Stereoselective Synthesis of Alcohols, XXX[1]

E- and *Z*-Pentenylboronates, Reagents for Simple Diastereoselection on Addition to Aldehydes

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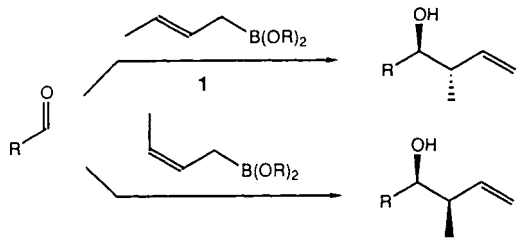
Pentenylboronates, either >90% *Z* (4) or >95% *E* (3), can be obtained by reaction of the pentenyl Grignard reagent with different borates. The *Z*-pentenylboronates 4 add to aldehydes under high simple diastereoselection to give the diastereomerically pure *syn*-homoallyl alcohols 10. The corresponding addition of the *E*-pentenylboronates leads to the *anti*-homoallyl alcohols *E*-(15)/*Z*-(17) mixtures.

Stereoselektive Synthese von Alkoholen, XXX[1]. – *E*- und *Z*-Pentenylboronsäureester, Reagenzien, die sich unter einfacher Diastereoselektivität an Aldehyde addieren

Durch Reaktion des Pentenyl-Grignard-Reagenzes 2 mit verschiedenen Borsäureestern erhält man Pentenylboronsäureester entweder zu >90% als *Z*-Isomer 4 oder zu >95% als *E*-Isomer 3. Addition der *Z*-Pentenylboronsäureester 4 an Aldehyde ergibt die diastereomerenreinen *syn*-Homoallylalkohole 10. Entsprechende Addition des *E*-Pentenylboronsäureesters 3 führt zu *anti*-Homoallylalkoholen als *E*-(15)/*Z*-(17)-Gemische.

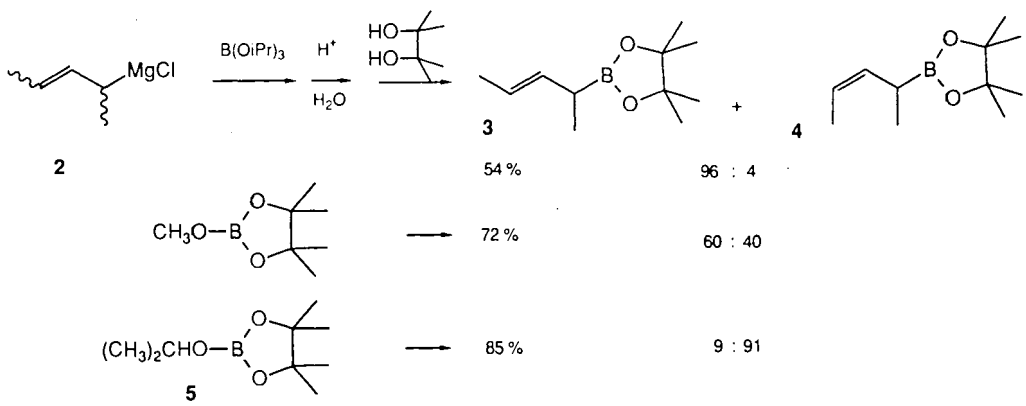
Stereogenic carbon–carbon bond forming reactions are of prime interest in stereoselective synthesis[2]. A well-established[3] reaction is the addition of *E*- and *Z*-crotylboronates[4–6] such as **1**, or of *E*- and *Z*-crotylboranes[7] to aldehydes, a reaction which proceeds with high simple diastereoselection.



These reagents are in general prepared by deprotonation of *E*- or *Z*-butene to *E*- or *Z*-butenylpotassium[8] followed by borylation. The generation of butenylpotassium does not lend itself to scale up readily. Of the other routes to such crotylboron compounds[9,10] some require separation of geometric isomers of a precursor [*E*/*Z*-1-bromopropene[10] or *E*/*Z*-crotylbis(dimethylamino)boranes[4]] in a spinning band column. As long as only simple diastereoselection on addition to aldehydes is concerned, the *E*- and *Z*-pentenylboronates **3** and **4** might do as well. The *E* reagent **3** can easily be prepared in a diastereomeric purity of >95% by reaction of the simple pentadienyl Grignard reagent **2** with triisopropylborate[11] and this has been achieved on a scale of up to 0.36 mole. However, for addition to aldehydes the crude product had to be used, since **3** has a tendency to decompose to a solid material on distillation (polymerisation?).

Further experiments showed that the **3**/**4** ratio depends on the borylating agent. Representative results are given in Scheme 1.

