Quenching Experiments (Table II and Figure 2). Aldehyde **3Z** or **3E** (0.5 mmol) was dissolved in 5 mL of methanol and rapidly mixed at $t = 0$ with a stirred methanol solution (total 5 mL) of 5 mmol of $Me_2NH_2^+Cl^-$ or $MeNH_3^+Cl^-$ plus $x/2$ mmol of NaOH (from 1.0 M methanol solution) at room temperature. At t min 1.0-mL aliquots (1/10) were withdrawn and quenched with 1.0-mL aliquots of a solution of 0.75 mmol of $NaBH_3CN$ in 10 mL of methanol. After reaction for ca. 1 h a portion of these mixtures was treated with 2 M HCl for some minutes. The samples were made alkaline with 2 M NaOH, extracted with ether, and analyzed on capillary GLC at 190–200 °C. The Z/E ratios are shown in Table II and Figure 2.

Europium-Induced Shifts in ^{1}H NMR. Solid tris-(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)europium [Eu(fod)$_3$] was added in increments to a $CDCl_3$ (0.5 mL) solution of the aldehyde **3Z** or **3E** (70 mg). The gradient G (slope) was calculated for the vinyl, aldehyde, and 2-pyridyl protons from plots of induced chemical shift vs. (concentration of Eu(fod)$_3$/concentration of **3**) as described earlier.[10] The gradient ratios G(vinyl)/G(2-pyridyl) and G(vinyl)/G(2-aldehyde) are given in the text.

Acknowledgment. We wish to thank colleagues at Astra Läkemedel and University of Kansas, especially Drs. B. Carnmalm and P. Krogsgaard-Larsen, for valuable discussions.

Registry No. **1E**, 56775-89-4; **1Z**, 56775-88-3; **2E**, 60324-58-5; **2Z**, 60324-59-6; **3Z**, 77470-68-9; **3E**, 83049-64-3; **4**, 70263-43-3; **5Z**, 77470-73-6; **5E**, 91671-06-6; **5E** (picrate), 91671-07-7; **6**, 91671-10-2; **7Z**, 91671-08-8; **7E**, 91671-09-9; **8Z**, 91671-11-3; **8E**, 91671-12-4; **9Z**, 91671-13-5; **9E**, 91671-14-6; $NaBH_3CN$, 25895-60-7; $Me_2NH_2^+Cl^-$, 506-59-2; $MeNH_3^+Cl^-$, 593-51-1.

Acyclic Stereoselection. 22. Diastereofacial Selectivity in the Lewis Acid Mediated Reactions of Allylsilanes with Chiral Aldehydes and Enones[1]

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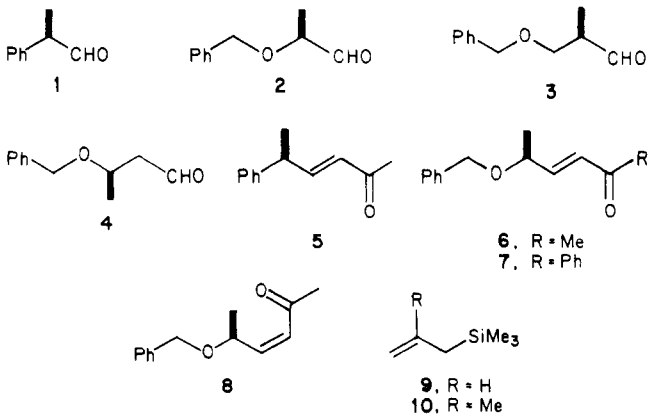
The Lewis acid mediated reactions of chiral aldehydes **1–4** and enones **5–8** with allylsilanes **9** and **10** have been investigated. With aldehyde **1** and enones **5–7**, modest diastereofacial preferences are seen, in the sense predicted by application of Felkin's model for asymmetric induction. Aldehydes **2–4** and enone **8** appear to react by way of chelated intermediates. With these four compounds, the diastereofacial preferences are rather large and are in the sense that is consistent with attack of the allylsilane on the least hindered face of the chelated intermediate. In the reactions of the trans and cis enones **6** and **8** with allyltrimethylsilane, a dramatic reversal of diastereofacial preference is observed; enone **6** gives a 84:14 ratio of products, while enone **8** provides a 10:90 mixture of the same products.

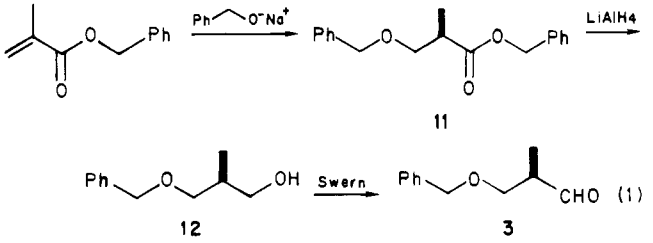
As a part of our investigation of the diastereoselectivity of carbon-carbon bond-forming reactions,[2] we have investigated the Lewis acid mediated reactions of allylsilanes with several chiral aldehydes and α,β-unsaturated ketones. In this paper, we report the results of that investigation.

Materials

The reactions of aldehydes **1–4** and enones **5–8** with allylsilane (**9**) and methallylsilane (**10**) in the presence of several Lewis acids were studied. Compound **1** may be



purchased from a commercial supplier,[3] although the material obtained is contaminated with about 15% acetophenone. However, this material may be readily purified (see Experimental Section). Compound **2** is prepared as previously reported.[4] Aldehyde **3** may be produced by the route summarized in eq 1. Addition of sodium benzyl



(1)

oxide to benzyl methacrylate gives **11**, which is reduced by lithium aluminum hydride to alcohol **12**. Swern oxidation[5] of the latter substance provides aldehyde **3**.[6]

(1) For part 21, see: Heathcock, C. H.; Jarvi, E. T.; Rosen, T. *Tetrahedron Lett.* **1984**, *25*, 243.
(2) Heathcock, C. H. *Science (Washington, D.C.)* **1981**, *214*, 395.
(3) Aldrich Chemical Company, catalog no. 24,136-9.
(4) Heathcock, C. H.; Young, S. D.; Hagen, J. P.; Pirrung, M. C.; White, C. T.; VanDerveer, D. *J. Org. Chem.* **1980**, *45*, 3846.
(5) (a) Mancuso, A. J.; Huang, S.-L.; Swern, D. *J. Org. Chem.* **1977**, *43*, 2480. (b) Mancuso, A. J.; Swern, D. *Synthesis* **1981**, 165.
(6) The enantiomerically homogeneous forms of aldehyde **6** are well-known synthetic intermediates. See inter alia: Paterson, I.; Patel, S.; Porter, J. R. *Tetrahedron Lett.* **1983**, *24*, 3395. Roush, W. R.; Adam, M. A.; Peseckis, S. M. *Ibid.* **1983**, *24*, 1377. Meyers, A. I.; Babiak, K. A.; Campbell, A. L; Comins, D. L.; Fleming, M. P.; Henning, R.; Heuschmann, M.; Hudspeth, J. P.; Kane, J. M. *J. Am. Chem. Soc.* **1983**, *105*, 5015. Schreiber, S. L.; Hoveyda, A. H.; Wu, H. J. *Ibid.* **1983**, *105*, 660. Lewis, M. D.; Kishi, Y. *Tetrahedron Lett.* **1982**, *23*, 2343. Nagoka, H.; Hudspeth, J. P. *Tetrahedron Lett.* **1981**, *22*, 3925. Schlessinger, R. H.; Poss, M. A. *J. Am. Chem. Soc.* **1982**, *104*, 357. Kishi, Y. *Pure Appl. Chem.* **1981**, *53*, 1163. Still, W. C.; Schneider, J. A. *Tetrahedron Lett.* **1980**, *21*, 1035. Johnson, M. R.; Kishi, Y. *Ibid.* **1979**, 4347. Johnson, M. R.; Nakata, T.; Kishi, Y. *Ibid.* **1979**, 4343.

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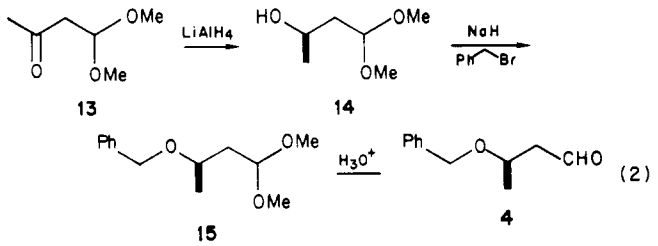
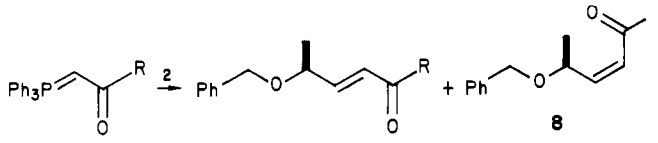
Compound **4** was produced by the method outlined in eq 2. Lithium aluminum hydride reduction of keto acetal



(2)

13 provides alcohol **14**. Benzylation of this material gives **15**, which is hydrolyzed to obtain **4**.

Enone **5** was obtained by the reaction of aldehyde **1** with (acetylmethylene)triphenylphosphorane (**16**); the major product is accompanied by 10% of a mixture of β,γ-unsaturated isomers. Similar treatment of aldehyde **2** with phosphorane **16** gives a 2:1 mixture of enones **6** and **8**.



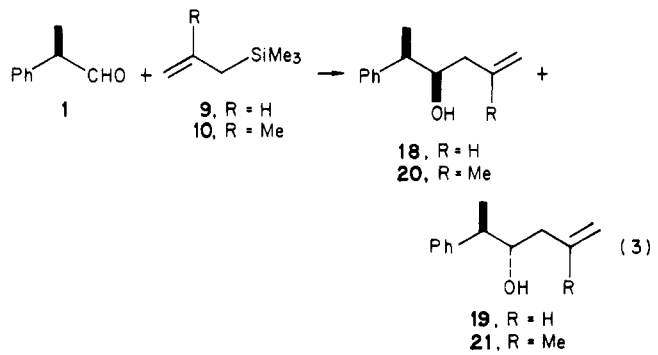
16: R = Me
17: R = Ph

6: R = Me
7: R = Ph

However, the analogous reaction of **2** with (benzoylmethylene)triphenylphosphorane (**17**) gives only the trans enone **7**.

Results and Discussion

The reactions of aldehyde **1** and the two allylsilanes were studied with three Lewis acids, boron trifluoride etherate, titanium tetrachloride, and stannic chloride (eq 3); the results are summarized in Table I. As shown in Table I



1

9, R = H
10, R = Me

18, R = H
20, R = Me

19, R = H
21, R = Me

(3)

all reactions studied give mixtures of the two diastereomers resulting from attack of the allylsilane on the two diastereotopic faces of the Lewis acid coordinated carbonyl groups. The relative stereochemistry of the two isomers has been assigned as shown on the basis of two arguments. First, the indicated major diastereomer is that expected on the basis of the Felkin model for asymmetric induction.[7] The observed chemical shifts of the vinyl methyl groups in isomers **20** and **21** (δ 1.68 and 1.74, respectively) are consistent with this assignment. Conversely, the acetyl methyl resonances in the derived acetates (**22** and **23**) occur at δ 2.02 and 1.90, respectively. Acyclic compounds having vicinal stereocenters, each bearing one hydrogen, normally exist predominantly in the conformation having the hydrogens anti, so as to minimize gauche interactions. In the

(7) Cherest, M.; Felkin, H.; Prudent, N. *Tetrahedron Lett.* **1968**, 2199. For a theoretical treatment of the Felkin model, see: Anh, N. T.; Eisenstein, O. *Nouv. J. Chim.* **1977**, *1*, 61.

