes and enolsilanes producing chelation-controlled adducts[5-7], a methodology that has since been applied successfully on numerous occasions[9].



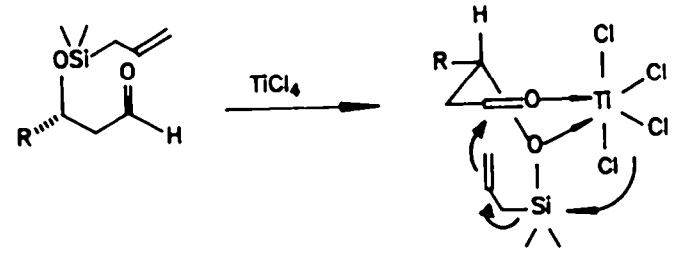
3) Reactions of $RTi(OiPr)_3$ (which are less Lewis acidic than $RTiCl_3$) with chiral α-alkoxy aldehydes and ketones to produce non-chelation controlled adducts[7-8,10-11].

4) Activation of α-chiral α- and β-alkoxy aldehydes by BF_3 followed by addition of allyl- and enolsilanes to afford non-chelation controlled adducts[11].

5) Use of ammonium enolates to form non-chelation controlled aldols[11].

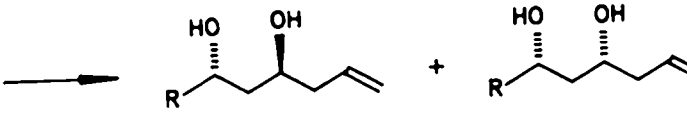
In addition to these methods, reagent control[12] in principle should allow for either chelation- or non-chelation control. This strategy has been applied elegantly by Braun[13] and Schöllkopf[14] in certain aldol additions to chiral alkoxy aldehydes. However, reagent control generally means a higher level of complexity and cost due to the requirement of optically active reagents.

Several years ago we devised yet another approach based on intramolecular allylsilane additions of chiral siloxy aldehydes 14[15]. We speculated that $TiCl_4$ could form a chelate such as 15, thereby reducing the number of degrees of freedom in the aldehyde and simultaneously triggering allyl addition intramolecularly. The direction of attack was expected to be opposite to that observed in intermolecular allylsilane additions to the related chelates 12. Indeed, in preliminary experiments reversal of diastereofacial selectivity was observed (anti isomer:syn isomer=16:17=<10: >90)[15]. In the present paper we describe the synthetic scope as well as mechanistic aspects of this novel reaction type.



14 a : R = CH_3
b : R = n-C_4H_9

15



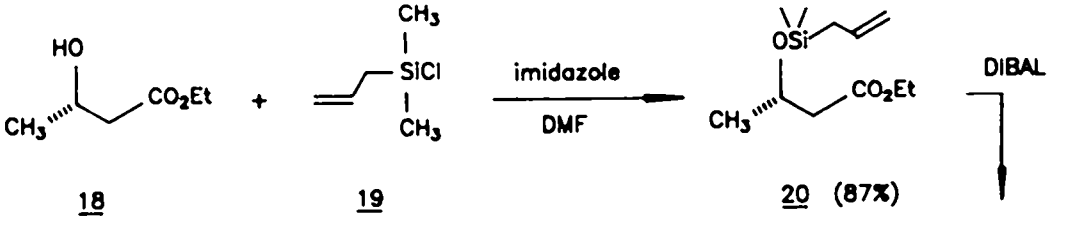
16 : 17

<10 : >90

RESULTS AND DISCUSSION

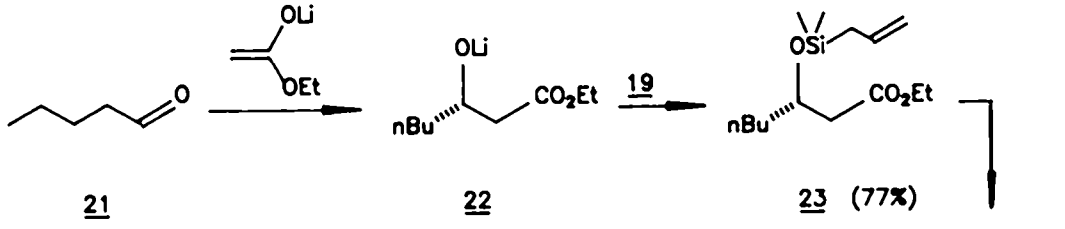
Reactions Involving 1,3 Asymmetric Induction

Silylation of the hydroxy ester 18 with commercially available allylchlorodimethylsilane 19[16] followed by reduction of the product 20 with diisobutylaluminum hydride (DIBAL) afforded the aldehyde 14a in good yield. 14b was prepared by quenching the aldolate 22 with 19 and reducing the ester 23. The DIBAL reductions must be worked up with a buffered aqueous solution (pH 4) in order to prevent desilylation.



