A General Route to 1-Alkoxy-3-[(trimethylsilyl)oxy]-1,3-butadienes: Vinylogous Transesterification

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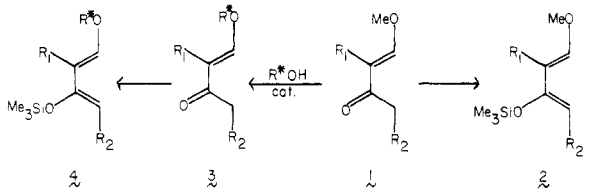
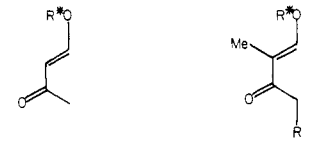
The value of butadienes of the type **2**, in cycloaddition reactions, has been demonstrated.[1] These compounds have been obtained by the enol silylation of the β-methoxy ketones **1**, which are often commercially available or can be prepared by standard methods.[2,3] For most purposes, the nature of the alkoxy group at the 1-position was of little consequence since the alcohol function was eliminated during the workup process.[4] Recently, in connection with our studies on the cycloaddition of activated dienes with aldehydes by Lewis acids, mild catalytic systems have been developed which allow for maintenance of the alkoxy function.[5] The alkoxy group thus emerges at the anomeric center.

It was therefore of interest to expand the scope of alkoxy dienes which can be prepared and used in the cycloaddition reactions. A particularly promising approach would involve the same enones **1** as the starting materials. The desired alkoxy groups would be installed by an exchange reaction of **1** with appropriate alcohols.[6] The resultant enones **3** would be converted to dienes **4** by the usual enol silylation.[1b] Herein we report on the reduction of this program to practice. The exchange reaction can be conducted with a large variety of alcohols both on the parent enone **5a** and on derivatives thereof.



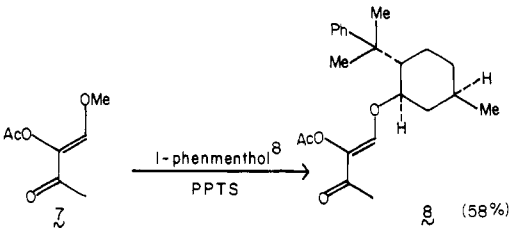
4 **3** **1** **2**

The exchange reactions were conducted in benzene under reflux with R*OH and the enone. Pyridinium *p*-toluenesulfonate (PPTS) was found to be an effective acid catalyst which is sufficiently mild to allow for survival of sensitive functionality both in the alcohol and in the enone components. The analogy to the application of this acid by Grieco and co-workers[7] to transacetalization reactions is apparent. With inexpensive volatile alcohols such as *tert*-butyl alcohol, R*OH was used in excess. When the alcohol is less readily available, nearly equivalent molar ratios were employed. In some instances, a 3:1 excess of enone was helpful in driving the exchange toward completion. In this fashion, readily available β-methoxy enones **5a**, **6a**, and **6d** were converted in the indicated yields to enones **5b–f**, **6b,c**, and **6e–g**, respectively.

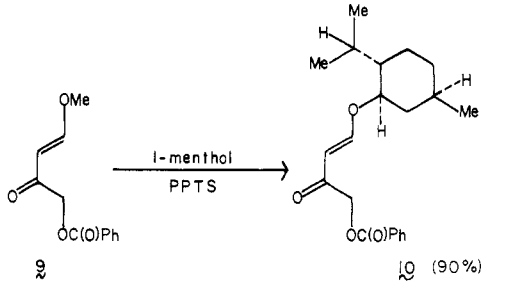


	R*	R
5a	Me	
b	^{t}Bu (55%)	
c	d- or l-menthyl (80%)	
d	l-phenmenthyl[8] (94%)	
e	d- or l-phenethyl[9] (72%)	
f	3-cholestanyl (92%)	
6a	Me	H
b	^{t}Bu	H (60%)
c	l-menthyl	H (58%)
d	Me	Me
e	l-menthyl[10]	Me (60%)
f	l-phenmenthyl[8]	Me (100%)
g	d- or l-phenethyl[9]	Me (69%)

A major incentive for the use of resolved chiral auxiliaries in the alkoxy group was the recent finding that such groups, particularly in tandem with chiral catalysts,[5b,11,12] can confer considerable diastereofacial bias to the cyclocondensation reaction. It was therefore of interest to probe the extendability of the exchange reaction to more challenging situations. The smooth conversions of **7** to **8** and **9** to **10** are reassuring in this regard.