Table I. Diastereomer Ratios in the Reactions of Allylsilanes with Aldehyde 1 (Eq 3)

entry	allylsilane	Lewis acid	conditn[a]	yield,[b] %	isomer ratio[c] (18/19 or 20/21)
1	**9**	$TiCl_4$	A	86	1.6:1
2	**9**	$TiCl_4$	B	81	1.3:1
3	**9**	$BF_3{\cdot}OEt_2$	A	47	2:1
4	**9**	$BF_3{\cdot}OEt_2$	B	51	1.7:1
5	**9**	$SnCl_4$	A	86	2.2:1
6	**10**	$TiCl_4$	A	66	2.8:1
7	**10**	$TiCl_4$	B	38	1.3:1[d]
8	**10**	$BF_3{\cdot}OEt_2$	A	64	7:1
9	**10**	$BF_3{\cdot}OEt_2$	B	53	2.8:1
10	**10**	$SnCl_4$	A	68	3.2:1

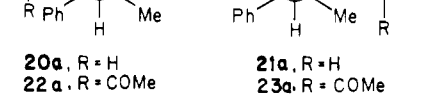
[a] Reaction conditions: aldehyde:allylsilane:Lewis acid ratio = 1.0:1.1:1.0; solvent = methylene chloride; A = −78 °C for 20–30 min, B = 25 °C for 2–5 min. [b] Isolated yield after silica chromatography; diastereomer pairs were not separated. [c] Isomer ratios were determined by 250-MHz ^1H NMR spectroscopy. [d] These products were isolated as chlorides, rather than as benzyl ethers; see text.

Table II. Allylsilane Additions to Enone 5[a] (Eq 4)

entry	Lewis acid	temp, °C	time, h	yield, %	ratio 25:26
1	$TiCl_4$	−78	1	74	4:1
2	$BF_3{\cdot}Et_2O$	−78→25	24	<50[b]	4:1
3	BF_3	−78→25	24	no reactn	
4	BCl_3	−78	32	<20	4:1
5	$BF_3{\cdot}Et_2O$, $CuBF_4$	−78→25	24	no reactn	
6	$ZnCl_2$[c]	−78	72	no reactn	
7	CF_3CO_2H	−78→25	24	no reactn	
8	$BF_3{\cdot}Et_2O$[d]	−78	24	43	4:1

[a] Methylene chloride was used as solvent unless otherwise noted. [b] Maximum yield, the product was not purified. [c] A 1:1 mixture of ether and methylene chloride was used as solvent. [d] Allyltributylstannane was used in place of allyltrimethylsilane.

case of **20–23**, the pertinent conformations are those shown below as **20a–23a**. In such a compound, a substituent



20a, R = H
22a, R = COMe

21a, R = H
23a, R = COMe

gauche to phenyl usually experiences an upfield shift, due to the net shielding effect of the aromatic ring.[8]

Several generalizations may be drawn from the data in Table I. First, diastereofacial selectivity with allylsilane is low in all cases, although there is a modest improvement at lower temperature (cf. entries **1** and **2** and **3** and **4**). The selectivity is lowest with $TiCl_4$ and highest with $SnCl_4$. Yields are good with both of the Lewis acids, and are poorer with $BF_3{\cdot}OEt_2$. Selectivity is higher with methallylsilane (cf. entries **1** and **6**, **3** and **8**, **4** and **9**, and **5** and **10**). With this silane the beneficial effect of lower temperature is also seen. In this case, $BF_3{\cdot}OEt_2$ was found to give the greatest stereoselection. In fact, the $BF_3{\cdot}OEt_2$-mediated reaction of aldehyde **1** with methallylsilane at −78 °C gives a preparatively useful 88:12 ratio of **20** and **21**. Finally, the reaction products isolated from the $TiCl_4$-mediated reaction of **1** with **10** at room temperature

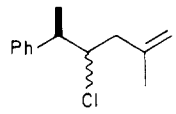
(8) Heathcock, C. H.; Lampe, J. *J. Org. Chem.* **1983**, *48*, 4330.

Table III. Observed ^{1}H NMR Chemical Shifts for Selected Resonances of Compounds 25 and 26

resonance	chemical shift, ppm: major isomer (25)	minor isomer (26)
acetyl methyl	2.07	1.94
α-keto methylene[a]	2.36	2.24
allylic methylene[a]	2.12, 2.32	2.29
vinyl methine	5.65	5.72
vinyl methylene	4.96	5.02

[a] Diastereotopic hydrogens.

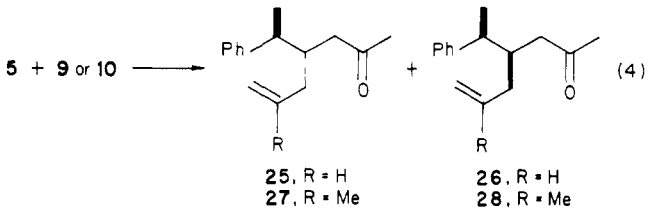
were chlorides (**24**) resulting from $TiCl_4$-mediated halogenation occuring after the addition reaction. No such



24

side reaction is seen with $SnCl_4$ or with $TiCl_4$ at −78 °C. Finally, it is noteworthy that the exceedingly high diastereofacial selectivity seen with aldehyde **1** and various enol silanes[9] is not observed with allylsilanes.

A similar study was carried out with the γ-phenyl-α,β-unsaturated ketone **5** (eq 4). Data are summarized in Table II. The relative stereochemistry of the two isomers

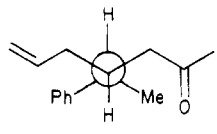


(4)

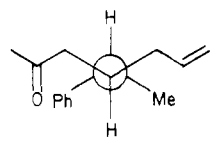
25, R = H
27, R = Me

26, R = H
28, R = Me

was assigned on the basis of arguments similar to those employed for assignment of stereostructures of unsaturated alcohols **18**–**21**. The assumed preferred conformations are **25a** and **26a** and the predicted shifts may be seen in five resonances (Table III). In this case, the preferred catalyst



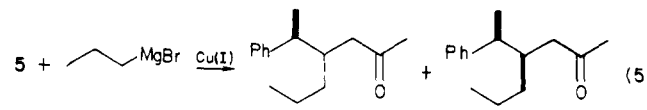
25a



26a

was found to be $TiCl_4$; reaction is smooth at −78 °C, giving a 4:1 mixture of diastereomeric adducts in 1 h in 74% yield. The reaction is much slower and proceeds in lower yield with BF_3·OEt_2 and BCl_3. However, the diastereofacial selectivity in these reactions (entries 2 and 4), as well as that seen in the BF_3·OEt_2-mediated reaction of enone **5** with allyltrimethylstannane (entry 8) is also 4:1. No significant reaction was seen with several other Lewis acids (entries 3, 5, and 6) or with trifluoroacetic acid. Again, the major diastereomer is that predicted on the basis of the Felkin model.

For further comparison, the copper-catalyzed addition of *n*-propylmagnesium bromide to enone **5** was examined. The product obtained in this reaction is a 4:1 mixture of ketones **29** and **30** (eq 5). An identical mixture of products was produced by catalytic hydrogenation of the mixture of unsaturated ketones **25** and **26** resulting from the reaction of **5** with allylsilane, thus allowing unambiguous

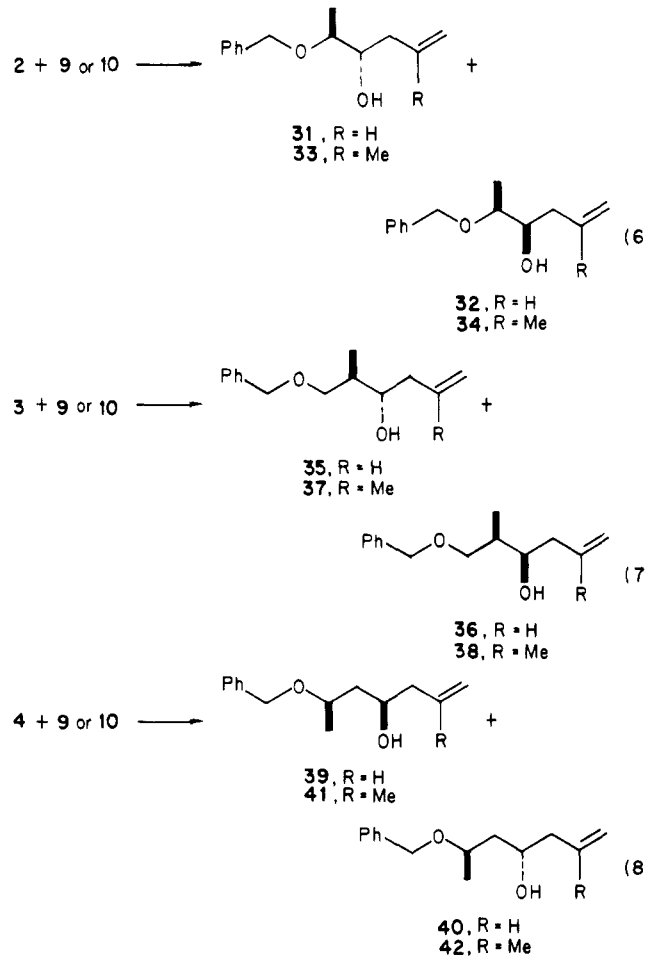


(5)

29 **30**

assignment of stereostructures to **29** and **30**.

Having found that no special diastereofacial preference is shown by aldehyde **1** or enone **5** in Lewis acid mediated reactions with allylsilanes, we turned our attention to the chiral, oxygen-containing aldehydes **2**–**4** and enones **6**–**8**. The reactions of aldehydes **2**–**4** and the two allylsilanes were studied with $TiCl_4$, $SnCl_4$, and BF_3·OEt_2 (eq 6–8). Results are presented in Table IV.



31, R = H
33, R = Me

(6)

32, R = H
34, R = Me

35, R = H
37, R = Me

(7)

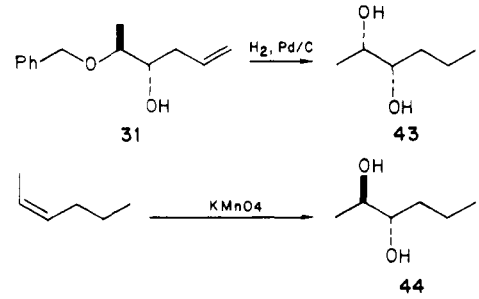
36, R = H
38, R = Me

39, R = H
41, R = Me

(8)

40, R = H
42, R = Me

The stereostructure of **31**, the major isomer produced in the reaction of aldehyde **2** with allyltrimethylsilane, was established by hydrogenation of the double bond and hydrogenolysis of the benzyl group to give (2*SR*,3*SR*)-2,3-heptanediol (**43**), which was clearly different from the diol (**44**) produced by permanganate oxidation of *cis*-2-hexene.[11]



31 **43**

44

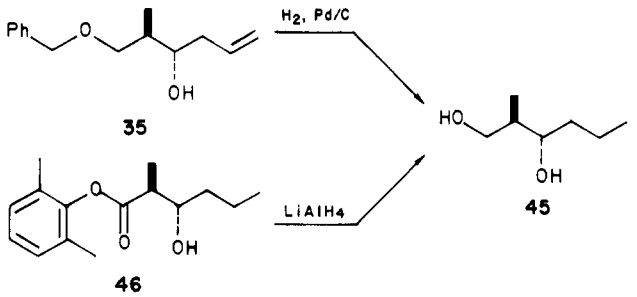
(9) Heathcock, C. H.; Flippin, L. A. *J. Am. Chem. Soc.* **1983**, *105*, 1667.
(10) Reetz, M. T.; Jung, A. *J. Am. Chem. Soc.* **1983**, *105*, 4833.
(11) Kiyooka, S.-I.; Heathcock, C. H. *Tetrahedron Lett.* **1983**, *24*, 4765.