18 19 20 (87%)

14a (60%)



21 22 23 (77%)

14b (63%)

In order to induce C-C bond formation, the aldehydes 14a-b were added to cooled (-78°C) solutions of CH_2Cl_2 containing equivalent amounts of the Lewis acids $TiCl_4$, $SnCl_4$ or $BF_3{\cdot}OEt_2$. Following aqueous workup and Kugelrohr distillation, the diastereomeric ratios 16:17 were determined by ^{13}C NMR spectroscopy (Table 1).

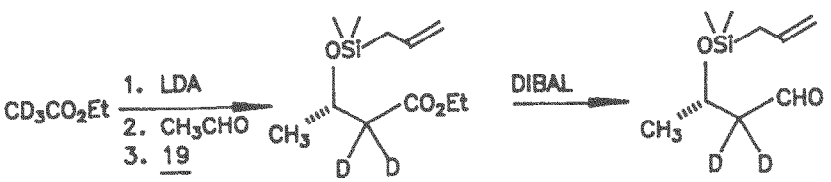
Table 1. Lewis acid induced allylation reaction of 14

Entry	Aldehyde	Lewis acid	Yield 16/17 (%)	Ratio 16 : 17
1	14a	$TiCl_4$	70	8 : 92*
2	14a	$SnCl_4$	70	92 : 8
3	14a	$BF_3 \cdot OEt_2$	60	70 : 30
4	14b	$TiCl_4$	80	10 : 90

*) In some runs slightly higher diastereoselectivities were observed (e.g., 5 : 95).

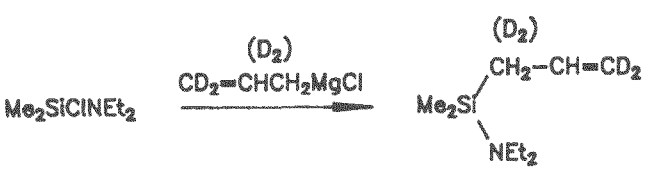
Surprisingly, $TiCl_4$ and $SnCl_4$ lead to opposite diastereoselectivities (syn versus anti diastereomers). The results of the $TiCl_4$ mediated reactions (entries 1 and 4 in Table 1) are in line with the original hypothesis of an intramolecular allyl transfer in which silicon and titanium act as templates (cf 15). However, the observed stereoselectivities do not strictly prove the proposed intramolecularity. The result of the $SnCl_4$ induced reaction is even more difficult to explain. Perhaps some kind of an intermolecular process related to the reaction of 12 with allylsilanes[6] is involved.

In order to put some of these speculations on a more sound basis, crossover experiments were performed. To this end, the D_2-labeled aldehyde 26 was synthesized in the following straightforward manner:

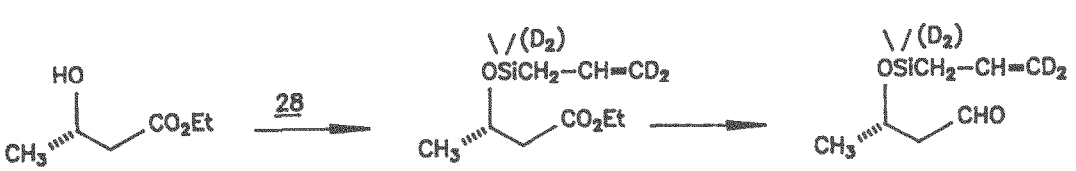


24 25 26

The synthesis of the D_2-labeled aldehyde 30 initially posed problems due to the loss of expensive material in the allylation of $(CH_3)_2SiCl_2$ with D_2-allylmagnesium chloride which leads to a mixture of mono- and di-allylated silanes. By using $Me_2SiClNEt_2$ (27), readily prepared from Me_2SiCl_2 and diethylamine according to the procedure of Wannagat[17], clean mono-allylation to 28 was accomplished. This paved the way for an efficient preparation of 30:



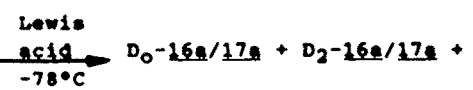
27 28



18 29 30

Crossover experiments were performed by adding a cooled 1:1 mixture of 26 and 30 to cooled solutions of $TiCl_4$ or $SnCl_4$ in CH_2Cl_2. Following aqueous workup the 1,3-diols were isolated and analyzed by ^{13}C NMR spectroscopy. As expected, the

diastereomer ratios of the $TiCl_4$ and $SnCl_4$ reactions were found to be anti:syn ≈5:95 and 95:5, respectively. The results of the mass spectroscopic analysis (CI) of the syn diol in the case of the $TiCl_4$ induced reaction and the anti diol obtained by the $SnCl_4$ mediated process, averaged over several runs, turned out to be as follows:



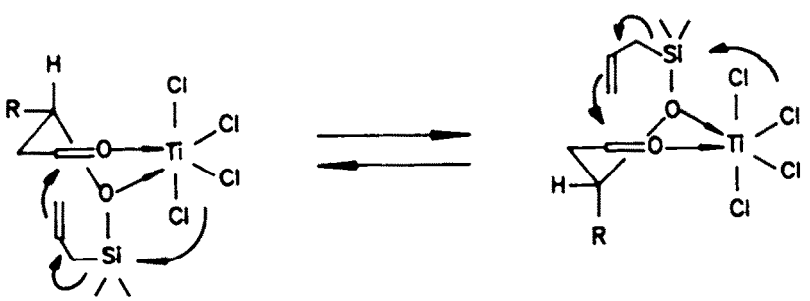
26 + 30 → D_o-16a/17a + D_2-16a/17a + D_4-16a/17a

$TiCl_4$: D_o : D_2 : D_4 = 5 : 93 : 2
$SnCl_4$: D_o : D_2 : D_4 = 28 : 50 : 22

Strict intramolecularity requires a theoretical ratio of D_o : D_2 : D_4 = 0:100:0. Within experimental errors this seems to be the case in the $TiCl_4$ induced allylation. In contrast, intermolecularity should result in a statistical ratio of D_o : D_2 : D_4 = 25 : 50 : 25. The result of the $SnCl_4$ reaction is very close to these values, pointing to intermolecular allyl transfer.

Although the experimental results are unambiguous, their interpretation is currently not straightforward. A helpful starting point is the analysis of the NMR spectra of $TiCl_4$ adducts of chiral alkoxy carbonyl compounds, which we reported several years ago. Whereas the addition of $TiCl_4$ to α-chiral α-alkoxy aldehydes[8,18] and ketones[7] affords discrete five-membered chelates (e.g. 8), the H NMR spectrum (CD_2Cl_2/-78°C) of the $TiCl_4$ adduct of the β-chiral β-alkoxy aldehyde 7 (R=CH_3) consists of broad lines and indicates the presence of several species as evidenced by the appearance of two large and a small peak in aldehydic proton absorption range[19]. Keck has also recorded the H NMR spectrum of $TiCl_4$/7 (R=CH_3) under slightly different conditions (-93°C) and also reports broad lines[20]. However, he concludes that a discrete bidentate complex is formed in which the methyl group at C_3 occupies an axial or pseudoaxial position, as in the case of the analogous $MgBr_2$ adduct which shows a clean H NMR spectrum with well resolved lines.

Assuming that siloxy aldehydes form the same type of chelates as the benzyloxy analogs, 15 and 31 are possible intermediates. The extension of Keck's model to the siloxy aldehydes leads to the proposition that 31 should be the favored chelate. However, even if 31 were the major component in solution, it is not necessarily the reacting conformer (Curtin-Hammett principle). Indeed, it would lead to the minor diastereomer 16. We therefore conclude that 15 is a reasonable mechanistic interpretation and do not feel the need to invoke alternative intermediates such as boat conformers[21].