Scheme 1



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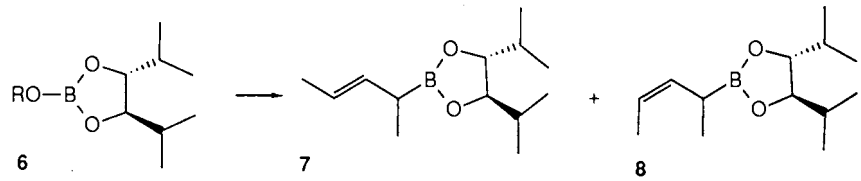
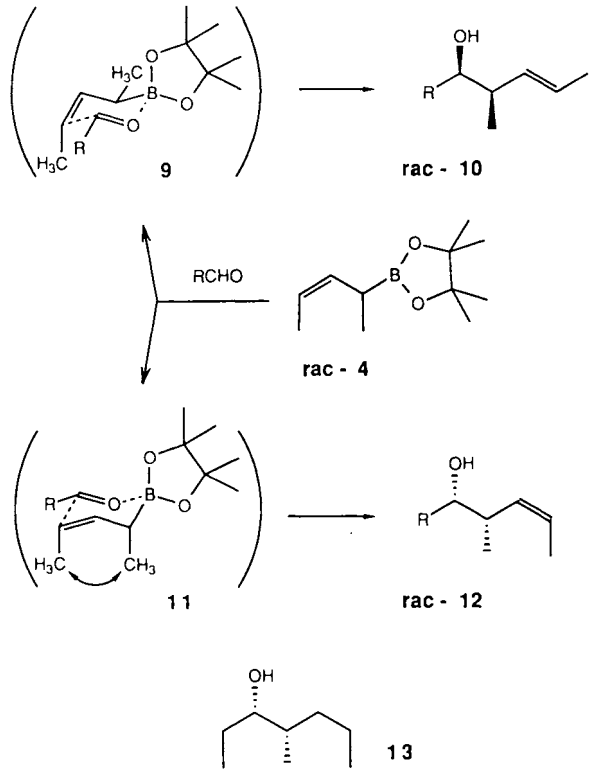


a	R = CH_3	81 %	64 : 36
b	R = $(CH_3)_2CH$	75 %	25 : 75
c	R = $(CH_3)_3C$	50 %	70 : 30

Such a variation of the *E*/*Z* ratio in the products formed from 1-methyl-2-butenyl Grignard reagents had been noted previously[12]. This variation is probably connected with the rapid metallotropic equilibrium between the isomeric η^1-Grignard reagents[13], which react with different relative rates with individual electrophiles depending on the steric demands of the latter. For the present purpose it is important, that the reaction of **2** with the 2-propanol-pinacol-borate **5** led to the *Z*-pentenylboronate **4** with a selectivity of ca. 90%. Preparation of the distillable and stable *Z*-pentenylboronate **4** was possible at least on a scale of 0.5 mole. By analogy to the reactions of the crotylboronate **1**[4], it was expected that the *E* isomer would react faster with aldehydes than the *Z* isomer. Hence, on treatment of a crude 9:1 mixture of **4**/**3** with 15% of benzaldehyde, major amounts of the *E* isomer **3** were consumed preferentially. Subsequent distillation furnished **4** containing only ca. 5% of **3**. Repetion of this process led to material which was 98% *Z*.

Addition of the *Z*-Pentenylboronate 4 to Aldehydes

As for the addition of other α-substituted crotylboronates to aldehydes[14,1], two transition states, **9**, **11**, have to be considered. They differ in the arrangement of the 2-methyl group. Equatorial arrangement gives rise to the *E*-homoallyl alcohol **10**, axial arrangement to the corresponding *Z* isomer.



Transition state **11** should, however, suffer from considerable allylic 1,3-strain[15], as compared with the transition state **9**. Therefore the formation of the homoallyl alcohol **10** with an *E* double bond should predominate. Indeed, a diastereoselectivity of >90% in favor of **10** was seen in all cases of Table 1.

Table 1. Formation of *syn*-homoallyl alcohols **10** from the *Z*-pentenylboronate **4** and aldehydes

	R in RCHO	Product **10** yield (%)	Diastereomeric purity (%)[a]
a	CH_3CH_2	92	96
b	$(CH_3)_2CH$	90	92
c	(*E*)-$CH_3-CH=CH-CH_2$	90	90
d	C_6H_5	95	94

[a] The diastereomeric purity reflects the *Z*/*E* purity of the pentenylboronate used.

In the case of **10a**[16] the *syn* disposition of the hydroxy and methyl groups was proven by catalytic hydrogenation to the known[17] alcohol **13**.

Addition of the *E*-Pentenylboronate 3 to Aldehydes

On addition of the *E*-pentenylboronate **3** to aldehydes the two competing most probable transition states **14** and **16** differ only little in energy. Therefore both homoallyl alcohols **15** and **17** result, cf. Table 2.