7 **8** (58%)



9 **10** (90%)

In our previous studies we had carried out enol silylations of a variety of vinylogous esters using chlorotrimethylsilane, zinc chloride, and triethylamine.[1b] With the availability of enones bearing elaborate alkoxy groups, it was more convenient to achieve silylation by using the milder methodology of Simchen[13] (trimethylsilyl triflate, triethylamine). Three instances of the application of the Simchen procedure to the synthesis of elaborated siloxy dienes are shown in Scheme I.

Applications of these and related dienes to problems in

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(2) (a) 4-Methoxy-3-buten-2-one is commercially available from Aldrich. (b) Sugasawa, S.; Yamada, S. I.; Harahashi, M. *J. Pharm. Soc. Jpn.* **1951**, *71*, 1345.

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(6) For a similar reaction catalyzed by sodium methoxide, see: Müller, R.; Plieninger, H. *Chem. Ber.* **1959**, *92*, 3009. Crottschalk, F. J.; Weyerstahl, P. *Ibid.* **1980**, *113*, 555.

(7) Miyashita, M.; Yoshikoshi, A.; Grieco, P. A. *J. Org. Chem.* **1977**, *42*, 3772.

(8) Corey, E. J.; Ensley, H. E. *J. Am. Chem. Soc.* **1975**, *97*, 6908.

(9) The *d*- and l-phenethyl alcohols are commercially available from Norse Laboratories, Newbury Park, CA 91320.

(10) In this case *p*-toluenesulfonic acid (TsOH) was used instead of PPTS.

(11) Bednarski, M.; Maring, C.; Danishefsky, S. *Tetrahedron Lett.* **1983**, *24*, 3451.

(12) Gupta, R. C.; Harland, P. A.; Stoodley, R. J. *J. Chem. Soc., Chem. Commun.* **1983**, *13*, 754.

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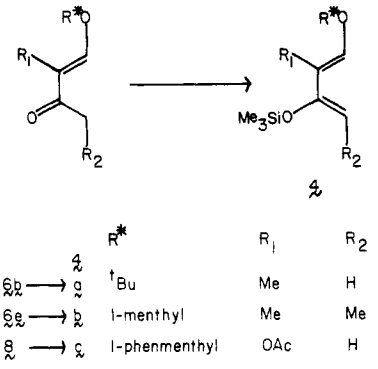
Scheme I



	R*	R_1	R_2
6a → 6	^{t}Bu	Me	H
6e → b	l-menthyl	Me	Me
8 → c	l-phenmenthyl	OAc	H

synthesis are of continuing interest in our laboratory and will be described in due course.

Experimental Section[14]

1-*tert*-Butoxy-2-methyl-1-buten-3-one (6b). A solution of enone **6a** (1.5 g, 13 mmol), *tert*-butyl alcohol (9 mL, 95 mmol), and PPTS (65 mg, 0.26 mmol) in benzene (15 mL) was refluxed for 22 h with continuous removal of methanol by using a Dean–Stark trap containing 4-Å molecular sieves. The reaction was concentrated to give a dark oil. Simple bulb-to-bulb distillation (approximately 0.1 mmHg, 65–75 °C) gave 1.3 g of an oil which was 95% pure by ^{1}H NMR (60% yield). Crystallization from hexane gave **6b** as white crystals: mp 58.5–59.5 °C; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.35 (s, 9 H), 1.70 (s, 3 H), 2.20 (s, 3 H), 7.53 (br s, 1 H); IR ($CHCl_3$) 2950, 1626, 1585, 1369 cm^{-1}; MS, *m/e* 156 (M^+).