Table IV. Diastereomer Ratios in the Reactions of Allylsilanes with Aldehydes 2–4 (Eq 6–8)[a]

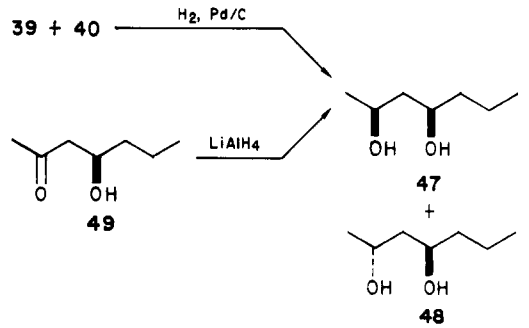
entry	aldehyde	allylsilane	Lewis acid	yield,[b] %	diastereomer ratio[c]
1	2	9	$SnCl_4$	94	35:1
2	2	9	$TiCl_4$	0[d]	
3	2	9	$BF_3{\cdot}Et_2O$	50	1:1.5
4	2	10	$SnCl_4$	81	45:1
5	2	10	$BF_3{\cdot}Et_2O$	40	1:2.6
6	3	9	$SnCl_4$	92	12:1
7	3	9	$BF_3{\cdot}Et_2O$	0[d]	
8	3	10	$SnCl_4$	83	10:1
9	4	9	$SnCl_4$	97	9:1
10	4	9	$TiCl_4$	0[d]	
11	4	9	$BF_3{\cdot}Et_2O$	0[d]	
12	4	10	$SnCl_4$	86	7:1

[a] Reaction conditions: aldehyde:allylsilane:Lewis acid = 1.0:1.1:1.0; solvent = methylene chloride. For $SnCl_4$, the aldehyde and Lewis acid were premixed at −78 °C; for $TiCl_4$ and $BF_3{\cdot}Et_2O$, the aldehyde and Lewis acid were premixed at 25 °C, and then cooled to −78 °C. All reactions were carried out at −78 °C for 20 min. [b] Isolated by silica gel chromatography; diastereomers were not separated. [c] Ratios were determined by 250-MHz ^1H NMR and 62.9 MHz ^{13}C NMR; ratios refer to **31:32** or **33:34** for aldehyde **2**, **35:36** or **37:38** for aldehyde **3**, and **39:40** or **41:42** for aldehyde **4**. [d] These reactions gave none of the normal product; see text.

The major unsaturated alcohol (**35**) from the reaction of aldehyde **3** with allyltrimethylsilane was reduced in a similar manner to obtain diol **45**. The same diol was produced when the anti β-hydroxy ester **46**[12] was reduced with lithium aluminum hydride.



The stereostructures of the products (**39** and **40**) obtained from the reaction of aldehyde **4** with allylsilane **9** were assigned by the Gerlach procedure.[14] Catalytic reduction of the 9:1 mixture gave a similar mixture of diols **47** and **48**, from which the major isomer was easily obtained. Lithium aluminum hydride reduction of aldol **49** gave the same two diols in a ratio of 3:7. Diol **47** was



condensed with benzaldehyde to give a single 1,3-dioxolane

(12) Aldol **46** was prepared as a 6:1 mixture of anti and syn diastereomers from the reaction of the lithium enolate of 2,6-dimethylphenyl propionate with butanal.[13]

(13) Heathcock, C. H.; Pirrung, M. C.; Montgomery, S. H.; Lampe, J. *Tetrahedron* **1981**, *37*, 4087.

(14) Gerlach, H.; Wetter, H. *Helv. Chim. Acta* **1974**, *57*, 2306.

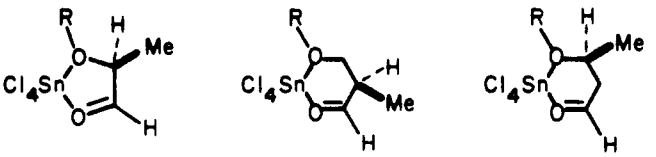
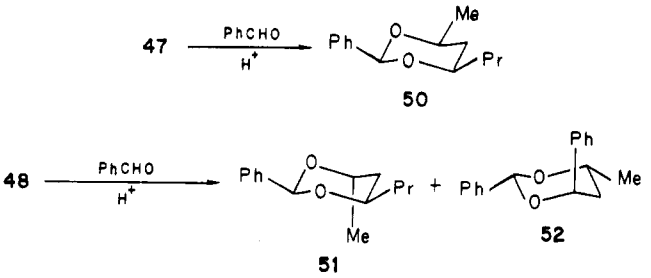


Figure 1. Chelated α- and β-alkoxy aldehydes.

(**50**), while similar treatment of diol **48** gave a 1:1 mixture of two dioxolanes, **51** and **52**. As shown in Table IV



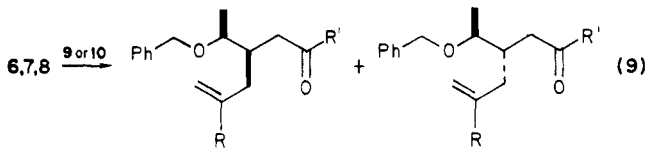
aldehyde **2** shows exceptional diastereofacial preference with both allylsilanes when $SnCl_4$ is used as catalyst (entries 1 and 4). With $BF_3{\cdot}OEt_2$, the diastereofacial preference is reversed, although the observed selectivity is not synthetically useful (entries 3 and 5). With $TiCl_4$, we obtained a complex mixture of chlorine-containing materials rather than the normal products, in contrast to the good yield and high stereoselectivity seen in a similar reaction by Reetz and Jung.[10] The reason for this apparent discrepancy was pointed out to us by Professor Reetz after our preliminary publication.[11] In the Reetz and Jung experiments, the aldehyde–$TiCl_4$ complex was formed by treating aldehyde with the Lewis acid at −78 °C. In our work, we formed the complex by mixing the reagents at room temperature. The resulting mixture was then cooled to −78 °C for reaction with the allylsilane. Apparently, the complex is not stable at the higher temperatures to which it was subjected in our experiments.[21]

With aldehydes **3** and **4**, the $SnCl_4$-mediated reactions are also smooth at −78 °C, giving the indicated adducts in excellent yields. With these aldehydes, the diastereofacial preference is not as great as it is with aldehyde **2**. Nevertheless, it is still very good (>90:10 with **3** and >88:12 with **4**), and the chemical yields are excellent.

The results obtained with aldehydes **2–4** may be interpreted in terms of chelation of $SnCl_4$ by the α-alkoxy and carbonyl oxygens (Figure 1). It would seem that the more rigid five-membered chelate produced from **2** results in a greater steric difference between the two diastereotopic faces of the carbonyl group than in the case of the chelates from **3** or **4**. In addition, it is noteworthy and understandable that the chelate derived from **3**, in which the stereocenter is directly adjacent to the carbonyl group, shows greater selectivity than that derived from **4**, in which the stereocenter is one position more distant. Finally, the results probably represent the minimum stereoselectivity that may be expected for compounds such as these. Chiral aldehydes related to **2–4**, but having groups larger than methyl, are expected to show correspondingly higher diastereofacial preferences.

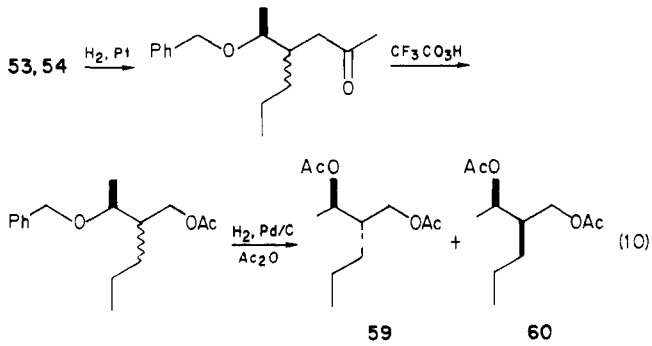
Enones **6–7** were studied only under the normal Sakurai conditions,[15] with $TiCl_4$ in methylene chloride at −78 °C (eq 9). As in all other reactions examined, mixtures of diastereomers were obtained (Table V). The stereostructures of the two isomers obtained from enone **6** and allyltrimethylsilane (**53** and **54**) were determined by con-

(15) Hosomi, A.; Sakurai, H. *J. Am. Chem. Soc.* **1977**, *99*, 1673.



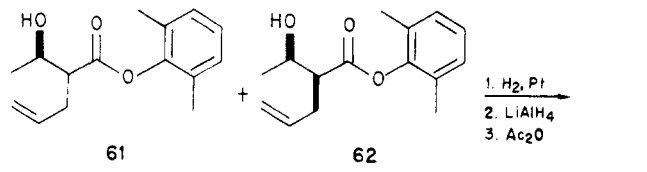
53, R = H, R' = Me
55, R = H, R' = Ph
57, R = Me, R' = Me
54 R = H, R' = Me
56, R = H, R' = Ph
58, R = Me, R' = Me

version into diacetates **59** and **60**, as shown in eq 10. As



59 **60**

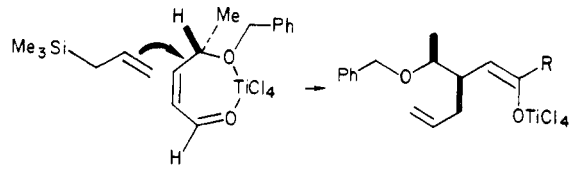
shown in eq 11, the diacetates were prepared independently from the diastereomeric mixture of aldols **61** and **62**,[13] whose stereostructures were established by ^{13}C NMR spectroscopy.[16]



61 **62**

59 + **60** (11)

As shown in Table IV trans enones **6** and **7** react with allyltrimethylsilane to give diastereomeric ratios of 7:1 and 8:1, respectively (entries 1 and 3). However, the cis enone **8** shows opposite diastereofacial preference, giving products **53** and **54** in a preparatively useful ratio of 1:10 (entry 4). The stereostructures of the major isomers produced in the reactions of **6** and **7** are those predicted by application of Felkin's model (Figure 2). The opposite diastereofacial preference shown by the cis enone **8** is probably due to the effect of chelation, which is not possible for geometric reasons with **6** and **7**. Although the chelate would be a seven-membered ring, the site of attack is adjacent to the stereocenter, and the observed diastereofacial preference of 10:1 seems reasonable, in light of the diastereofacial preferences seen in the reactions of alkoxy aldehydes **2**–**4**.



The behavior of allylsilane **10** with enones **6** and **8** is puzzling. With both compounds, the diastereofacial selectivity with this allylsilane is greatly reduced, being only 4:1 with compound **6** and 1:1 with compound **8**. It will be recalled that, in Lewis acid mediated reactions with chiral α-alkoxy aldehydes, methallyltrimethylsilane shows slightly greater stereoselectivity than does allyltrimethylsilane (Table IV).

The results obtained with the isomeric trans and cis enones **6** and **8** may be compared with those recently reported by Roush and Lesur for the addition of lithium divinylcuprate to a γ-alkoxy-α,β-unsaturated ketone.[17] In his system, Roush found a high diastereofacial preference (>97:3), with both trans and cis enones giving the same diastereomer; in both cases, the major isomer was that predicted by application of the Felkin model.

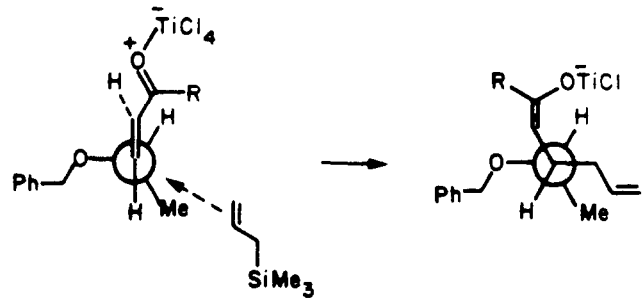


Figure 2. Proposed trajectory of attack of allylsilane **9** on enones **6** and **7**.

Table V. Diastereomer Ratios in the Reactions of Allylsilanes with Enones 6–8 (Eq 9)[a]

entry	enone	allylsilane	yield,[b] %	diastereomer ratio[c]
1	**6**	**9**	83	7:1
2	**6**	**10**	80	4:1
3	**7**	**9**	82	8:1
4	**8**	**9**	70	1:10
5	**8**	**10**	78	1:1

[a] Reaction conditions: aldehyde:$TiCl_4$:allylsilane = 1.0:1.2:1.5; solvent = methylene chloride; −78 °C; 90 min. [b] Isolated by silica gel chromatography; diastereomers were not separated. [c] Ratios were determined by 250-MHz ^1H NMR and 62.9-MHz ^{13}C NMR; ratios refer to **53**:**54** for entries 1 and 4, **57**:**58** for entries 2 and 5, and **55**:**56** for entry 3.

Conclusion

In summary, we have studied the reactions of chiral aldehydes **1**–**4** and chiral enones **5**–**8** with both allyltrimethylsilane and methallyltrimethylsilane. Aldehyde **1** and enones **5**–**7** show modest diastereofacial preferences, consistent with application of the Felkin model for asymmetric induction. In this set of compounds, stereoselectivity is generally greater with the enones than with the aldehyde **1**. Aldehydes **2**–**4** and enone **8**, which are all capable of reaction by way of chelated intermediates, show greater diastereofacial preferences, in the sense consistent with attack of the allylsilane on the less hindered face of the chelated intermediate.