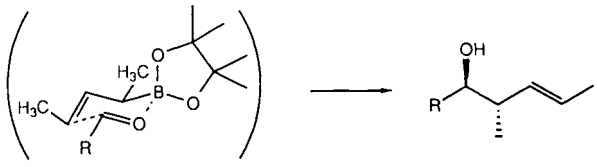
Table 2. Formation of homoallyl alcohols **15**/**17** from the *E*-pentenylboronate **3**[a] and aldehydes

	R in RCHO	Product yield (%)	*Z*-**17**:*E*-**15**
a	CH_3CH_2	81	65:35
b	$(CH_3)_2CH$	90	75:25
c	(*E*)-$CH_3-CH=CH-CH_2$	90	77:23
d	C_6H_5	92	80:20

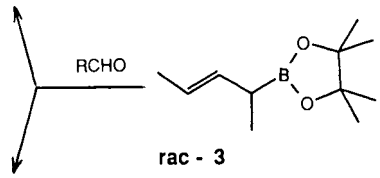
[a] The starting *E*-pentenylboronate **3** contained ca. 4% of the *Z* isomer **4**. Due to the slower reaction of the latter this was of no consequence as long as no excess of the aldehyde was used.

The weak preference for the formation of the *Z* isomer **17** is probably a consequence of the steric bulk of the pinacol

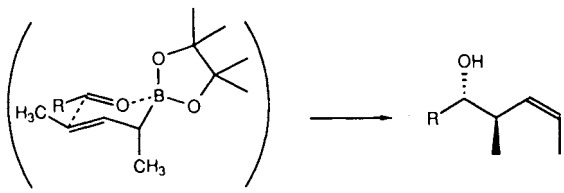
residue on boron destabilizing somewhat the equatorial disposition of the methyl group in the transition state **14**. A similar weak *Z* preference was noted on reaction of the related pinacol α-methylallylboronate[18], whereas in the reaction of the *E*-pentenylstannanes corresponding to **3** a marked *Z* selectivity[19] was noted.



14 **rac - 15**



rac - 3



16 **rac - 17**

On reaction of a chiral aldehyde with **3** four products may result[20], cf. the conversion of **18** into the *E*/*Z* pairs of products **19** and **20**. On reaction of a racemic reagent with a racemic substrate mutual kinetic resolution may occur[21], so that product selectivity is higher than that obtained on substrate based asymmetric induction alone[22]. Since we had an interest in the conversion of the aldehyde **18** to the product of the relative configuration **19**, we were curious, whether on reaction of **18** with the boronate **3** the diastereoselectivity could be increased by mutual kinetic resolution beyond the Cram/*anti*-Cram selectivity of 85:15 found in the reaction of the aldehyde **18** with the simple crotylboronate **1**. Enhanced selectivity due to mutual kinetic resolution can in principle also be attained by reacting the enantiomerically pure aldehyde with an excess of the racemic reagent **3**. Hence, a 1.5-fold excess of *rac*-*E*-pentenylboronate **3** was allowed to react with the chiral aldehydes **18**[20] and **21**[23].

The products were obtained as 2–3:1 mixtures of the *E*/*Z* isomers. The Cram/*anti*-Cram selectivity **19**/**20** or **22**/**23** was not noticeable increased even using a three-fold excess of the boronate **3**. Thus, in order to prepare the homoallyl alcohols of type **19** in high diastereomeric purity[1], we had to rely eventually on reagent control of diastereoselectivity[24].

Apart from the fact that the pentenylboronates **3** and **4** do not display mutual kinetic resolution on addition to chiral aldehydes, they are equivalent and easily accessible substitutes for the crotylboronates. Like the latter they add to aldehydes in high yields with good *syn*/*anti* selectivity.

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Experimental

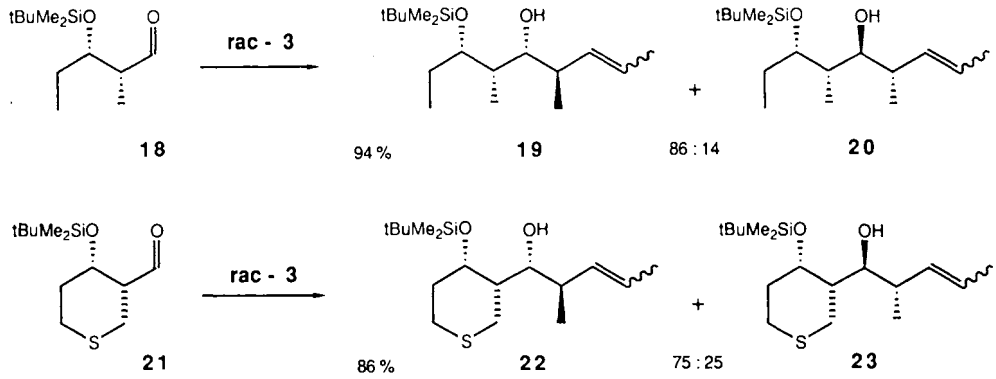
All temperatures quoted are not corrected. – ^{1}H NMR: Bruker AM 300 and WH 400. – ^{13}C NMR: Bruker AM 300, WH 400 and Varian XL 100. – Preparative gas chromatography: Wilkens Aerograph A 90-P-3, 1.5 m × 0.6 cm column with 5% SE 30 on chromosorb G, AW-DMCS, 60–80 mesh, 200 ml He/min. – Analytical gas chromatography: Perkin-Elmer 900, 3 m × 0.3 cm column with 5% SE 52 on chromosorb G, AW-DMCS, 80–100 mesh, 30 ml N_2/min. – Rotations: Perkin-Elmer polarimeter 141.