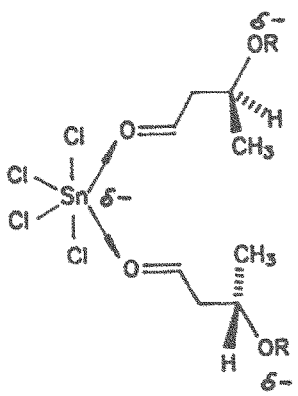


15 ⇌ 31

15 → 17

31 → 16

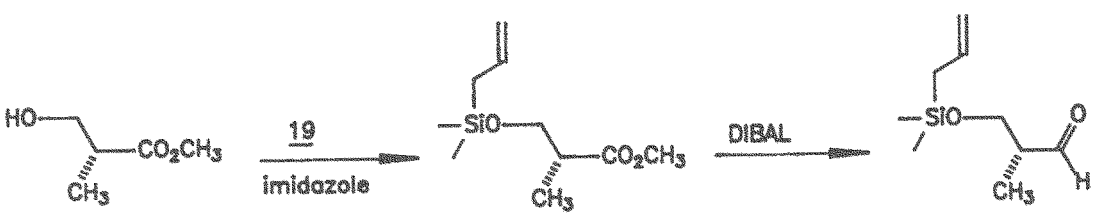
The mechanistic picture of the intermolecular $SnCl_4$ induced allylation is less clear. The benzyloxy aldehyde 7 (R=CH_3) is known to react with $SnCl_4$ to form several species[20], among others probably octahedral 2:1 adducts of the type 32a[22]. Due to electrostatic repulsion a "rigid" conformation of the carbon chain as shown may well pertain. In the case of 32b, this would result in preferential intermolecular attack from the less hindered π-face with the formation of 16. Such an effect, if actually operating, is reminiscent of our previous report concerning the BF_3 induced reaction of aldehyde 7 (R=CH_3) with allyltrimethylsilane which affords 91% of diastereomer 13[11]. This means that BF_3, having only one coordination site, is simulating chelation, probably on the basis of electrostatic repulsion (rigid carbon chain)[11].



32 a) R = CH_2Ph
b) R = $Si(Me)_2CH_2CH=CH_2$

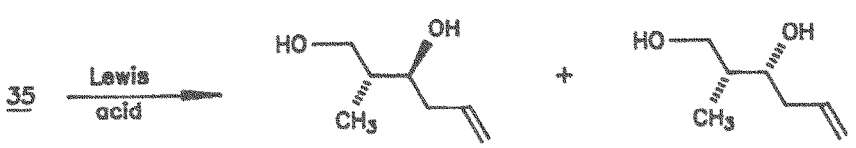
Reactions Involving 1,2-Asymmetric Induction

In order to test whether O-silyl protected α-chiral β-hydroxy aldehydes related to 6 also undergo stereoselective allyl addition reactions, aldehyde 35 was synthesized. Although the synthesis of the key ester 34 proceeded smoothly via silylation of 33, the isolated yield of 35 did not exceed 35% due to problems with the DIBAL reduction.



33 34 35

Upon adding 35 to cooled solutions or suspensions of Lewis acids in CH_2Cl_2, diols 36/37 were formed with 92-98% conversion and varying degrees of 1,2-asymmetric induction (Table 2).



36 37

Table 2. Lewis acid induced*) allylation reactions of 35

Entry	Lewis acid	Yield 36/37 (%)	Ratio 36/37
1	$TiCl_4$	95	64:36
2	$SnCl_4$	98	77:23
3	$AlCl_3$	94	55:45
4	$EtAlCl_2$	92	85:15
5	$MgBr_2$	--	---

*) In all cases 1 eq of Lewis acid in CH_2Cl_2 at -78°C was used (exception: $EtAlCl_2$ reaction in toluene). No reasonable amounts of 36/37 were formed in the case of $MgBr_2$ (entry 5).

In all cases studied, diastereomer 36 was formed preferentially. Thus, the direction of diastereofacial selectivity is the same as in the reaction of complex 10 (R=CH_3) with allyltrimethylsilane (80:20 diastereomer ratio)[11]. The present reaction is most stereoselective if $EtAlCl_2$ is used as the Lewis acid, but the difference relative to $SnCl_4$ is not pronounced. Since the O-silyl protected aldehyde 35 is not as readily accessible as the O-benzyl analog 6 (R=CH_3), the synthetic advantage of the former is not apparent. We therefore did not carry out any more studies such as crossover experiments, and prefer not to offer speculations concerning the mechanism.