Experimental Section

General Methods. Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Ether, tetrahydrofuran (THF), and benzene were distilled from sodium/benzophenone immediately prior to use. Methylene chloride, triethylamine, and diisopropylamine were distilled from calcium hydride prior to use. Titanium tetrachloride was distilled from copper powder and stored under nitrogen. All reactions involving organometallic reagents were conducted under a nitrogen atmosphere. Upon workup, solvents were evaporated by using a Büchi rotary evaporator, unless otherwise indicated. Boiling points and melting points (Pyrex capillary) are uncorrected. Infrared spectra (IR) were determined with a Perkin-Elmer 297 infrared recording spectrophotometer. ^1H NMR spectra were determined with the following spectrometers: Varian EM 390, UCB 200, or UCB 250 (super-conducting, FT instruments operating at 200 and 250 MHz, respectively). ^{13}C NMR spectra were measured at 62.89 Hz with the UCB 250. Chemical shifts

(16) Heathcock, C. H.; Pirrung, M. C.; Sohn, J. E. *J. Org. Chem.* **1979**, *44*, 4294.

(17) Roush, W. R.; Lesur, B. M. *Tetrahedron Lett.* **1983**, *24*, 2231.

are expressed in ppm downfield from internal tetramethylsilane. Significant ^{1}H NMR data are tabulated in order: multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), number of protons, coupling constant(s) in Hertz. ^{13}C NMR data are listed separately for each isomer; for those samples containing mixtures of diastereomers, the resonances for all carbons of the minor isomers were not always discernible. High-performance liquid chromatography (HPLC) was done with a Waters Model ALC/GPC-244 liquid chromatograph. "Flash chromatography" refers to the procedure of Still, Kahn, and Mitra.[18] Elemental analyses were performed by the Microanalytical Laboratory, University of California, Berkeley, CA.

(*RS*)-2-Phenylpropanal (1). Commercial material[3] was found to be contaminated with 15% acetophenone. A mixture of 25 g (186 mmol) of this mixture and 150 mL of 4 M $NaHSO_3$ solution was stirred vigorously for 12 h, during which time the mixture became thick and pasty. The mixture was triturated with ether and the pasty solid was separated. The solid material was stirred with 400 mL of warm water and 50 g of $NaHCO_3$ was added slowly. The resulting mixture was stirred for 3 h and then extracted twice with 75-mL portions of CH_2Cl_2. The organic layer was dried over $MgSO_4$ and the solvent was then removed at reduced pressure with a rotary evaporator. The residue was distilled to provide 16 g of a clear, colorless liquid, bp 54–56 °C (1.2 torr). This material was shown by ^{1}H NMR spectroscopy to contain only 3.5% acetophenone.

(*RS*)-3-(Phenylmethoxy)-2-methylpropanal (3). A solution of 10.0 g (0.116 mol) of methacrylic acid and 10.8 g (0.10 mol) of benzyl alcohol in 100 mL of dry benzene with a small amount of *p*-toluenesulfonic acid was refluxed for 15 h under a Dean–Stark trap. The mixture was cooled to room temperature and washed with dilute $NaHCO_3$. The benzene layer was dried over $MgSO_4$ and the solvent was removed with a rotary evaporator. The residue was distilled using a short-path still to afford 15 g (85%) of benzyl methacrylate: bp 73–76 °C (1 torr); ^{1}H NMR ($CDCl_3$) δ 1.94 (3 H, s), 5.16 (2 H, s), 5.50 (1 H, m), 6.12 (1 H, br s), 7.32 (5 H, br s).

Under nitrogen, 41 mg (1.7 mmol) of NaH was added to 3.24 g (30 mmol) of benzyl alcohol. The resulting solution was stirred at room temperature for 30 min and 3.0 g (17 mmol) of benzyl methacrylate was then added dropwise. After stirring at room temperature for 18 h, the reaction mixture was quenched with aqueous $NaHCO_3$ and extracted with ether. The ethereal solution was washed with water and dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by flash chromatography (100 g silica gel, 1:19 ethyl acetate/hexanes) to afford 4.21 g (86%) of benzyl 3-(phenylmethoxy)-2-methylpropanoate (**11**): IR (neat) 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20 (3 H, d, J = 7), 2.70–3.20 (1 H, m), 3.50–3.83 (2 H, m), 4.59 (2 H, s), 5.27 (2 H, s), 7.45 (10 H, br s).

To a dispersion of 2 g (52.8 mmol) of lithium aluminum hydride in 100 mL of THF was added slowly 15 g (52.8 mmol) of ester **11**. The resulting solution was stirred at room temperature for 15 h, cooled to 0 °C, quenched with 5% hydrochloric acid, and extracted with ether. The ethereal layer was washed with aqueous $NaHCO_3$ and water and dried over $MgSO_4$. After evaporation of the solvent, the residue was distilled using a short-path still to afford 7.5 g (79%) of 3-(phenylmethoxy)-2-methylpropan-1-ol (**12**): bp 117 °C (1 torr); ^{1}H NMR ($CDCl_3$) δ 0.87 (3 H, d, J = 7), 1.90–2.30 (1 H, m), 2.54 (1 H, br s), 3.33–3.75 (4 H, m), 4.60 (2 H, s), 7.48 (5 H, m).

To a solution of 4.2 g (33.1 mmol) of oxalyl chloride in 100 mL of CH_2Cl_2 at −50 °C under nitrogen was added 4.7 mL (5.15 g, 65.9 mmol) of dimethyl sulfoxide by syringe pump over a 20-min period. After stirring for 10 min, 5 g (28 mmol) of alcohol **12** was added to the mixture at −50 °C by syringe pump over a 10-min period. After stirring for 15 min, 20.3 mL (14.7 g, 145 mmol) of triethylamine was added and the resulting solution was stirred for 10 min. The reaction mixture was allowed to warm to room temperature over a 1-h period, 100 mL of water was added, and the mixture was stirred overnight. The organic layer was washed with dilute hydrochloric acid and water and dried over Na_2SO_4. After the volatile materials were removed with a rotary evaporator, the residue was distilled with a Kugelrohr apparatus [bath temp 70–90 °C (1 torr)] to afford 4.8 g (95%) of **3**: ^{1}H NMR ($CDCl_3$) δ 1.14 (3 H, d, J = 7), 2.65–2.68 (1 H, m), 3.67 (2 H, m), 4.53 (2 H, s), 7.33 (5 H, br s), 9.73 (1 H, s).

(*RS*)-3-(Phenylmethoxy)butanal (4): To a dispersion of 1.90 g (50 mmol) of lithium aluminum hydride in 150 mL of diethyl ether was added dropwise 13.2 g (100 mmol) of acetylacetaldehyde dimethyl acetal (**13**). The mixture was stirred at room temperature for 5 h, cooled to 0 °C, quenched with aqueous $NaHCO_3$, and extracted with ether. The ethereal solution was dried over $MgSO_4$. After evaporation of the solvent, the residue was distilled using a short-path still to afford 9.4 g (74%) of 3-hydroxybutanal dimethyl acetal (**14**): bp 89 °C (23 torr); ^{1}H NMR ($CDCl_3$) δ 1.18 (3 H, d, J = 6), 1.63–1.86 (2 H, m), 2.98 (1 H, br s), 3.33 (3 H, s), 3.36 (3 H, s), 3.76–4.10 (1 H, m), 4.52 (1 H, t, J = 5).

To a dispersion of 1.75 g (70 mmol) of NaH in 100 mL of dry dimethyl sulfoxide was added dropwise 9.40 g (70 mmol) of acetal **14**. The resulting mixture was stirred for 30 min and 8.07 mL (8.88 g, 70 mmol) of benzyl chloride was added dropwise. After stirring at room temperature for 12 h, the reaction mixture was quenched with water and extracted with ether. The ethereal layer was washed with aqueous NH_4Cl and water and dried over $MgSO_4$. After evaporation of the solvent, the residue was distilled using a short-path still to afford 15.2 g (96%) of 3-(phenylmethoxy)-butanal dimethyl acetal (**15**): bp 103–105 °C (0.5 torr); IR (neat) 1125, 1060 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20 (3 H, d, J = 6), 1.50–2.06 (2 H, m), 3.30 (6 H, s), 3.47–3.84 (1 H, m), 4.30–4.67 (3 H, m), 7.31 (5 H, br s).

Acetal **15** (5.0 g, 22.3 mmol) was stirred in 60 mL of a mixed solvent of acetic acid and water (1:1) at room temperature for 16 h. To the resulting solution was added dropwise with cooling aqueous $NaHCO_3$. After extraction with ether, the ethereal solution was dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was purified by flash chromatography (30 g silica gel, 1:10 ethyl acetate/hexanes) to afford 3.2 g (81%) of **4**: IR (neat) 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.23 (3 H, d, J = 6), 2.23–2.87 (2 H, m), 3.85–4.25 (1 H, m), 4.35–4.70 (2 H, m), 7.33 (5 H, br s), 9.84 (1 H, m).

(*E*,*SR*)-5-Phenylhex-3-en-2-one (5). A solution of 3.50 mL (3.53 g, 26.3 mmol) of 2-phenylpropanal and 7.58 g (23.8 mmol) of (acetylmethylene)triphenylphosphorane (**16**) in 10 mL of dry CH_2Cl_2 was heated at reflux for 16 h. The reaction mixture was cooled to room temperature and the solvent was evaporated. The residue was shaken vigorously with hexane until a white, granular precipitate was evident. The solvent was decanted and the precipitate was washed three times with hexane. The combined hexane layers were washed with brine and dried over Na_2SO_4. The solvent was evaporated and the residue (4.26 g) was distilled to provide 2.36 g (52%) of a clear, colorless liquid: bp 83–84.5 °C (0.05 torr); IR (film) 1675, 1450, 1360 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.43 (d, 3 H, J = 7), 2.23 (s, 3 H), 3.63 (double quintet, 1 H, J = 1, 7), 6.06 (dd, 1 H, J = 1, 16), 6.92 (dd, 1 H, J = 7, 16), 7.27 (m, 5 H). Anal. Calcd for $C_{11}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.68; H, 7.91.

(*E*,*SR*)- and (*Z*,*SR*)-5-(Phenylmethoxy)hex-3-en-2-one (6 and 8). A solution of 1.18 g (7.19 mmol) of 2-(phenylmethoxy)propanal and 2.55 g (8.01 mmol) of (acetylmethylene)triphenylphosphorane (**16**) in 5 mL of dry CH_2Cl_2 was heated at reflux for 24 h. The reaction mixture was cooled to room temperature and the solvent was evaporated. The residue was shaken with hexane until a white, granular precipitate was evident. The solvent was decanted and the precipitate was washed three times with hexane. The combined hexane layers were washed with brine and dried over Na_2SO_4, and the solvent was evaporated. The residue (1.51 g) was purified by chromatography on 50 g of silica gel with 7:93 ether/hexane as eluant to afford 421 mg (29%) of **8**: a clear, colorless oil, R_f 0.17; IR (film): 1680, 1450, 1360, 1255 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.31 (d, 3 H, J = 7), 2.21 (s, 3 H), 4.41 (d, 1 H, J = 12), 4.48 (d, 1 H, J = 12), 5.04 (quintet, 1 H, J = 7), 6.08 (dd, 1 H, J = 7, 12), 6.19 (d, 1 H, J = 12), 7.30 (s, 5 H). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.79; C, 7.79. Further elution with 1:4 ether/hexane provided 876 mg (60%) of **6**: a clear, colorless oil, R_f 0.07 with 7:93 ether/hexane as eluant; IR (film) 1680, 1450, 1360, 1255 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.34 (d, 3 H, J = 6), 2.26 (s, 3 H), 4.13 (double quintet, 1 H, J = 1, 6), 4.45 (d, 1 H, J = 12), 4.54 (d, 1 H, J = 12), 6.22 (dd, 1

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

H, J = 1, 16), 6.68 (dd, 1 H, J = 6, 16), 7.33 (s, 5 H). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.25; H, 7.78.