Preparation of Borate Esters

1) *2-Isopropyloxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**5**): From a solution of 93.0 g (0.5 mol) of triisopropyl borate and 59.1 g (0.5 mol) of pinacol in 700 ml of hexane, a 2-propanol/hexane azeotrope was slowly distilled off at 55–60°C. The residual solvents were removed at 15 Torr, and the residue was distilled at 0.1 Torr into a cold trap from a 40°C bath. The condensate was distilled to give 83.0 g (89%) of the product, b.p. 66–68°C/12 Torr. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18 (d, *J* = 6.2 Hz, 6H), 1.23 (s, 12H), 4.31 (sept, *J* = 6.2 Hz, 1H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 24.0, 24.3, 66.9, 82.0.

$C_9H_{19}BO_3$ (186.1) Calcd. C 58.10 H 10.29
Found C 58.21 H 10.35

2) *(4S,5S)-4,5-Diisopropyl-2-methoxy-1,3,2-dioxaborolane* (**6a**): From 2.70 g (26.0 mmol) of trimethoxy borate, 3.80 g (26.0 mmol) of (3*S*,4*S*)-2,5-dimethyl-3,4-hexanediol[25] and 50 ml of cyclohexane, a methanol/cyclohexane azeotrope was distilled off over a 1 h period. After addition of 50 ml of cyclohexane the distillation was



18 94% **19** 86:14 **20**

21 86% **22** 75:25 **23**

repeated. The mixture was concentrated at 12 Torr and the residue was bulb-to-bulb distilled at 0.1 Torr (dry ice cooling) from a 40°C bath affording 4.00 g (83%) of the product as a colorless oil. – ^{1}H NMR: (300 MHz, $CDCl_3$): δ = 0.85 (dd, *J* = 6.8 and 3.1 Hz, 12H), 1.52 (m, 2H), 3.60 (s, 3H), 3.75 (dd, *J* = 4.1 and 1.1 Hz, 2H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.6, 17.9, 33.2, 52.8, 83.5.

$C_9H_{19}BO_3$ (186.7) Calcd. C 58.10 H 10.29
Found C 58.16 H 10.39

3) *(4S,5S)-4,5-Diisopropyl-2-isopropyloxy-1,3,2-dioxaborolane* (**6b**): A mixture of 5.70 g (30.0 mmol) of triisopropyl borate, 4.40 g (30.0 mmol) of (3*S*,4*S*)-2,5-dimethyl-3,4-hexanediol[25] and 100 ml of *n*-hexane afforded as described above 5.1 g (81%) of the product as a clear oil. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.82 (dd, *J* = 6.8 and 2.0 Hz, 12H), 1.10 (dd, *J* = 6.1 and 2.0 Hz, 6H), 1.60 (m, 3H), 3.70 (dd, *J* = 4.0 and 0.9 Hz, 2H), 4.25 (m, 1H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.4, 17.7, 24.0, 33.0, 67.3, 82.9.

$C_{11}H_{23}BO_3$ (214.1) Calcd. C 61.70 H 10.83
Found C 61.69 H 10.83

4) *(4S,5S)-2-tert-Butyloxy-4,5-diisopropyl-1,3,2-dioxaborolane* (**6c**): From 4.00 g (17.4 mmol) of tri-*tert*-butyl borate[26], 2.30 g (17.4 mmol) of (3S,4S)-2,5-dimethyl-3,4-hexanediol and 100 ml of cyclohexane was obtained as above 3.20 g (80%) of the product as a clear oil. – ^{1}H NMR (300 MHz, $CDCl_3$): 0.85 (dd, *J* = 6.7 and 1.4 Hz, 12H), 1.30 (s, 9H), 1.60 (m, 2H), 3.70 (dd, *J* = 3.9 and 0.9 Hz, 2H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.6, 17.9, 29.9, 30.1, 33.1, 73.9, 82.8.

$C_{12}H_{25}BO_3$ (228.1) Calcd. C 63.18 H 11.05
Found C 63.23 H 10.95

Preparation of the Pentenylboronates

A solution of 12.5 g (0.12 mol) of 2-chloro-3-pentene[27] in 50 ml of THF was added dropwise over 2 h to a suspension of 15.0 g (0.60 mol) of magnesium in 150 ml of THF at 0°C. After 2 h at room temperature, the mixture was filtered under nitrogen and the filtrate was titrated.