1-(*l*-Menthyloxy)-2-methyl-1-penten-3-one (6e). A solution of enone **6d** (750 mg, 5.8 mmol), *l*-menthol (880 mg, 5.6 mmol), and *p*-toluenesulfonic acid (30 mg, 0.15 mmol) in benzene (10 mL) was refluxed for 10 h with continuous removal of methanol by using a Dean–Stark trap with 4-Å molecular sieves. Flash chromatography of crude reaction mixture (30 g silica gel, 15:85 ethyl acetate/hexane) gave the crystalline enone **6e** (880 mg, 60%): mp 65–67 °C; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.60–2.20 [m, 24 H, includes 1.72 (s, 3 H) and 1.05 (t, *J* = 7 Hz, 3 H)], 2.50 (q, *J* = 7 Hz, 2 H), 3.65 (dt, *J* = 11, 4 Hz, 1 H), 7.39 (br s, 1 H); IR ($CHCl_3$) 1638 cm^{-1}; $[\alpha]^{23}_D$ −48° (*c* 1.0, $CHCl_3$); MS, *m/e* 252 (M^+).

1-(*l*-Phenmenthyloxy)-2-acetoxy-1-buten-3-one (8). The mixture of the enone **7** (347.9 mg, 2.2 mmol), *l*-phenmenthol (464.7 mg, 2.0 mmol), and PPTS (10.1 mg, 0.40 mmol) in benzene (4 mL) was refluxed for 8.5 h with continuous removal of methanol by using a Dean–Stark distilling apparatus containing 4-Å molecular sieves. The reaction mixture was evaporated in vacuo and purified by flash chromatography to give the desired enone **8** (413.1 mg, 58%): ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.70–2.40 [m, 23 H, includes 0.87 (d, *J* = 6 Hz, 3 H), 1.33 (s, 6 H), 2.11 (s, 3 H), 2.19 (s, 3 H)], 3.50–3.90 (m, 1 H), 7.06 (s, 1 H), 7.24 (s, 5 H); IR ($CHCl_3$) 2940, 2900, 1760, 1640, 1195, 755, 695 cm^{-1}; $[\alpha]^{23}_D$ −41.0° (*c* 2.43, $CHCl_3$); MS, *m/e* 358 (M^+).

1-(*l*-Menthyloxy)-4-(benzoyloxy)-1-buten-3-one (10). A solution of enone **9** (881 mg, 4.0 mmol), *l*-menthol (640 mg, 4.1 mmol), and PPTS (50 mg, 0.2 mmol) in benzene (40 mL) was stirred at reflux for 24 h with continuous removal of methanol by using a Dean–Stark trap containing 4-Å molecular sieves. The reaction was concentrated in vacuo and chromatographed on silica gel (100 g) in 10% ethyl acetate/hexane to give **10** (1.25 g, 90%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.77 (d, *J* = 6.9 Hz, 3 H), 0.80–1.12 (m, 9 H), 1.40–1.45 (m, 2 H), 1.61–1.71 (m, 2 H), 1.99–2.04 (m, 2 H), 3.76–3.81 (m, 1 H), 4.91 (s, 3 H), 5.84 (d, *J* = 12.1 Hz, 1 H), 7.46–7.49 (m, 2 H), 7.58–7.62 (m, 1 H), 7.72 (d, *J* = 12.1 Hz, 1 H), 8.11–8.14 (m, 2 H); IR ($CHCl_3$) 2940, 2900, 2840, 1720, 1686, 1672, 1585, 1448 cm^{-1}; $[\alpha]^{23}_D$ −46.0° (*c* 1.55, $CHCl_3$); MS, *m/e* 344 (M^+).

Similarly, the following enones were obtained by using an appropriate procedure from the above cases and the indicated alcohols.

5b: ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.33 (s, 9 H), 2.14 (s, 3 H), 5.68 (d, *J* = 12 Hz, 1 H), 7.64 (d, *J* = 12 Hz, 1 H); IR ($CHCl_3$) 2960, 1675, 1627, 1597, 1366 cm^{-1}; MS, *m/e* 142 (M^+).

5c (*l*-menthol): mp 57–59 °C; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.60–2.25 [m, 21 H, includes 2.12 (s, 3 H)], 3.72 (dt, *J* = 11, 4 Hz, 1 H), 6.62 (d, *J* = 12 Hz, 1 H), 7.48 (d, *J* = 12 Hz, 1 H); IR ($CHCl_3$) 1680, 1632, 1600 cm^{-1}; $[\alpha]^{23}_D$ −84.4° (*c* 1.6, $CHCl_3$); MS, *m/e* 224 (M^+).