(*E*,4*SR*)-1-Phenyl-4-(phenylmethoxy)pent-2-en-1-one (7). A solution of 1.22 g (7.44 mmol) of 2-(phenylmethoxy)propanal and 2.83 g (7.44 mmol) of (benzoylmethylene)triphenylphosphorane (**17**) in 5 mL of dry CH_2Cl_2 was heated at reflux for 24 h. The reaction mixture was cooled to room temperature and the solvent was evaporated. The residue was shaken vigorously with hexane until a white, granular precipitate was evident. The solvent was decanted and the precipitate was washed five times with hexane. The combined hexane layers were washed with brine and dried over Na_2SO_4, and the solvent was evaporated. The residue (1.78 g) was purified by chromatography on 50 g of silica gel with 7:93 ether/hexane as eluant to afford 1.52 g (77%) of a clear, colorless oil: IR (film) 1670, 1625, 1450, 1280 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.39 (d, 3 H, J = 7), 4.25 (double quintet, 1 H, J = 1, 6), 4.51 (d, 1 H, J = 12), 4.63 (d, 1 H, J = 12), 6.98 (dd, 1 H, J = 6, 16), 7.10 (dd, 1 H, J = 1, 16), 7.36 (s, 5 H), 7.47 (m, 3 H), 7.94 (d, 2 H, J = 7). Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.03; H, 6.73.

General Procedure for Reactions of Allylsilanes with Aldehydes. (4*SR*,5*SR*)- and (4*RS*,5*SR*)-5-(Phenylmethoxy)hex-1-en-4-ol (31 and 32). A solution of 0.117 mL (260 mg, 1 mmol) of stannic chloride in 4 mL of dry CH_2Cl_2 was cooled to −78 °C. To the solution was added dropwise a solution of 164 mg (1 mmol) of 2-(phenylmethoxy)propanal in 0.5 mL of dry CH_2Cl_2 with a syringe over a 2-min period. The solution was stirred for 3 min and 0.175 mL (125 mg, 1.1 mmol) of allyltrimethylsilane (**9**) was added in one portion. After stirring at −78 °C for 15 min, the clear reaction mixture was quenched with water. The reaction mixture was allowed to warm to room temperature and was extracted with ether. The ethereal layer was dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by flash chromatography (9 g silica gel; 1:15 ethyl acetate/hexanes) to afford 193 mg (94%) of a clear, colorless liquid, which was a 35:1 mixture of the diastereomers **31** and **32**, respectively: IR (neat) 3450 cm^{-1}; ^1H NMR ($CDCl_3$) major isomer (**31**) δ 1.19 (3 H, d, J = 7), 2.12–2.40 (2 H, m), 2.69 (1 H, br s), 3.40–3.60 (2 H, m), 4.42 (1 H, d, J = 11), 4.63 (1 H, d, J = 11), 5.00–5.20 (2 H, m), 5.80–6.00 (1 H, m), 7.31 (5 H, br s), minor isomer (**32**) δ 1.20 (3 H, d, J = 7), 4.52 (1 H, d, J = 11), 4.64 (1 H, d, J = 11); ^{13}C NMR ($CDCl_3$) major isomer (**31**) δ 15.2, 37.3, 70.8, 74.0, 77.2, 116.9, 127.5, 127.6 (2 C), 128.2 (2 C), 134.7, 138.2. Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.37; H, 8.62.

(4*SR*,5*SR*)- and (4*RS*,5*SR*)-2-Methyl-5-(phenylmethoxy)hex-1-en-4-ol (33 and 34). The reaction (stannic chloride) of **2** and **10** was performed on 1-mmol scale. The crude product was purified by flash chromatography (the same conditions mentioned above) to afford 178 mg (81%) of a clear, colorless liquid, which was a 45:1 mixture of the diastereomers **33** and **34**, respectively: IR (neat) 3445 cm^{-1}; ^1H NMR ($CDCl_3$) major isomer (**33**) δ 1.20 (3 H, d, J = 7), 1.77 (3 H, s), 2.10–2.30 (2 H, m), 2.56 (1 H, br s), 3.44 (1 H, m), 3.65 (1 H, m), 4.43 (1 H, d, J = 11.5), 4.63 (1 H, d, J = 11.5), 4.77 (1 H, m), 4.82 (1 H, m), 7.32 (5 H, m), minor isomer (**34**) δ 1.20 (3 H, d, J = 7), 1.77 (3 H, s), 2.14–2.30 (2 H, m), 4.48 (1 H, d, J = 11), 4.61 (1 H, d, J = 11); ^{13}C NMR ($CDCl_3$) major isomer (**33**) δ 15.3, 22.3, 41.2, 70.8, 72.3, 77.3, 112.7, 127.4, 127.5 (2 C), 128.2 (2 C), 138.2, 142.5. Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 75.94; H, 8.85.

(4*SR*,5*RS*)- and (4*RS*,5*RS*)-5-Methyl-6-(phenylmethoxy)hex-1-en-4-ol (35 and 36). The reaction (stannic chloride) of **3** and **9** was performed on a 1-mmol scale. The crude product was purified by flash chromatography (the same conditions mentioned above) to afford 202 mg (92%) of a clear, colorless liquid, which was a 12:1 mixture of the diastereomers **35** and **36**, respectively: IR (neat) 3450 cm^{-1}; ^1H NMR ($CDCl_3$) major isomer (**35**) δ 0.90 (3 H, d, J = 7), 1.80–1.95 (1 H, m), 2.10–2.40 (2 H, m), 3.33 (1 H, br s), 3.42–3.66 (3 H, m), 4.48 (2 H, s), 5.05–5.10 (2 H, m), 5.80–6.00 (1 H, m), 7.30 (5 H, m), minor isomer (**36**) δ 0.94 (3 H, d, J = 7.25), 3.74–3.85 (1 H, m); ^{13}C NMR ($CDCl_3$) major isomer (**35**) δ 13.6, 37.7, 39.1, 73.2, 74.3, 74.5, 116.9, 127.4 (2 C), 127.5, 128.2 (2 C), 135.0, 137.7, minor isomer (**36**) δ 10.5, 37.3, 38.7, 72.5, 74.2, 125.6, 128.1, 135.4. Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.06; H, 9.04.

(4*SR*,5*RS*)- and (4*RS*,5*RS*)-2,5-Dimethyl-6-(phenylmethoxy)hex-1-en-4-ol (37 and 38). The reaction (stannic chloride) of **3** and **10** was performed on a 1-mmol scale. The crude product was purified by flash chromatography (the same conditions mentioned above) to afford 194 mg (83%) of a clear, colorless liquid, which was a 10:1 mixture of the diastereomers **37** and **38**, respectively: IR (neat) 3455 cm^{-1}; ^1H NMR ($CDCl_3$) major isomer (**37**) δ 0.96 (3 H, d, J = 7), 1.76 (3 H, s), 1.87 (1 H, m), 2.00–2.30 (2 H, m), 2.93 (1 H, d, J = 3.25), 3.50–3.60 (2 H, m), 3.66–3.72 (1 H, m), 4.50 (2 H, s), 4.78 (1 H, m), 4.85 (1 H, m), 7.31 (5 H, m), minor isomer (**38**) δ 3.89–3.98 (1 H, m); ^{13}C NMR ($CDCl_3$) major isomer (**37**) δ 13.9, 22.3, 38.4, 43.3, 72.2, 73.2, 73.8, 112.9, 127.5 (2 C), 128.3 (2 C), 137.9, 143.0. Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.92; H, 9.56.

(4*RS*,6*RS*)- and (4*SR*,6*RS*)-6-(Phenylmethoxy)hept-1-en-4-ol (39 and 40). The reaction (stannic chloride) of **4** and **9** was performed on a 1-mmol scale. The crude product was purified by flash chromatography (the same conditions mentioned above) to afford 215 mg (97%) of a clear, colorless liquid, which was a 9:1 mixture of the diastereoisomers, **39** and **40**, respectively: IR (neat) 3420 cm^{-1}; ^1H NMR ($CDCl_3$) major isomer (**39**) δ 1.26 (3 H, d, J = 6.35), 1.64–1.69 (2 H, m), 2.19–2.25 (2 H, m), 2.72 (1 H, d, J = 3.8), 3.84–4.08 (2 H, m), 4.45 (1 H, d, J = 11.75), 4.63 (1 H, d, J = 11.8), 5.05–5.14 (2 H, m), 5.78–5.88 (1 H, m), 7.33 (5 H, m), minor isomer (**40**) δ 1.25 (3 H, d, J = 6), 4.42 (1 H, d, J = 11.5), 4.67 (1 H, d, J = 11.5); ^{13}C NMR ($CDCl_3$) major isomer (**39**) δ 19.2, 41.9, 42.3, 67.4, 70.4, 72.4, 117.2, 127.4, 127.5 (2 C), 128.2 (2 C), 134.8, 138.3, minor isomer (**40**) δ 19.4, 41.9, 43.0, 70.1, 128.3. Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.15; H, 9.00.

(4*RS*,6*RS*)- and (4*SR*,6*RS*)-2-Methyl-6-(phenylmethoxy)hept-1-en-4-ol (41 and 42). The reaction (stannic chloride) of **4** and **10** was performed on a 1-mmol scale. The crude product was purified by flash chromatography (the same conditions mentioned above) to afford 201 mg (86%) of a clear, colorless liquid, which was a 7:1 mixture of diastereoisomers, **41** and **42**, respectively: IR (neat) 3450 cm^{-1}; ^1H NMR ($CDCl_3$) major isomer (**41**) δ 1.26 (3 H, d, J = 6), 1.60–1.70 (2 H, m), 1.75 (3 H, s), 2.10–2.25 (2 H, m), 2.60 (1 H, d, J = 3), 3.80–4.00 (1 H, m), 4.00–4.15 (1 H, m), 4.46 (1 H, d, J = 11.5), 4.63 (1 H, d, J = 11.5), 4.76 (1 H, m), 4.84 (1 H, m), 7.33 (5 H, m), minor isomer (**42**) δ 1.25 (3 H, d, J = 6.25), 2.19 (1 H, d, J = 2.75), 4.43 (1 H, d, J = 10); ^{13}C NMR ($CDCl_3$) major isomer (**41**) δ 19.4, 22.4, 43.0, 46.1, 65.8, 70.6, 72.5, 112.8, 127.5, 127.6 (2 C), 128.3 (2 C), 138.5, 142.7. Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 77.14; H, 9.60.

(3*RS*,2*RS*)- and (3*RS*,2*SR*)-2-Phenylhex-5-en-3-ol (18 and 19). The reaction (stannic chloride) of **1** and **9** was performed on a 1-mmol scale. The crude product was purified by flash chromatography (the same conditions mentioned above) to afford 151 mg (86%) of a clear, colorless liquid, which was a 2.2:1 mixture of the diastereomers, **18** and **19**, respectively: IR ($CHCl_3$) 3600 cm^{-1}; ^1H NMR ($CDCl_3$) major isomer (**18**) δ 1.32 (3 H, d, J = 7), 1.78 (1 H, br s), 1.96–2.24 (2 H, m), 2.68–2.84 (1 H, m), 3.62–3.77 (1 H, m), 5.02–5.16 (2 H, m), 5.70–5.97 (1 H, m), 7.14–7.36 (5 H, m), minor isomer (**19**) δ 1.28 (3 H, d, J = 7); ^{13}C NMR ($CDCl_3$) major isomer (**18**) δ 16.3, 39.4, 45.3, 74.9, 117.9, 126.3, 127.7, 128.4 (2 C), 135.0, 143.2, 144.3, minor isomer (**19**) δ 17.6, 38.9, 117.5, 126.5, 128.1 (2C). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 82.08; H, 8.93.

(3*RS*,2*RS*)- and (3*RS*,2*SR*)-5-Methyl-2-phenylhex-5-en-3-ol (20 and 21). The reaction (stannic chloride) of **1** and **10** was performed on a 1-mmol scale. The crude product was purified by flash chromatography (the same conditions mentioned above) to afford 122 mg (68%) of a clear, colorless liquid, which was a 3.2:1 mixture of the diastereoisomers **20** and **21**, respectively: IR (neat) 3450 cm^{-1}; ^1H NMR ($CDCl_3$) major isomer (**20**) δ 1.35 (3 H, d, J = 7), 1.68 (3 H, s), 1.88–2.14 (2 H, m), 2.74 (1 H, m), 3.79 (1 H, m), 4.76 (1 H, m), 4.84 (1 H, m), 7.16–7.36 (5 H, m), minor isomer (**21**) δ 1.31 (3 H, d, J = 7.25), 1.74 (3 H, s); ^{13}C NMR ($CDCl_3$) major isomer (**20**) δ 16.5, 22.0, 43.8, 45.7, 72.9, 113.2, 126.3, 127.6, 128.1, 128.3 (2 C), 142.9, 144.5, minor isomer (**21**) δ 17.5, 22.3, 43.0, 45.5, 113.2, 126.4, 127.8, 128.2 (2 C), 142.8. Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.87; H, 9.31.