5) *4,4,5,5-Tetramethyl-2-[(2Z)-1-methyl-2-butenyl]-1,3,2-dioxaborolane* (**4**): To a solution of 7.5 g (48 mmol) of 2-isopropyloxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5**) in 75 ml of THF was added at –78°C an equivalent of a 0.95 M Grignard solution dropwise over 2 h. After 2 h at room temperature, the mixture was poured into a mixture of 48 ml of 1 N aqueous HCl, 50 ml of saturated aqueous NH_4Cl solution and 400 ml of petroleum ether (b.p. 40–60°C). The phases were separated and the aqueous phase was extracted two times with 100 ml of petroleum ether each. The combined organic phases were washed with 100 ml each of saturated NaCl solution until the pH of the aqueous phase indicated neutrality. The organic phase was dried with $MgSO_4$, filtered through 25 g of flash silica gel and concentrated affording 8.7 g (95%) of **4** as a 91:9 *Z*/*E* mixture. Distillation yielded 7.7 g (85%) of **4** as a colorless liquid of b.p. 75°C/12 Torr. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06 (d, *J* = 7.4 Hz, 3H), 1.23 (s, 12H), 1.59–1.61 (m, 3H), 2.09–2.15 (m, 1H), 5.33–5.45 (m, 2H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 12.9, 15.9, 24.6, 83.0, 122.3, 133.2.

$C_{11}H_{21}BO_2$ (196.1) Calcd. C 67.37 H 10.79
Found C 67.11 H 10.76

To 9.0 g (48 mmol) of **4** as obtained above was added at room temperature 0.80 g (7.5 mmol) of benzaldehyde. The mixture was stirred for 1 h, diluted with 30 ml of petroleum ether (b.p. 40–60°C) and filtered through 20 g of silica gel. Concentration and distillation yielded 7.2 g (80%) of **4** as a 95:5 *Z*/*E* mixture.

6) *(4S,5S)-4,5-Diisopropyl-2-[(2Z)-1-methyl-2-butenyl]-1,3,2-dioxaborolane* (**8**): 1.50 g (8.1 mmol) of (4*S*,5*S*)-4,5-diisopropyl-2-methoxy-1,3,2-dioxaborolane (**6a**) in 20 ml of THF and an equivalent of an 0.78 M Grignard solution afforded as described above 1.45 g (81%) of the boronate **8** as a 64:36 *E*/*Z* mixture.

Z-**8**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.80 (dd, *J* = 6.8 and 3.7 Hz, 12H), 1.01 (d, *J* = 7.3 Hz, 3H), 1.55 (d, *J* = 7.0 Hz, 3H), 1.80 (m, 2H), 2.15 (m, 1H), 3.72 (dd, *J* = 3.8 and 1.1 Hz, 2H), 5.30 (m, 2H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.9, 16.2, 16.6, 17.7, 33.1, 83.8, 122.1, 133.3. The diastereomers regarding the chiral center of the pentenyl group are not differentiated.

E-**7**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.58 (d, *J* = 7.0 Hz, 3H), 5.45 (ddq, *J* = 16, 7.0 and 2 Hz, 1H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.3, 15.2, 16.6, 17.7, 33.1, 83.8, 122.4, 133.4. The diastereomers regarding the chiral center of the pentenyl group are not differentiated.

$C_{13}H_{25}BO_2$ (224.1) Calcd. C 69.66 H 11.24
Found C 69.60 H 11.33

Addition of 4 to Aldehydes

7) *(3R*,4R*)-(E)-4-Methyl-5-hepten-3-ol* (**10a**): A solution of 0.50 g (2.5 mmol) of **4**, 0.15 g (2.6 mmol) of propionaldehyde in 10 ml of CH_2Cl_2 was left for 20 h at room temperature. 0.38 g (2.5 mmol) of triethanolamine was added and the mixture was stirred for 3 h and concentrated at 12 Torr. The residue was chromatographed with CH_2Cl_2 over 100 g of alumina (basic, activity III) to give 0.30 g (92%) of **10a**. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, *J* = 7.5 Hz, 3H), 0.97 (d, *J* = 6.9 Hz, 3H), 1.27–1.38 (m, 1H), 1.48–1.58 (m, 1H), 1.67 (d, *J* = 6 Hz, 3H), 1.95 (dd, *J* = 6.9 and 1.5 Hz, 1H), 2.22 (m, 1H), 3.33 (tt, *J* = 5 and 4 Hz, 1H), 5.34 (ddq, *J* = 15.4, 7.5 and 1.5 Hz, 1H), 5.49 (dqd, *J* = 15.4, 6.2, and 1.0 Hz, 1H), cf. ref.[16]. – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 10.3, 14.8, 18.0, 26.7, 42.2, 76.5, 125.6, 133.7.