5d: ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.70–2.30 [m, 20 H, includes 0.88 (d, *J* = 5.1 Hz, 3 H), 1.29 (s, 3 H), 1.33 (s, 3 H), 2.11 (s, 3 H)], 3.75 (dt, *J* = 10.5, 3.9 Hz, 1 H), 5.40 (d, *J* = 12.6 Hz, 1 H), 7.13–7.31 (m, 6 H); IR (thin film) 2940, 2900, 1680, 1655, 1630, 1600, 1200, 695 cm^{-1}; $[\alpha]^{23}_D$ −22.7° (*c* 2.10, $CHCl_3$); MS, *m/e* 300 (M^+).

5e ((+)-phenethyl alcohol): mp 71–74 °C; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.56 (d, *J* = 6.3 Hz, 3 H), 2.06 (s, 3 H) 5.02 (q, *J* = 6.9 Hz, 1 H), 5.60 (d, *J* = 12.6 Hz, 1 H), 7.29 (s, 5 H), 7.44 (d, *J* = 12.6 Hz, 1 H); IR (thin film) 1680, 1655, 1630, 1600, 1195, 695 cm^{-1}; $[\alpha]^{23}_D$ 35.8° (*c* 2.56, $CHCl_3$); MS, *m/e* 190 (M^+).

5f: mp 100–103 °C; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.40–2.20 (m, 46 H), 2.14 (s, 3 H), 3.65–4.10 (m, 1 H), 5.61 (d, *J* = 12.5 Hz, 1 H), 7.48 (d, *J* = 12.5 Hz, 1 H); IR (Nujol) 1685, 1675, 1635, 1600, 1225, 950 cm^{-1}; $[\alpha]^{23}_D$ 13.2° (*c* 2.34, $CHCl_3$); MS, *m/e* 456 (M^+).

6c: ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.70–2.30 [m, 24 H, includes 1.72 (s, 3 H), 2.21 (s, 3 H)], 3.70 (dt, *J* = 11, 4 Hz, 1 H), 7.30 (s, 1 H); IR ($CHCl_3$) 1675, 1640 cm^{-1}; MS, *m/e* 238 (M^+).

6f: ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.70–2.20 [m, 23 H, includes 0.85 (d, *J* = 6.0 Hz, 3 H), 1.10 (t, *J* = 7.5 Hz, 3 H), 1.33 (s, 3 H), 1.37 (s, 3 H), 1.51 (s, 3 H)], 2.49 (q, *J* = 7.5 Hz, 2 H), 3.66 (dt, *J* = 10.2, 3.9 Hz, 1 H), 7.14 (s, 1 H), 7.24 (s, 5 H); IR (liquid film) 2940, 2900, 1630, 1200, 985, 695 cm^{-1}; $[\alpha]^{23}_D$ 5.4° (*c* 2.25, $CHCl_3$); MS, *m/e* 328 (M^+).

6g ((+)-phenethyl alcohol): ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.01 (t, *J* = 7.5 Hz, 3 H), 1.61 (d, *J* = 7.2 Hz, 3 H), 1.79 (d, *J* = 1.2 Hz, 3 H), 2.42 (q, *J* = 7.2 Hz, 2 H), 5.00 (q, *J* = 5.0 Hz, 1 H), 7.28 (d, *J* = 1.2 Hz, 1 H), 7.33 (s, 5 H); IR (liquid film) 1640, 1200, 1065, 695 cm^{-1}; $[\alpha]^{23}_D$ −8.0° (*c* 2.47, $CHCl_3$); MS, *m/e* 218 (M^+).