The mixture of diastereomeric acetates (**22a** and **22b**) was prepared by the following procedure. A solution of 270 mg (1.42 mmol) of the 3.2:1 mixture of **20** and **21** and 163 mg of acetic anhydride in 3 mL of dry pyridine was stirred at room temperature

for 2 days. The reaction mixture was quenched with water and extracted with ether. The ethereal layer was dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by flash chromatography (9 g silica gel, 1:19 ethyl acetate/hexanes) to afford 243 mg (74%) of acetate: IR (neat) 1735, 1235 cm^{-1}; ^1H NMR ($CDCl_3$) major isomer (**22a**) δ 1.27 (3 H, d, J = 6.75), 1.66 (3 H, s), 2.02 (3 H, s), 2.08–2.20 (2 H, m), 2.82–3.02 (1 H, m), 4.65 (1 H, m), 4.72 (1 H, m), 5.25 (1 H, m), 7.15–7.35 (5 H, m), minor isomer (**22b**) δ 1.71 (3 H, s), 1.90 (3 H, s); ^{13}C NMR ($CDCl_3$) major isomer (**22a**) δ 17.3, 20.9, 22.1, 41.1, 43.9, 75.4, 113.1, 126.6, 127.6 (2 C), 128.4 (2 C), 141.8, 143.4, 170.5, minor isomer (**22b**) δ 17.2, 20.8, 22.3, 40.3, 43.3, 75.0, 113.1, 126.4, 128.0 (2 C), 128.1 (2 C), 141.7, 142.5.

4-Chloro-5-phenyl-1-hexenes. The reaction (titanium tetrachloride) of **1** and **9** was performed at room temperature. The isolated product was a 1.3:1 mixture of diastereomeric chlorides: IR (neat) 3460, 760, 705 cm^{-1}; ^1H NMR ($CDCl_3$) major isomer δ 1.34 (3 H, d, J = 7), 1.55 (6 H, s), minor isomer δ 1.30 (3 H, d, J = 7), 1.59 (6 H, s). Anal. Calcd for $C_{13}H_{19}Cl$: C, 68.86; H, 8.45. Found: C, 69.23; H, 8.35.

(2*SR*,3*SR*)-Hexane-2,3-diol (43). Unsaturated alcohol **31** (150 mg, 0.68 mmol) was dissolved in 7 mL of 1:10 formic acid/ethanol and 40 mg of 10% Pd/C was added. The mixture was stirred under an atmosphere of hydrogen for 20 h. After removal of the catalyst by filtration through Celite, the solvent was evaporated to afford 66 mg (83%) of diol **43**: IR (neat) 3360 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 (3 H, t, J = 6), 1.18 (3 H, d, J = 6.25), 1.32–1.62 (4 H, m), 2.95 (2 H, br s), 3.33 (1 H, m), 3.58 (1 H, m).

(2*RS*,3*SR*)-Hexane-2,3-diol (44). A solution of 2.34 g (14.8 mmol) of $KMnO_4$ and 0.5 g (12.5 mmol) of NaOH in 80 mL of water was cooled to 0 °C and added quickly with vigorous stirring to a cold mixture (−10 °C) of 100 mL of *tert*-butyl alcohol, 20 mL of water, and 50 g of cracked ice containing 0.84 g (10 mmol) of *cis*-2-hexene. After 5 min, most of the permanganate color had been discharged. The precipitate of manganese dioxide was filtered through Celite. Most of the *tert*-butyl alcohol was removed by distillation at atmospheric pressure. The resulting solution was concentrated to about 25 mL under reduced pressure and extracted with ether. After drying over $MgSO_4$, the ethereal solution gave 1.02 g (86%) of **44** as a colorless oil: IR (neat) 3360 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 (3 H, t, J = 7), 1.13 (3 H, d, J = 6.25), 1.30–1.62 (4 H, m), 2.90 (1 H, br s), 2.97 (1 H, br s), 3.63 (1 H, m), 3.77 (1 H, m).

(2*RS*,3*SR*)-2-Methylhexane-1,3-diol (45). (a) A 2:1 mixture of 70 mg (0.299 mmol) of unsaturated alcohols **35** and **36** was hydrogenated, using 20 mg of 10% Pd/C, to afford 347 mg (88%) of a mixture of diols: IR ($CHCl_3$) 3610, 3480 cm^{-1}; ^1H NMR ($CDCl_3$) major isomer (**45**) δ 0.87 (3 H, d, J = 6.75), 0.93 (3 H, t, J = 6.75), 1.30–1.60 (4 H, m), 1.60–1.80 (1 H, m), 3.48–3.64 (2 H, m), 3.68–3.78 (1 H, m), 4.22 (1 H, br s), 4.40 (1 H, br s); ^{13}C NMR ($CDCl_3$) major isomer (**45**) δ 13.7, 14.0, 18.3, 37.1, 39.6, 67.0, 76.3.

(b) To a dispersion of 450 mg (11.8 mmol) of lithium aluminum hydride in 10 mL of THF was added dropwise a solution of 450 mg (1.67 mmol) of 2,6-dimethylphenyl 3-hydroxy-2-methylhexanoate (**46**).[19] The resulting solution was stirred overnight and quenched with 5% hydrochloric acid. The mixture was extracted with ether and the ethereal solution was dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by flash chromatography (9 g silica gel, 1:4 ethyl acetate/hexanes) to afford 148 mg (67%) of **43**, identical by ^1H NMR and ^{13}C NMR with the major isomer of the mixture of diols prepared in part a.

(2*SR*,4*RS*)- and (2*RS*,4*RS*)-Heptane-2,4-diol (47 and 48). (a) A 7:1 mixture of 70 mg (0.299 mmol) of unsaturated alcohols **39** and **40** was hydrogenated, using 20 mg of 10% Pd/C to afford 36 mg (92%) of diol: IR ($CHCl_3$) 3600, 3460 cm^{-1}; ^1H NMR ($CDCl_3$) major isomer (**48**) δ 0.92 (3 H, t, 6.25), 1.20 (3 H, d, J = 6), 1.30–1.50 (4 H, m), 1.50–1.62 (2 H, m), 3.89 (2 H, br s), 4.09 (2 H, m); ^{13}C NMR ($CDCl_3$) major isomer (**48**) δ 13.9, 18.8, 32.2, 39.4, 44.2, 64.9, 68.5.

(b) To a dispersion of 760 mg (20 mmol) of lithium hydride in 30 mL of THF was added dropwise a solution of 2.6 g (20 mmol) of 4-hydroxy-2-heptanone (**49**).[20] The resulting solution was stirred overnight and quenched with 5% hydrochloric acid. The mixture was extracted with ether and the ethereal solution was dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by flash chromatography (120 g silica gel, 1:4 ethyl acetate/hexanes) to afford two isomers (2.18 g, 83%): 1.51 g of **47** and 669 mg of **48**.

Compound 47: IR ($CHCl_3$) 3600, 3480 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (3 H, t, J = 6.5), 1.18 (3 H, d, J = 6.25), 1.30–1.50 (4 H, m), 1.50–1.60 (2 H, m), 3.82 (1 H, br s), 4.02 (1 H, br s), 4.45 (1 H, m), 4.59 (1 H, m); ^{13}C NMR ($CDCl_3$) δ 13.8, 18.3, 23.7, 40.0, 44.2, 68.5, 72.1.

Compound 48: The spectra of isomer **48** were identical with those reported for the major isomer produced in part a.

(2*SR*,4*SR*,6*RS*)-4-Methyl-2-phenyl-6-propyl-1,3-dioxane (50). A solution of 132 mg (1 mmol) of **47** and 127 mg (1.2 mmol) of benzaldehyde in 10 mL of benzene with 5 mg of *p*-toluenesulfonic acid was refluxed under a Dean–Stark water separator for 3 h. The mixture was washed with 2 N NaOH and water. The organic layer was dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by flash chromatography (9 g silica gel, 1:100 ethyl acetate/hexanes) to give 162 mg (74%) of **50**: ^1H NMR ($CDCl_3$) δ 0.93 (3 H, t, J = 7), 1.28 (3 H, d, J = 6), 1.30–1.70 (6 H, m), 3.76 (1 H, m), 3.92 (1 H, m), 5.49 (1 H, s), 7.22–7.60 (5 H, m).

(2*SR*,4*RS*,6*RS*)- and (2*RS*,4*RS*,6*RS*)-4-Methyl-2-phenyl-6-propyl-1,3-dioxane (51 and 52). The reaction was performed with 132 mg (1 mmol) of **48** to afford 177 mg (80%) of **51** and **52**: IR (neat) 1130, 1020, 995 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 (3 H, t, J = 7), 0.98 (3 H, t, J = 7.25), 1.28 (3 H, d, J = 6.25), 1.47 (3 H, d, J = 7), 1.34–1.72 (4 H, m), 1.90–2.20 (2 H, m), 3.96–4.50 (2 H, m), 5.76 (1 H, s), 5.81 (1 H, s), 7.30–7.60 (5 H, m). The NMR signals at δ 0.94 and 0.98 (methyl group on the propyl substituent), δ 1.28 and 1.47 (methyl group), and δ 5.76 and 5.81 (methine proton from benzaldehyde) show two isomers in a ratio of 1:1.

General Procedure for Allylsilane Conjugate Additions. 4-(1-Phenylethyl)hept-6-en-2-ones (25 and 26). A solution of 258 mg (1.48 mmol) of enone **5** in 6.5 mL of dry CH_2Cl_2 was cooled to −78 °C. Titanium tetrachloride (0.20 mL, 350 mg, 1.8 mmol) was added to the stirring reaction mixture in one portion, giving rise to a deep red solution in which a yellow precipitate was evident. After 5 min, a solution of 0.35 mL (250 mg, 2.2 mmol) of allyltrimethylsilane in 1 mL of dry CH_2Cl_2 was added dropwise over a 30-min period. The dark purple mixture was stirred an additional 60 min, and 2 mL of water was then added over a 10-min period. The reaction mixture was allowed to warm to room temperature, during which time it became colorless. The mixture was partitioned between ether and brine. The ethereal layer was dried over sodium sulfate and the solvent was evaporated. The residue (356 mg) was purified by chromatography on 12 g of silica gel with 1:24 ether/hexane as eluant to afford 236 mg (74%) of a clear, colorless oil shown by ^1H and ^{13}C NMR spectroscopy to be a 4:1 mixture of diastereomers: IR (film) 1710, 1450, 1360, 1160, 990, 915 cm^{-1}; ^{13}C NMR ($CDCl_3$) major isomer (**25**) δ 17.2, 30.1, 36.2, 39.1, 41.5, 44.4, 116.3, 125.8, 127.5, 128.0, 136.5, 145.1, 208.0, minor isomer (**26**) δ 18.3, 35.3, 39.2, 41.9, 45.1, 116.6, 136.1, 145.4. Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C,

(19) Compound **46** was prepared as a 6:1 mixture of anti and syn diastereomers by the procedure previously reported (ref 13). The spectral properties of the anti diastereomer are as follows: IR (neat) 3500, 1740, 1155 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.80–1.10 (3 H, m), 1.38 (3 H, d, J = 7), 1.20–1.70 (4 H, m), 2.13 (6 H, s), 2.40–3.00 (2 H, m), 3.65–4.00 (1 H, m), 7.01 (3 H, s).

(20) Compound **49** was prepared by addition of the lithium enolate of acetone to butanal: ^1H NMR ($CDCl_3$) δ 0.80–1.10 (3 H, m), 1.20–1.60 (4 H, m), 2.20 (3 H, s), 2.50–2.70 (2 H, m), 3.18 (1 H, br s), 4.07 (1 H, m).