8) *(3R*,4R*)-4-Methyl-3-heptanol* (**13**): 0.30 g (2.3 mmol) of **10a** in 15 ml of methyl acetate was hydrogenated with 0.10 g 10% Pd on carbon under 1 bar of hydrogen. The mixture was filtered through 5 g of alumina (basic, activity IV) and concentrated to give 0.30 g (93%) of **13**. The material was purified by chromatography with petroleum ether (b.p. 40–60°C)/ether = 4:1 over a 15 × 1 cm column with silica gel. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85 (d, *J* = 6.8 Hz, 3H), 0.89 (t, *J* = 7.1 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H), 1.14–1.53 (m, 7H), 1.36 (s, 1H), 3.40 (m, 1H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 10.5, 13.4, 14.3, 20.4, 27.2, 35.6, 37.5, 76.7, cf. ref.[17a,17b].

9) *(3R*,4R*)-(E)-2,4-Dimethyl-5-hepten-3-ol* (**10b**): From 7.8 g (0.04 mol) of **4**, 3.04 g (0.04 mol) of isobutyraldehyde, and 6.72 g (0.04 mol) of triethanolamine as described under 10): The reaction mixture was filtered through 20 g of silica gel with ether/petroleum ether = 1:8. Removal of the solvents at 15 Torr afforded 5.46 g (90%) of **10b**. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (d, *J* = 6.7 Hz, 3H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.99 (d, *J* = 6.7 Hz, 3H), 1.36 (d, *J* = 4.0 Hz, 1H), 1.68 (d, *J* = 6 Hz, 3H), 1.75 (sept, *J* = 6.7 Hz, 1H), 2.3 (q,*J* = 6.7 Hz, 1H), 3.12 (q, *J* = 4 Hz, 1H), 5.37 (ddq, *J* = 15, 7 and 1.5 Hz, 1H), 5.47 (dqd, *J* = 15, 6.0 and 1 Hz, 1H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 14.2, 17.0, 18.1, 19.7, 30.4, 39.6, 79.9, 125.1, 134.5.

$C_9H_{18}O$ (143.2) Calcd. C 75.98 H 12.76
Found C 75.80 H 12.51

10) *(2E,4R*,5R*,6E)-5-Methyl-2,6-octadien-4-ol* (**10c**): To a solution of 0.20 g (1.02 mmol) of **4** in 15 ml of petroleum ether (b.p. 40–60°C) was added at –78°C 71 mg (1.02 mmol) of crotonal-

dehyde. The mixture was allowed to reach room temperature and was stirred until TLC analysis indicated completion of the reaction. A solution of 0.20 g (1.2 mmol) of triethanolamine in 1 ml of CH_2Cl_2 was added. After stirring for 24 h the mixture was filtered and the filtrate was partitioned between petroleum ether (b.p. 40–60°C) and saturated aqueous $NaHCO_3$ solution. The aqueous phase was washed twice with petroleum ether. The combined organic extracts were dried with $MgSO_4$ and concentrated i.vac. Flash chromatography over 10 g of silica gel with ether/petroleum ether (b.p. 40–60°C) = 1:8 afforded 0.13 g (90%) of **10c** as a clear liquid. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96 (d, *J* = 6.9 Hz, 3H), 1.68 (d, *J* = 7.0 Hz, 3H), 1.70 (d, *J* = 7.0 Hz, 3H), 2.30 (m, 1H), 3.90 (m, 1H), 5.30 (dd, *J* = 15.5 and 8.0 Hz, 1H), 5.70 (dd, *J* = 15.0 and 6.5 Hz, 1H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.5, 17.7, 18.0, 42.7, 76.1, 126.3, 127.4, 131.6, 132.7.

$C_9H_{16}O$ (140.2) Calcd. C 77.09 H 11.50
Found C 77.28 H 11.61

11) *(1R*,2S*,3E)-2-Methyl-1-phenyl-3-penten-1-ol* (**10d**): From 0.20 g (1.02 mmol) of **4**, 0.11 g (1.0 mmol) of benzaldehyde, and 0.15 g (1.0 mmol) of triethanolamine as described under 10): 0.17 g (95%) **10d** as a colorless oil, which was identified by its ^{1}H and ^{13}C NMR spectra[28].

Addition of 3 to Aldehydes

12) *(3R*,4S*)-4-Methyl-5-hepten-3-ol* (**15a**/**17a**): 4.0 g (20 mmol) of **3** and 1.16 g (20 mmol) of propionaldehyde were allowed to react as described under 10). After chromatography the product was bulb-to-bulb distilled at 15 Torr from a bath of 130°C to give 1.37 g (54%) of the product as a colorless oil. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.9–1.75 (m, 12H), 2.5 (m, 1H), 3.25 (m, 1H), 5.3 (m, 1H), 5.6 (m, 1H). – ^{13}C NMR (100 MHz, $CDCl_3$): **17a**: δ = 9.8, 12.8, 16.8, 26.8, 36.8, 76.5, 125.0, 132.5; **15a**: δ = 9.8, 16.5, 17.7, 26.8, 42.4, 76.2, 126.2, 132.9.