1-*tert*-Butoxy-3-[(trimethylsilyl)oxy]-2-methyl-1,3-butadiene (4a). To a solution of enone **6b** (400 mg, 2.56 mmol) in triethylamine (0.9 mL, 6.4 mmol) and ether (15 mL) at 0 °C under nitrogen was added trimethylsilyl trifluoromethanesulfonate (0.511 mL, 2.64 mmol) via syringe. The reaction was stirred for 0.5 h and then diluted with triethylamine (2 mL) and pentane (50 mL). The reaction mixture was transferred to a separatory funnel and washed with saturated $NaHCO_3$ solution (10 mL) and brine (10 mL) and dried over anhydrous $MgSO_4$. Removal of the solvent in vacuo gave **4a** (580 mg, 99%): ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.20 (s, 9 H), 1.30 (s, 9 H), 1.69 (s, 3 H), 4.07 (s, 1 H), 4.18 (s, 1 H), 6.82 (br s, 1 H).

1-(*l*-Menthyloxy)-3-[(trimethylsilyl)oxy]-2,4-dimethyl-1,3-butadiene (4b). To a solution of enone **6e** (430 mg, 1.7 mmol) and triethylamine (0.700 mL, 4.8 mmol) in carbon tetrachloride (5 mL) at 0 °C under nitrogen was added trimethylsilyl trifluoromethanesulfonate (0.400 mL, 2.0 mmol). The reaction mixture was stirred for 1 h at 0 °C and then allowed to warm to room temperature. The reaction was diluted with an additional 5 mL of carbon tetrachloride and quenched with 3 mL of saturated $NaHCO_3$ solution. The organic layer was washed once with $NaHCO_3$ solution and dried over $MgSO_4$. Evaporation of solvent in vacuo gave diene **4b** (450 mg, 82%): ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.15 (s, 9 H), 0.60–2.35 (m, 24 H), 3.35 (dt, *J* = 11, 4 Hz, 1 H), 4.65 (q, *J* = 7 Hz, 1 H), 6.40 (br s, 1 H).

1-(Phenmenthyloxy)-3-[(trimethylsilyl)oxy]-2-acetoxy-1,3-butadiene (4c). To a solution of the enone **8** (355.0 mg, 0.99 mmol) and triethylamine (2.06 mL, 1.5 mmol) in ether (2 mL) at 0 °C was added trimethylsilyl trifluoromethanesulfonate (0.198 mL, 1.1 mmol). The mixture was stirred for 4 h at 0 °C. The ether layer was separated from an oily precipitate which was washed with hexane. The combined ether and hexane solution was washed with ice-cold saturated $NaHCO_3$ solution and brine,

(14) Reagents and solvents were purified and dried by using standard methods, and spectra were recorded on the following instruments: IR, Perkin-Elmer spectrophometer 710 B; ^{1}H NMR; Varian EM-390 (90 MHz) and Bruker WM-500 (500 MHz); mass spectra; Hewlett-Packard 5985; optical rotations; Perkin-Elmer 241 polarimeter. NMR spectra were obtained by using $CDCl_3$ as the solvent. Melting points were determined with a Thomas-Hoover melting point apparatus and are uncorrected.

and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave the diene **4c** (353.7 mg, 83%): ^1H NMR ($CDCl_3$, 90 MHz) δ 0.25 (s, 9 H), 0.45–2.30 [m, 20 H, includes 0.85 (br d, J = 5.5 Hz, 3 H), 1.34 (s, 3 H), 1.37 (s, 3 H), 2.13 (s, 3 H)], 3.45 (dt, J = 10.1, 2.0 Hz, 1 H), 4.16 (dd, J = 4.8, 2.0 Hz, 2 H), 6.36 (s, 1 H), 7.23 (br s, 5 H).

Acknowledgment. This research was supported by PHS Grant HL49784. NMR spectra were obtained through the auspices of the Northeast Regional NSF/NMR Facility at Yale University which was supported by NSF Chemistry Division Grant CHE 7916210. A Dox Fellowship to Mark Bednarski and a Heyl Fellowship to Clarence Maring are gratefully acknowledged.