CONCLUSIONS

The intramolecular $TiCl_4$ mediated reaction of (allyl)siloxy aldehydes 14 is a synthetically useful way to achieve 1,3 asymmetric induction. It remains to be seen whether other C-nucleophiles such as enolates and cyano moieties can be transferred stereoselectively in a similar manner. Relevant is the interesting report by Davis concerning intramolecular silicon hydride reductions of ketones[23] and Molander's intruiging SmI_2-promoted intramolecular Reformatsky-type reactions[24].

EXPERIMENTAL

General information. All reactions were performed in dry flasks under an atmosphere of N_2. Solvents were dried according to standard techniques. NMR spectra ($CDCl_3$) were recorded on Bruker WH 90 (90 MHz) or Bruker WH 400 (400 MHz) instruments. Mass spectroscopic studies were carried out using chemical ionization (reactant gas NH_3) on a Vacuum Generators 70-70 instrument. All chiral compounds were used in racemic form.

Ethyl 3-(allyldimethylsiloxy)butanoate (20). The mixture of ethyl 3-hydroxybutanoate (12.5 g, 95 mmol), imidazole (23.4 g, 343 mmol) and allylchlorodimethylsilane (13.6 g, 100 mmol) in 45 ml of dry DMF was stirred for 12 h at room temperature. After pouring on H_2O and extracting several times with pentane, the organic phase was washed with a NaCl soln, dried over Na_2SO_4 and concentrated. The residue was distilled in a Kugelrohr (100°C/9 torr) to afford 19 g (87%) of a colorless liquid: H-NMR δ 0.11 (s,6H), 1.17 (d,J=6.4Hz, 3H), 1.26 (t,J=7.1Hz, 3H), 1.61 (broad d,J=8.1Hz, 2H), 2.42 (mc, 2H), 4.13 (q,J=7.1Hz, 2H), 4.05-4.48 (m, 1H), 4.70-6.12 (m, 3H); ^{13}C-NMR δ -2.2, 14.0, 23.7, 24.7, 44.5, 59.9, 65.6, 113.4, 133.7, 170.9; found: C, 57.20; H, 9.74; calcd for $C_{11}H_{22}O_3Si$: C, 57.35; H, 9.63.

3-(Allyldimethylsiloxy)butanal (14a). the soln of 1.15 g (5 mmol) 20 in 25 ml of pentane was slowly treated at -78°C with 5.1 ml of a 1.0 N hexane soln of diisobutylaluminum hydride (DIBAL). After stirring for 5 h at -78°C, the mixture was poured on 10 ml of a buffer soln (pH 4). The insoluble material was extracted several times with ether and the ether phases were washed with NaCl-soln and dried over Na_2SO_4. After removal of the solvent, the residue was purified by MPLC

(40-60 pet ether/ether 2:1) to afford 0.56 g (60%) of a colorless liquid: H-NMR δ 0.13 (s, 6H), 1.24 (d,J=6.1Hz, 3H), 1.5-1.7 (m, 2H), 2.5 (mc, 2H), 4.4 (mc, 1H), 4.7-6.1 (m, 3H), 9.8 (t, 1H); ^{13}C-NMR δ -2.2, -2.1, 23.9, 24.6, 52.6, 64.1, 113.5, 133.5, 201.1; found: C, 57.85; H, 10.09; calcd for $C_9H_{18}O_2Si$: C, 58.02; H, 9.74.