$C_8H_{16}O$ (128.2) Calcd. C 74.94 H 12.58
Found C 74.80 H 12.55

13) *(4R*,5S*)-2,4-Dimethyl-5-hepten-3-ol* (**15b**/**17b**): From 0.23 g (3.2 mmol) of isobutyraldehyde, 0.63 g (3.2 mmol) of **3**, and 0.61 g (3.84 mmol) of triethanolamine: 0.41 g (90%) of the product as a colorless oil. – ^{1}H NMR (300 MHz, $CDCl_3$): **17b**: δ = 0.87 (t, *J* = 6.5 Hz, 6H), 0.91 (d, *J* = 5.5 Hz, 3H), 1.58 (dd, *J* = 6.7 and 1.8 Hz, 3H), 2.20 (m, 1H), 2.60 (m, 1H), 3.02 (dd, *J* = 6.8 and 4.8 Hz, 1H), 5.25 (ddq, *J* = 12, 12 and 2.0 Hz, 1H), 5.50 (dqd, *J* = 11.0, 7.0 and 1 Hz, 1H). *E*-**15b**: δ = 1.62 (dd, *J* = 6.3 and 1.5 Hz, 3H), 2.96 (t, *J* = 5.9 Hz, 1H). – ^{13}C NMR (75 MHz, $CDCl_3$): *Z*-**17b**: δ = 13.2, 15.7, 17.2, 20.0, 29.9, 34.8, 79.7, 125.4, 132.6; *E*-**15b**: δ = 16.1, 17.3, 17.9, 19.8, 30.1, 40.3, 79.4, 126.8, 133.0.

$C_9H_{18}O$ (142.2) Calcd. C 75.98 H 12.76
Found C 76.37 H 12.71

14) *(2E,4R*,5S*)-5-Methyl-2,6-octadien-4-ol* (**15c**/**17c**): From 0.22 g (3.2 mmol) of crotonaldehyde, 0.63 g (3.2 mmol) of **3**, and 0.61 g (3.8 mmol) of triethanolamine: 0.40 g (90%) of the product as a clear oil. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84 (d, *J* = 6.8 Hz, 3H), 1.58 (dd, *J* = 6.8 and 1.8 Hz, 3H), 1.65 (dd, *J* = 6.8 and 1.3 Hz, 3H), 1.90 (s, 1H), 2.45 (m, 1H), 3.65 (t, *J* = 7.5 Hz, 1H), 5.16 (ddq, *J* = 10.0, 10.0 and 2 Hz, 1H), 5.37 (ddq, *J* = 15.0, 8.0 and 1.8 Hz, 1H), 5.58 (m, 2H). – ^{13}C NMR (75 MHz, $CDCl_3$): **17c**: δ = 13.0, 16.5, 17.6, 37.8, 76.8, 126.0, 128.3, 131.9, 132.7; **15c**: δ = 16.5, 17.6, 17.9, 43.5, 75.9, 127.1, 128.0, 132.0, 133.2.

$C_9H_{16}O$ (140.2) Calcd. C 77.09 H 11.50
Found C 77.05 H 11.42

15) *(1R*,2R*)-2-Methyl-1-phenyl-3-penten-1-ol* (**15d**/**17d**): From 0.24 g (2.3 mmol) of benzaldehyde, 0.40 g (2.3 mmol) of **3**, and 0.44 g (2.8 mmol) of triethanolamine: 0.37 g (92%) as a colorless oil. – ^{1}H NMR (300 MHz, $CDCl_3$): **17d**: δ = 0.82 (d, *J* = 6.6 Hz, 3H), 1.70 (dd, *J* = 6.8 and 1.7 Hz, 3H), 2.85 (m, 1H), 4.30 (d, *J* = 8.1 Hz, 1H), 5.35 (ddq, *J* = 11.0, 11.0 and 2.0 Hz, 1H), 5.70 (dqd, *J* = 11.7, 7.0 and 1.0 Hz, 1H), 7.35 (m, 5H), cf. ref.[19]. **15d**: δ = 1.7 (dd, *J* = 6.4 and 1.6 Hz, 3H). – ^{13}C NMR (75 MHz, $CDCl_3$): **17d**: δ = 13.2, 17.0, 39.8, 78.6, 126.9, 127.4, 127.5, 128.1, 132.7, 142.5; **15d**: δ = 16.9, 18.0, 45.4, 78.0, 126.9, 127.4, 128.1, 133.3, 142.5.