(21) **Note added in proof.** In a recent communication,[22] Reetz and co-workers have commented on our preliminary disclosure of the reactions of alkoxy aldehydes with allylsilanes.[11] As has already been pointed out, these authors report that the complexes of $TiCl_4$ and BF_3 with β-alkoxy aldehydes **3** and **4** are not stable at ambient temperatures. Therefore, it is necessary to form the aldehyde–Lewis acid complexes at −78 °C before addition of the allylsilane. With aldehyde **1**, Reetz and co-workers have confirmed our report that the the $SnCl_4$ complex is stable at room temperature, while the $TiCl_4$ complex is not, and that $SnCl_4$ is probably a superior catalyst for sensitive aldehyd

(22) Reetz, M. T.; Kesseler, K.; Jung, A. *Tetrahedron Lett.* **1984**, *25*, 729.

83.09; H, 9.25. A sample of each diastereomer was separated by analytical HPLC with 1:49 ether/hexane as eluant: ^{1}H NMR ($CDCl_3$) major isomer (**25**) δ 1.21 (d, 3 H, J = 7), 1.83 (m, 1 H), 2.07 (s, 3 H), 2.12 (m, 1 H), 2.32 (m, 1 H), 2.35 (br s, 1 H), 2.81 (m, 1 H), 4.96 (m, 2 H), 5.65 (m, 1 H), 7.27 (m, 5 H), minor isomer (**26**) δ 1.26 (d, 3, J = 7), 1.94 (s, 3 H), 2.07 (m, 1 H), 2.24 (m, 2 H), 2.29 (m, 2 H), 2.70 (m, 1 H), 5.02 (m, 2 H), 5.72 (m, 1 H), 7.23 (m, 5 H).

The following compounds were prepared in a manner analogous to that described above:

4-[1-(Phenylmethoxy)ethyl]hept-6-en-2-ones (53 and 54). (a) The reaction was performed with 179 mg (0.877 mmol) of enone **6**, 0.12 mL (210 mg, 1.1 mmol) of titanium tetrachloride, and 152 mg (1.33 mmol) of allyltrimethylsilane. The crude product was purified by chromatography on silica gel with 1:19 ether/hexane as eluant to afford 180 mg (83%) of a clear, colorless oil shown to be a 7:1 mixture of diastereomers: IR (film) 3070, 3030, 1710, 1450, 1360, 990, 910 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.17 (d, 3 H, J = 6), 2.03 (m, 1 H), 2.09 (s, 3 H), 2.26 (m, 2 H), 2.46 (dd, 2 H, J = 6, 13), 3.51 (m, 1 H), 4.40 (d, 1 H, J = 11), 4.58 (d, 1 H, J = 11), 5.02 (dd, 2 H, J = 1, 12), 5.72 (m, 1 H), 7.34 (s, 5 H); ^{13}C NMR ($CDCl_3$) major isomer (**53**) δ 16.5, 30.1, 35.3, 38.9, 43.6, 70.3, 75.9, 116.4, 127.1, 127.3, 128.0, 136.5, 138.6, 208.1, minor isomer (**54**) δ 15.2, 30.3, 34.7, 37.4, 42.9, 70.2, 75.5, 116.1, 136.7. Anal. Calcd for $C_{16}H_{22}O_2$: C, 77.51; H, 8.94. Found: C, 77.74; H, 8.68.

(b) The reaction was performed with 103 mg (0.505 mmol) of enone **8**, 0.070 mL (120 mg, 0.64 mmol) of titanium tetrachloride, and 86.5 mg (0.757 mmol) of allyltrimethylsilane. The crude product was purified by chromatography on silica gel with 1:19 ether/hexane as eluant to give 88 mg (70%) of a clear, colorless oil shown to be a 10:1 mixture of diastereomers: ^{13}C NMR ($CDCl_3$) major isomer (**54**) δ 15.3, 30.5, 34.9, 37.6, 43.1, 70.3, 75.6, 116.3, 127.3, 127.5, 128.2, 136.8, 138.8, 208.6, minor isomer (**53**) δ 35.4, 39.0, 70.5, 76.1, 104.6, 116.5, 127.2.

1-Phenyl-4-[1-(phenylmethoxy)ethyl]hex-5-en-1-ones (55 and 56). The reaction was performed with 230 mg (0.863 mmol) of enone **7**, 0.12 mL (210 mg, 1.10 mmol) of titanium tetrachloride, and 179 mg (1.57 mmol) of allyltrimethylsilane. The crude product was purified by chromatography on silica gel with 1:19 ether/hexane as eluant to afford 218 mg (82%) of a clear, colorless oil shown to be a 8:1 mixture of diastereomers: IR (film) 3060, 3030, 1685, 1450, 1000, 910 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.28 (d, 3 H, J = 6), 2.21 (m, 1 H), 2.43 (m, 1 H), 2.56 (m, 1 H), 3.02 (dd, 1 H, J = 7, 17), 3.17 (dd, 1 H, J = 7, 17), 3.70 (quintet, 1 H, J = 6), 4.48 (d, 1 H, J = 12), 4.67 (d, 1 H, J = 12), 5.08 (m, 2 H), 5.84 (m, 1 H), 7.38 (s, 5 H), 7.50 (m, 2 H), 7.57 (m, 1 H), 8.02 (d, 2 H, J = 7); ^{13}C NMR ($CDCl_3$) major isomer (**55**) δ 16.6, 35.2, 38.2, 39.1, 70.4, 75.7, 116.5, 127.1, 127.4, 127.8, 128.0, 128.2, 132.5, 136.6, 137.2, 138.7, 199.7, minor isomer (**56**) δ 38.1, 70.3, 75.5, 116.3, 126.9, 127.0, 127.3, 127.6, 136.8. Anal. Calcd for $C_{22}H_{24}O_2$: C, 81.78; H, 7.84. Found: C, 81.57; H, 7.72.

6-Methyl-4-[1-(phenylmethoxy)ethyl]hept-6-en-2-ones (57 and 58). (a) The reaction was performed with 161 mg (0.789 mmol) of enone **6**, 0.11 mL (190 mg, 1.0 mmol) of titanium tetrachloride, and 190 mg (1.47 mmol) of methallyltrimethylsilane. The crude product was purified by chromatography on silica gel with 1:19 ether/hexane as eluant to afford 164 mg (80%) of a clear, colorless oil shown to be a 4:1 mixture of diastereomers: IR (film) 1710, 1450, 890 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.10 (d, 3 H, J = 6), 2.04 (s, 3 H), 3.47 (m, 1 H), 4.35 (d, 1 H, J = 12), 4.52 (d, 1 H, J = 12), 4.60 (s, 1 H), 4.71 (s, 1 H), 7.28 (s, 1 H); ^{13}C NMR ($CDCl_3$) major isomer (**57**) δ 16.8, 22.0, 30.3, 37.0, 39.6, 43.8, 70.6, 76.3, 112.4, 127.3, 127.6, 128.2, 138.8, 144.1, 208.6, minor isomer (**58**) δ 21.9, 30.3, 35.4, 38.9, 70.4, 75.6, 112.3, 128.1. Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29 Found: C, 78.18; H, 9.25.

(b) The reaction was performed with 108 mg (0.527 mmol) of enone **8**, 0.070 mL (120 mg, 0.64 mmol) of titanium tetrachloride, and 212 mg (2.29 mmol) of methallyltrimethylsilane. The crude product was purified by chromatography on silica gel with 1:19 ether/hexane as eluant to afford 107 mg (78%) of a clear, colorless oil: ^{13}C NMR ($CDCl_3$) the resonances observed correspond to a 52:48 mixture of **57** and **58**. Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.18; H, 9.08.

4-(1-Phenylethyl)-2-heptanones (29 and 30). (a) A mixture of olefins **25** and **26** (90.6 mg, 0.419 mmol) was dissolved in 20 mL of absolute ethanol and 10 mg of platinum oxide was added. The mixture was stirred under an atmosphere of hydrogen until the uptake of hydrogen had ceased. The catalyst was removed by filtration through Celite and the solvent was evaporated to afford 86.2 mg (94%) of a mixture of **29** and **30**: IR (film) 1710, 1450, 1360 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85 (t, 3 H, J = 7), 1.19 (d, 3 H, J = 7), 1.30 (m, 4 H), 2.03 (s, 3 H), 2.23 (m, 1 H), 2.29 (m, 2 H), 2.85 (m, 1 H), 7.23 (m, 5 H); ^{13}C NMR ($CDCl_3$) major isomer (**29**) δ 14.1, 16.2, 20.0, 30.1, 34.1, 39.6, 41.2, 45.1, 125.8, 127.7, 128.0, 145.4, 208.8, minor isomer (**30**) δ 14.3, 19.5, 30.2, 40.0, 42.3, 46.1, 125.9. Anal. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 82.38; H, 10.04.

(b) To a vigorously stirring suspension of 52.0 mg (2.14 mmol) of magnesium turnings in 0.5 mL of dry THF at room temperature was added 3 drops of 1-bromopropane and a small crystal of iodine. After several minutes the violet color disappeared and the reaction was diluted with 1 mL of dry THF. The remaining 1-bromopropane [a total volume of 0.075 mL (100 mg, 0.83 mmol) of 1-bromopropane was added] was added dropwise over a 30-min period. After stirring an additional 30 min, the mixture was cooled to −20 °C and 27 mg (0.14 mmol) of purified copper(I) iodide was added. After stirring for another 30-min period, 117 mg (0.670 mmol) of enone **5** in 1 mL of dry THF was added dropwise over a 45-min period. After stirring for 30 min, the reaction mixture was allowed to warm to room temperature, during which time the mixture turned black, and was subsequently poured into a vigorously stirring 4:1 mixture of saturated aqueous ammonium chloride solution and concentrated aqueous ammonia. The resulting mixture was extracted twice with ether. The combined ether extracts were washed once each with 4:1 ammonia buffer and brine and then dried over Na_2SO_4. The solvent was evaporated. The residue (109 mg) was purified by chromatography on 5 g of silica gel with 1:24 ether/hexane as eluant to afford 48 mg (41%) of a clear, colorless oil shown to be a 4:1 mixture of diastereomers: ^{13}C NMR ($CDCl_3$) the resonances observed for the major and minor diastereomers correspond to those obtained for the hydrogenated allylsilane products **29** and **30**.

(2*SR*,3*RS*)- and (2*RS*,3*RS*)-2-Propyl-1,3-butanediol Diacetates (59 and 60). (a) A 7:1 mixture of compounds **53** and **54** (411 mg, 1.66 mmol), obtained from allylsilane addition to trans enone **6**, was dissolved in 25 mL of ethyl acetate. Platinum oxide (19 mg) and potassium carbonate (30 mg) were added, and the mixture was stirred under an atmosphere of hydrogen until the uptake of hydrogen had ceased. The catalyst was removed by filtration through Celite, and the solvent was evaporated to afford 412 mg (99%) of diastereomeric 5-(phenylmethoxy)-4-propyl-2-heptanones: IR (film) 1710, 1450, 1360 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.91 (t, 3 H, J = 7), 1.12 (m, 1 H), 1.17 (d, 3 H, J = 6), 1.26 (m, 2 H), 1.45 (m, 1 H), 2.12 (s, 3 H), 2.38 (dd, 1 H, J = 6, 17), 2.53 (dd, 1 H, J = 6, 17), 3.48 (quintet, 1 H, J = 6), 4.41 (d, 1 H, J = 12), 4.59 (d, 1 H, J = 12), 7.34 (s, 5 H); ^{13}C NMR ($CDCl_3$) major isomer δ 14.2, 16.7, 20.1, 30.1, 33.1, 39.3, 44.7, 70.5, 76.4, 127.2, 127.5, 128.1, 138.8, 208.7, minor isomer δ 20.5, 25.8, 30.4, 37.4, 39.5, 43.6, 70.2, 127.4. Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.37; H, 9.74. Found: C, 77.45; H, 9.54.