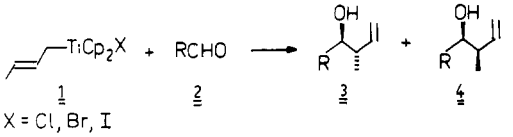
Registry No. **4a**, 88146-66-1; **4b**, 90130-49-7; **4c**, 90084-13-2; **5a**, 4652-27-1; **5b**, 79010-92-7; **5c** (*l*-menthol), 90084-14-3; **5d**, 90084-15-4; **5e** ((+)-phenethyl), 90084-16-5; **5f**, 90084-17-6; **6a**, 56279-34-6; **6b**, 90084-18-7; **6c**, 90084-19-8; **6d**, 56279-35-7; **6e**, 90084-20-1; **6f**, 90084-21-2; **6g** ((+)-phenethyl), 90084-22-3; **7**, 74441-37-5; **8**, 90084-23-4; **9**, 90084-24-5; **10**, 90084-25-6; *l*-phenmenthol, 65253-04-5; *l*-menthol, 2216-51-5; (+)-phenethyl alcohol, 1517-69-7; trimethylsilyl trifluoromethanesulfonate, 27607-77-8; 3-cholestanol, 80-97-7.

Communications

Reversal of Diastereoselectivity in the BF_3-Promoted Addition of Halobis(cyclopentadienyl)crotyltitanium Compounds to Aldehydes

Summary: Diastereoselectivity in the reaction of halobis(cyclopentadienyl)crotyltitanium reagents with aldehydes is reversed if BF_3 is added, erythro adducts being formed preferentially.

Sir: The idea that crotylmetal reagents can be used as enolate equivalents in the stereoselective construction of β-hydroxy carbonyl compounds has been applied in numerous cases.[1] Generally, the stereochemical outcome (threo or erythro adducts) depends upon the geometry of the crotylmetal reagent (*E* or *Z* configuration, respectively). For example, Sato's titanium compounds **1**, which are



accessible only in the *E* form, react with aldehydes to afford threo adducts **3** preferentially.[2,3] The necessity of having to prepare prochirally pure *E* or *Z* reagents does not apply to the BF_3-promoted addition of crotyltin compounds, which react stereoconvergently to produce erythro adducts **4**.[4] This surprising result has been explained by Yamamoto on the basis of an open-chain transition state as opposed to the conventional cyclic mechanism.[4] In this communication we report that *diastereoselectivity in the addition of 1 to aldehydes can be reversed by the use of BF_3.*

The reaction of the crotyltitanium reagents **1** with a mixture of aldehyde **2** and BF_3 at −78 °C afforded erythro adducts **4** preferentially as summarized in Table I. The data is relevant to the present preoccupation with cyclic vs. noncyclic transition states.[4,5] The degree of threo selectivity in the noncatalyzed reaction depends markedly upon the nature of the halogen ligand, and this has been interpreted by Sato by assuming the conventional pericyclic transition state.[1,2] The use of BF_3 in the present reactions not only favors the formation of erythro adducts but the degree of diastereoselectivity is also almost independent of the nature of the halogen at titanium. Al-

Table I. Addition[a] of 1 to Aldehydes 2

X	R	threo:erythro with BF_3[b]	threo:erythro without BF_3 according to Sato[2]
Cl	C_6H_5	14:86 (98)	60:40
Cl	n-C_6H_{13}	9:91 (85)	
Cl	$(CH_3)_2CH$	9:91 (85)	
Cl	$(C_2H_5)_2CH$	7:93 (84)	
Br	C_6H_5	14:86 (90)	100:0
Br	$(CH_3)_2CH$	9:91 (75)	99:1
Br	$(C_2H_5)_2CH$	6:94 (90)	
I	C_6H_5	24:76 (90)	94:6
I	$(C_2H_5)_2CH$	12:88 (70)	

[a] In the catalyzed reaction a mixture of 10 mmol of aldehyde and 20 mmol of BF_3 etherate in 5 mL of THF was added at −78 °C to 10 mmol of the crotyltitanium reagent **1**[2] in THF. After 2 h aqueous workup afforded the products **3**/**4**, the ratio of which was determined by GC. Configurational assignments were made by comparison of the NMR spectra of authentic samples reported in ref 2 and 4 as well as by Zeiss (Zeiss, H. J. Dissertation, University of Marburg, 1980) and Hoffmann and Zeiss (Hoffmann, R. W.; Zeiss, H. J. *J. Org. Chem.* **1981**, *46*, 1309). [b] Numbers in parentheses refer to percent conversion.

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