$C_{12}H_{16}O$ (176.3) Calcd. C 81.77 H 9.15
Found C 81.64 H 9.22

Reaction of 3 with Chiral Aldehydes

16) *Reaction with (2R,3S)-3-(tert-Butyldimethylsilyloxy)-2-methylpentanal* (**18**): From 2.80 g (14 mmol) of **3**, 2.35 g (10.2 mmol) of the aldehyde **18**[20], and 2.10 g (14 mmol) of triethanolamine as described under 10) 2.95 g of crude **19** and **20** were obtained. – ^{1}H NMR (400 MHz, $CDCl_3$): *Z*-**19**: δ = 0.060 (s, 3H), 0.064 (s, 3H), 0.8–0.95 (m, 9H), 0.88 (s, 9H), 1.5–1.7 (m, 3H), 1.64 (dd, *J* = 6.8 and 1.8 Hz, 1H), 2.19 (m, 1H), 2.63 (m, 1H), 3.40 (m, 1H), 3.7 (m, 1H), 5.32 (m, 1H), 5.57 (m, 1H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = –4.5, –4.0, 7.2, 9.2, 17.2, 18.1, 18.2, 25.9, 27.0, 35.1, 37.2, 77.0, 77.2, 125.1, 133.6. – The following signals of *E*-**19** could be recorded: δ = 1.67 (dd, *J* = 6.3 and 1.3 Hz) and δ = 13.1, 40.9, 126.2, 134.0.

For analysis a sample was purified by preparative gas chromatography at 160°C.

$C_{17}H_{36}O_2Si$ (300.6) Calcd. C 67.94 H 12.07
Found C 67.72 H 12.26

17) *Addition to (3R,4S)-4-(tert-Butyldimethylsilyloxy)-tetrahydro-2H-thiopyran-3-carbaldehyde* (**21**): The aldehyde was prepared as described in ref.[23]; $[\alpha]_D^{20}$ = –33.0 (*c* = 3.63, $CHCl_3$). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = –0.01 (s, 3H), 0.05 (s, 3H), 0.84 (s, 9H), 1.89 (m, 1H), 2.07 (m, 1H), 2.31 (m, 1H), 2.54 (m, 2H), 2.98 (m, 1H), 3.09 (m, 1H), 4.56 (m, 1H), 9.56 (s, 1H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = –5.3, –4.4, 17.8, 22.0, 22.4, 22.5, 34.7, 55.0, 65.6, 202.2.

From 3.50 g (13.4 mmol) of the aldehyde **21**, 4.00 g (20 mmol) of **3**, and 2.6 g (17 mmol) of triethanolamine as described under 10) to give 3.80 g (86%) of **22** and **23**. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.05–0.1 (4 s, 6H), 0.85–1.1 (m, 15H), 1.6–3.5 (m, 11H), 5.4–5.6 (m, 2H). – ^{13}C NMR (100 MHz, $CDCl_3$): *Z*-**22**: δ = –5.2, –4.0, 12.9, 17.9, 21.7, 23.1, 25.7, 33.4, 35.4, 38.2, 46.1, 69.2, 77.6, 124.0, 131.5. – *E*-**22**: δ = 44.8, 69.0, 124.1. – *Z*-**23**: δ = 46.3, 68.6, 77.1, 126.0, 130.5.

For analysis a sample was purified by preparative gas chromatography at 190°C.

$C_{17}H_{34}O_2SSi$ (330.6) Calcd. C 61.76 H 10.37
Found C 61.55 H 10.25

CAS Registry Numbers

3: 120788-89-8 / **4**: 120828-73-1 / **5**: 61676-62-8 / **6a**: 120788-90-1 / **6b**: 120788-91-2 / **6c**: 120788-94-5 / **7** (≡**8**): 120828-74-2 / **10a**: 120851-00-5 / **10b**: 120788-95-6 / **10c**: 120851-05-0 / **10d**: 120851-06-1 / **13**: 63707-89-1 / **15a**: 120851-01-6 / **15b**: 120788-96-7 / **15c**: 120851-07-2 / **15d**: 120851-09-4 / **17a**: 120851-02-7 / **17b**: 80357-60-4 / **17c**: 120851-08-3 / **17d**: 120851-10-7 / **18**: 108815-17-4 / (*Z*)-**19**: 120788-92-3 / (*E*)-**19**: 120851-11-8 / (*Z*)-**20**: 120851-03-8 / (*E*)-**20**: 120851-12-9 / **21**: 92119-95-4 / (*Z*)-**22**: 120788-93-4 / (*E*)-**22**: 120851-13-0 / (*Z*)-**23**: 120851-04-9 / (*E*)-**23**: 120851-14-1 / $B(OiPr)_3$: 5419-55-6 / $(CH_3)_2CHCHO$: 78-84-2 / pinacol: 76-09-5 / trimethoxy borate: 121-43-7 / (3*S*,4*S*)-2,5-dimethyl-3,4-hexanediol: 109785-53-7 / tri-*tert*-butyl borate: 7397-43-5 / 2-chloro-3-pentene: 1458-99-7 / propionaldehyde: 123-38-6 / crotonaldehyde: 4170-30-3 / benzaldehyde: 100-52-7

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