Ethyl 3-(allyldimethylsiloxy)heptanoate (23). To a cooled (-78°C) soln of 11 mmol LDA (prepared from 1.11 g diisopropylamine and 11 mmol n-butyllithium) in 30 ml THF was added 0.88 g (10 mmol) of ethyl acetate and the mixture stirred for 30 min. Pentanal (0.86 g, 10 mmol) was added, the mixture stirred at -78°C for 1 h and 1.75 g (13 mmol) allylchlorodimethylsilane added. The mixture was allowed to come to room temp overnight and worked up as in the case of 20. Kugelrohr distillation (120°C/0.01 torr) afforded 1.77 g (77%) of 23. H-NMR δ 0.12 (s, 6H), 0.9 (broad t, 3H), 1.1-1.7 (m, 8H), 1.34 (t,J=7.1Hz, 3H), 2.43 (d,J=6.4Hz, 2H), 4.13 (q, J=7.1Hz, 2H), 4.0-4.2 (m, 1H), 4.7-6.1 (m, 3H); ^{13}C-NMR δ -1,9, 14.0, 14.2, 22.7, 25.1, 27.5, 37.4, 43.0, 60.2, 69.8, 113.6, 134.1, 171.9; found: C, 61.99; H, 10.46; calcd for $C_{14}O_{28}O_3Si$: C, 61.72; H, 10.36.

3-(Allyldimethylsiloxy)heptanal (14b). The same procedure as in the synthesis of 14a afforded after Kugelrohr distillation (200°C/0.01 torr) 63% of 14b: H-NMR δ 0.13 (s, 6H), 0.90 (broad t, 3H), 1.1-1.8 (m, 8H), 2.51 (mc, 2H), 4.2 (mc, 1H), 4.7-6.1 (m,3H), 9.80 (t, 1H); ^{13}C-NMR δ -2.2, -2.1, 13.6, 22.3, 24.7, 27.1, 37.2, 50.7, 67.9, 113.4, 133.4, 201.1; found: C, 63.03; H, 10.78; calcd for $C_{12}H_{24}O_2Si$: C, 63.10; H, 10.59.

General procedure for Lewis acid promoted reactions of 14a-b. The soln of 2 mmol $TiCl_4$, $SnCl_4$ or $BF_3 \cdot OEt_2$ in 50 ml of cooled (-78°C) CH_2Cl_2 was slowly treated with a cooled soln of an aldehyde 14a-b (2 mmol in 10 ml CH_2Cl_2) within 2 h. The mixture was poured on H_2O, the aqueous phase extracted several times with CH_2Cl_2 and the combined org phases were washed with $NaHCO_3$ and NaCl solutions and dried over $MgSO_4$. Following Kugelrohr distillation the products were examined with NMR spectroscopy.

Diol 16a[6,25]. H-NMR δ 1.24 (d,J=6.4Hz, 3H), 1.56 (mc, 2H), 2.8 (broad t, 2H), 3.8 (broad s, 2H), 4.0 (mc, 2H), 4.9-6.1 (m, 3H); ^{13}C-NMR δ 23.3, 41.8, 43.6, 64.8, 68.0, 117.4, 134.7.

Diol 17a[6,25]. H-NMR δ 1.21 (d, J=6.1Hz, 3H), 1.5-1.7 (m, 2H), 2.2 (broad t, 2H), 3.2 (s, 2H), 3.7-4.3 (m, 2H), 4.9-6.1 (m, 3H); ^{13}C-NMR δ 24.1, 42.6, 44.1, 68.9, 71.9, 118.1, 134.3.

Diol 16b[6]. ^{13}C-NMR δ 14.0, 22.6, 27.9, 37.1, 41.8, 41.9, 68.1, 69.0, 117.7, 134.7.

Diol 17b[6]. H-NMR δ 0.9 (broad t, 3H), 1.1-1.8 (m, 8H), 2.3 (broad t, 2H), 3.2 (broad s, 2 H), 3.7-4.2 (m, 2H), 4.9-6.1 (m, 3H); ^{13}C-NMR δ 14.0, 22.6, 27.5, 37.8, 42.2, 42.5, 71.9, 72.8, 117.9, 134.3; results of the CH-analysis of the 10:90 mixture of 16b/17b; calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. The configurational assignment was made by comparison with the diol prepared by deprotection of the known O-benzylated compound 13 (R=n-C_6H_9).

Synthesis of labeled compounds

Compound 25 (yield 79%) was prepared using the same procedure as in the preparation of 23. The DIBAL reduction to 26 proceeded in the same manner as in the case of 14a.