A solution of peroxytrifluoroacetic acid was prepared by dropwise addition of 2.20 mL (3.27 g, 1.56 mmol) of trifluoroacetic anhydride to a mixture of 0.35 mL (12.8 mmol) of 90% aqueous hydrogen peroxide solution and 2.2 mL of dry CH_2Cl_2 at 0 °C.[2,3] The resulting solution was stirred for a 30-min period. Over a subsequent 20-min period, 0.5 mL of the peroxytrifluoroacetic acid solution was added to a suspension of 215 mg (0.859 mmol) of the foregoing mixture of diastereomeric methyl ketones and 620 mg (4.37 mmol) of disodium hydrogen phosphate (Na_2HPO_4) in 2 mL of dry CH_2Cl_2. When the addition was complete, the reaction mixture was heated at reflux for 1 h, during which time a precipitate formed. The mixture was diluted with CH_2Cl_2 and filtered, and the collected precipitate was washed with CH_2Cl_2. The combined CH_2Cl_2 layers were washed with 10% aqueous sodium carbonate solution. The aqueous layer was extracted two times with ether. The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated. The residue (224 mg) was purified by chromatography on 8 g of silica gel with 1:19 ether/hexane as eluant to afford 146 mg (64%) of a clear, colorless liquid: IR (film) 1640, 1450, 1240 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.94 (t, 3 H, J = 6), 1.23 (d, 2 H, J = 6), 2.04 (s, 3 H), 3.60 (quintet, 1 H, J = 6), 4.17 (t, 2 H, J = 5), 4.45 (d, 1 H, J = 12), 4.62 (d,

1 H, J = 12), 7.36 (s, 5 H). Anal. Calcd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.81; H, 9.14.

The foregoing acetoxy benzyl ether (101 mg, 0.380 mmol) was dissolved in 10 mL of acetic anhydride, to which 51 mg of platinum oxide and 1 drop of perchloric acid were added. The mixture was stirred under an atmosphere of hydrogen until the uptake of hydrogen had ceased. The catalyst was removed by filtration through Celite, and the filter cake was washed with ethyl acetate. The filtrate was poured into cold, aqueous saturated sodium bicarbonate solution and the resulting mixture was shaken vigorously for 10 min. The layers were separated and the aqueous layer was extracted with ether. The combined organic layers were washed with brine and dried over sodium sulfate. The volatile components were evaporated and the residue (405 mg) was purified by chromatography on 8 g of silica gel with 1:9 ether/hexane as eluant to provide 80 mg (97%) of a clear, colorless oil shown to be a 7:1 mixture of diastereomers: IR (film) 1740, 1370, 1240 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (t, 3 H, J = 6), 1.15 (two overlapping doublets, 3 H, J = 6), 1.28 (m, 2 H), 1.78 (m, 1 H), 1.96 (s, 3 H), 1.99 (s, 3 H), 4.02 (m, 2 H), 4.93 (quintet, 1 H, J = 6); ^{13}C NMR ($CDCl_3$) major isomer (**59**) δ 13.9, 16.9, 20.6, 20.9, 29.4, 41.7, 63.2, 70.2, 170.0, 170.7, minor isomer (**60**) δ 16.3, 19.9, 20.2, 29.0, 41.4, 63.5. Anal. Calcd for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32. Found: C, 61.07; H, 9.27.

(b) To a solution of 0.85 mL (614 mg, 6.06 mmol) of dry diisopropylamine in 7 mL of dry THF at −10 °C was added 3.35 mL (5.52 mmol) of a 1.65 M solution of n-butyllithium in hexane. After 10 min the solution was cooled to −78 °C, and 1.074 g (5.26 mmol) of 2,6-dimethylphenyl 4-pentenoate[16] in 3 mL of dry THF was added dropwise over a 30-min period. After the addition was complete, the mixture was stirred an additional 1.5 h at −78 °C and 0.310 mL (244 mg, 5.54 mmol) of distilled acetaldehyde was added as rapidly as possible by means of a syringe. After 5 min the reaction was quenched by the addition of saturated aqueous ammonium chloride solution and the mixture was allowed to warm to room temperature. The reaction mixture was diluted with water and extracted three times with ether. The combined ether extracts were washed with 1% aqueous hydrochloric acid and brine and dried over Na_2SO_4. The solvent was evaporated and the residue (1.23 g) was purified by chromatography on 30 g of silica gel with 100 mL of 1:9 ether/hexane, followed by 1:3 ether/hexane as eluant to afford 836 mg (64%) of a clear, colorless, viscous oil shown to be a 73:27 mixture of diastereomers: IR (film) 3470, 3070, 1640, 1470, 990, 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (d, 3 H, J = 6), 2.17 (s, 6 H), 2.58 (t, 2 H, J = 7), 2.79 (t, 1 H, J = 7), 2.86 (m, 1 H), 4.19 (m, 1 H), 5.16 (m, 2 H), 5.89 (m, 1 H), 7.05 (s, 3 H); ^{13}C NMR ($CDCl_3$) major isomer (**61**) δ 16.7, 21.0, 33.1, 52.1, 67.5, 117.7, 125.8, 128.5, 130.0, 134.5, 147.9, 172.4, minor isomer (**62**) δ 20.2, 31.5, 51.6, 67.7, 117.2, 129.9, 135.3, 172.0. Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.58; H, 8.06.

The foregoing mixture of unsaturated hydroxy esters **61** and **62** (275 mg, 1.10 mmol) was dissolved in 20 mL of absolute ethanol and 25 mg of platinum oxide was added. The mixture was stirred under an atmosphere of hydrogen until the uptake of hydrogen had ceased. After removal of the catalyst by filtration through Celite, the solvent was evaporated. The residue (297 mg) was purified by chromatography on 8 g of silica gel with 1:3 ether/hexane as eluant to afford 268 mg (97%) of a clear, colorless oil: IR (film) 3460, 1750, 1460, 1255 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (t, 3 H, J = 7), 1.31 (two overlapping doublets, 3 H, J = 6), 2.19 (s, 6 H), 2.71 (m, 1 H), 3.07 (m, 1 H), 4.10 (m, 1 H), 7.05 (s, 3 H); ^{13}C NMR ($CDCl_3$) major isomer δ 13.8, 16.5, 20.4, 20.9, 30.7, 52.6, 67.8, 125.6, 128.4, 129.8, 147.9, 172.9, minor isomer δ 20.1, 20.8, 29.3, 51.7, 172.5. Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 72.20; H, 8.67.

A suspension of 82 mg (2.16 mmol) of lithium aluminum hydride in 5 mL of dry ether was heated at reflux for 30 min. The mixture was cooled to room temperature and 229 mg (0.912 mmol) of the foregoing mixture of esters in 1 ml of dry ether was added dropwise at such a rate so as to maintain a gentle reflux. When the addition was complete, the reaction mixture was heated at reflux for 3 h. The mixture was cooled to room temperature and quenched by the dropwise addition of 0.08 mL of water, 0.08 mL of 15% aqueous sodium hydroxide solution, and 0.25 mL of water. The resulting mixture was heated at reflux for 30 min, cooled to room temperature, and filtered. The solvent was evaporated and the residue (221 mg) was purified by chromatography on 8 g of silica gel with 3:2 ether/petroleum ether as eluant to afford 119 mg (99%) of a clear, colorless, viscous oil: IR (film) 3330, 1030 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.82 (t, 3 H, J = 6), 1.12 (two doublets, 3 H, J = 6); ^{13}C NMR ($CDCl_3$) major isomer δ 14.2, 20.2, 21.6, 30.4, 45.8, 64.2, 71.6, minor isomer δ 18.3, 20.7, 28.3, 44.5, 63.7, 70.5. Anal. Calcd for $C_7H_{16}O_2$: C, 63.60; H, 12.20. Found: C, 63.26; H, 12.03.

A solution of 68.5 mg (0.518 mmol) of the foregoing diol, 10 mg (0.082 mmol) of 4-(*N*,*N*-dimethylamino)pyridine, 1.0 mL (730 mg, 7.2 mmol) of dry triethylamine, 1.0 mL (1.10 mg, 11.0 mmol) of acetic anhydride, and 1 mL of dry CH_2Cl_2 was stirred at room temperature for 48 h. The reaction mixture was poured into cold water and extracted three times with ether. The combined ethereal layers were washed twice with 2 N aqueous hydrochloric acid, twice with saturated aqueous sodium bicarbonate solution, and once with brine. The organic layer was dried over Na_2SO_4 and the solvent was evaporated. The residue (139 mg) was purified by chromatography on 5 g of silica gel with 1:9 ether/hexane as eluant to afford 103 mg (92%) of a clear, colorless liquid shown to be a 73:27 mixture of diastereomers: ^{13}C NMR ($CDCl_3$) the resonances observed for the major and minor diastereomers correspond to those obtained for the acetylated diol in part a.

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Registry No. (±)-**1**, 34713-70-7; (±)-**2**, 41954-96-5; (±)-**3**, 74130-31-7; (±)-**4**, 90458-77-8; (±)-**5**, 91711-97-6; (±)-**6**, 91711-98-7; (±)-**7**, 91711-99-8; (±)-**8**, 91712-00-4; **9**, 762-72-1; **10**, 18292-38-1; (±)-**11**, 91796-44-0; (±)-**12**, 64839-09-4; **13**, 5436-21-5; (±)-**14**, 91796-45-1; (±)-**15**, 91712-01-5; **16**, 1439-36-7; **17**, 859-65-4; (±)-**18**, 74333-47-4; (±)-**19**, 74333-46-3; (±)-**20**, 91712-02-6; (±)-**21**, 91712-03-7; (±)-**25**, 91712-04-8; (±)-**26**, 91712-05-9; (±)-**27**, 91712-06-0; (±)-**28**, 91712-07-1; (±)-**29**, 91712-08-2; (±)-**30**, 91712-09-3; (±)-**31**, 87938-26-9; (±)-**32**, 90458-78-9; (±)-**33**, 87938-27-0; (±)-**34**, 91796-46-2; (±)-**35**, 91796-47-3; (±)-**36**, 91796-48-4; (±)-**37**, 91796-49-5; (±)-**38**, 91796-50-8; (±)-**39**, 91796-51-9; (±)-**40**, 91796-52-0; (±)-**41**, 91796-53-1; (±)-**42**, 91796-54-2; (±)-**43**, 82360-68-7; (±)-**44**, 82360-67-6; (±)-*syn*-**45**, 91712-27-5; (±)-*anti*-**45**, 91712-10-6; (±)-*syn*-**46**, 91712-28-6; (±)-*anti*-**46**, 91712-11-7; (±)-**47**, 91712-12-8; (±)-**48**, 91712-13-9; (±)-**49**, 91712-14-0; (±)-**50**, 91712-15-1; (±)-**51**, 91796-55-3; (±)-**52**, 91796-56-4; (±)-**53**, 91712-16-2; (±)-**53** (dihydro deriv), 91741-61-6; (±)-**54**, 91712-17-3; (±)-**54** (dihydro deriv), 91712-29-7; (±)-**55**, 91712-18-4; (±)-**56**, 91712-19-5; (±)-**57**, 91712-20-8; (±)-**58**, 91741-76-3; (±)-**59**, 91712-21-9; (±)-**59** (diol), 91712-34-4; (±)-**60**, 91712-22-0; (±)-**60** (diol), 91712-35-5; (±)-**61**, 91712-23-1; (±)-**61** (dihydro deriv), 91712-32-2; (±)-**62**, 91712-24-2; (±)-**62** (dihydro deriv), 91712-33-3; $TiCl_4$, 7550-45-0; BF_3, 7637-07-2; $BF_3{\cdot}OEt_2$, 109-63-7; BCl_3, 10294-34-5; $SnCl_4$, 7646-78-8; $ZnCl_2$, 7646-85-7; CF_3CO_2H, 76-05-1; $CH_2{=}C(CH_3)CO_2H$, 79-41-4; $PhCH_2OH$, 100-51-6; $CH_2{=}C(CH_3)CO_2CH_2Ph$, 2495-37-6; $PhCH_2Cl$, 100-44-7; (±)-(*R**,*R**)-$PhCH(CH_3)CHCl(CH_2)_2CH_3$, 91712-25-3; (±)-(*R**,*S**)-$PhCH(CH_3)CHCl(CH_2)_2CH_3$, 91712-26-4; *cis*-$CH_3CH{=}CH(CH_2)_2CH_3$, 7688-21-3; PhCHO, 100-52-7; $CH_3(CH_2)_2Br$, 106-94-5; (±)-(*R**,*R**)-$PhCH_2OCH(CH_3)CH(CH_2OAc)(CH_2)_2CH_3$, 91712-31-1; (±)-(*R**,*S**)-$PhCH_2OCH(CH_3)CH(CH_2OAc)(CH_2)_2CH_3$, 91712-30-0; CH_3CHO, 75-07-0; 2,6-dimethylphenyl 4-pentenoate, 81819-00-3; allyltributylstannane, 24850-33-7; acetone lithium enolate, 62415-84-3; butanal, 123-72-8.