Ester 29. The solution of D_2-allylmagnesium chloride (14 mmol in THF) was treated with 1.7 g (10 mmol) of chlorodiethylaminodimethylsilane (27) at room temp and stirred for 12 h. The THF was removed by distillation and the residue triturated with pentane. After filtration from the Mg salts the solution was concentrated: >95% conversion to 28 which was used without further purification. The soln of 3.30 g (25 mmol) 18 in 5 ml of acetone was treated with the

equivalent amount of crude 28 at 0°C. After stirring at room temp for 1 h the mixture was poured on H_2O, extracted with pentane and dried over Na_2SO_4. The drying agent and solvent were removed and the crude product chromatographed (MPLC; 40-60 pet ether/ether, 2:1) to afford 3.02 g (65%) of 29.

Aldehyde 30. This compound was prepared from 29 using the same procedure as in the synthesis of 14a.

Crossover experiments

The mixture of 380 mg (2 mmol) of 26 and 2 mmol of 30 in 15 ml of CH_2Cl_2 was slowly added to 760 mg (4 mmol) of $TiCl_4$ in 50 ml of CH_2Cl_2 at -78°C. After 4 h the cold soln was worked up as usual. The crude product was distilled using a Kugelrohr and then chromatographed (MPLC). The crossover experiment using $SnCl_4$ (1.04 g, 4 mmol) was performed similarly. The mass spectrum (chemical ionization/NH_3 as reactant gas) showed (M^++1) peaks at 131, 133 and 135 in a ratio of 5:93:2 ($TiCl_4$ reaction) and 28:50:22 ($SnCl_4$ reaction).

Methyl 2-methyl-3-allyldimethylsiloxypropanoate (34) was prepared in the same manner as 20. Starting from 2.36 (20 mmol) of 33, 4.1 g (95%) of 34 were isolated (Kugelrohr distillation at 135°C/20 torr): H-NMR δ 0.09 (s, 6H), 1.13 (d,J=7.1Hz, 3H), 1.53-1.63 (m, 2H), 2.59-2.68 (m, 1H), 3.59-3.80 (m, 2H), 3.67 (s, 3H), 4.82-4.93 (m, 2H), 5.71-5.82 (m, 1H); ^{13}C-NMR δ -2.7, 13.5, 24.2, 42.3, 51.4, 64.8, 113.6, 133.8, 175.2; found: C, 55.48; H, 9.55; calcd for $C_{10}H_{20}O_3Si$: C, 55.50; H, 9.33.

2-Methyl-3-allyldimethylsiloxypropanal (35). The soln of 1.62 g (7.5 mmol) of ester 34 in 100 ml of CH_2Cl_2 was treated with DIBAL (7.88 ml of a 1 M hexane soln) at -78°C. After 2 h the mixture was allowed to reach room temp and poured on 20 ml of a buffer (pH 4). The emulsion was extracted several times with ether, and the ether phases were washed with a NaCl soln and dried over $MgSO_4$. Removal of solvent afforded 1.05 g of crude product containing about 18% of 34. Purification by GC (SE 30 column; 100-110°C) gave 460 mg (33%) of 35: H-NMR δ 0.1 (s, 6H), 1.08 (d,J=4.9Hz, 3H), 1.59-1.61 (m, 2H), 2.49-2.55 (m, 1H), 3.80 (d,J=5.9Hz, 2H), 4.84-4.91 (m, 2H), 5.71-5.82 (m, 1H), 9.71 (d,J=2.5Hz, 1H); ^{13}C-NMR δ -2.7, 10.3, 24.1, 48.6, 63.0, 113.8, 133.6, 204.3; found: C, 58.14, H, 9.73; calcd for $C_9H_{18}O_2Si$: C, 58.00, H, 9.76.

Lewis acid induced reactions of 35 were carried out in the same manner as in the case of 14. $AlCl_3$ and $MgBr_2$ form suspensions (not solutions) in CH_2Cl_2.

Diols 36/37. ^{13}C-NMR of the major isomer (36): δ 13.6, 39.6, 39.8, 67.3, 75.7, 118.1, 134.6; ^{13}C-NMR of the minor isomer (37): δ 10.1, 38.7, 38.8, 66.7, 72.1, 117.6, 135.2; found: C, 64.54, H, 10.85; calcd for $C_7H_{14}O_2$: C, 64.57; H, 10.86. The configurational assignment was made by hydrogenating the compounds to the known saturated diols[26].

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