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Stereoselective Synthesis of Alcohols, XXII[1]

E/Z-Selectivity on Addition of α-Substituted Allylboronates to Aldehydes

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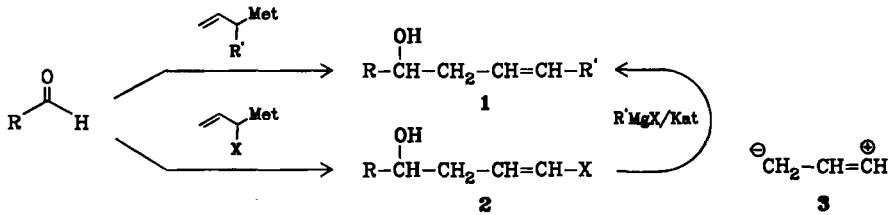
α-Heterosubstituted allylboronates **7** are prepared. Addition of **7** to aldehydes results in *E/Z*-isomeric homoallyl alcohols **13** and **14**. The reasons for the predominant formation of the *Z*-isomer **14** are discussed. The *Z*-bromo olefins **16** and **20** obtained in this way serve as starting point for chain extension or formation of δ-lactones **21**.

Stereoselektive Synthese von Alkoholen, XXII[1]

***E/Z*-Selektivität bei der Addition α-substituierter Allylboronsäureester an Aldehyde**

α-Heterosubstituierte Allylboronsäureester **7** werden dargestellt. Ihre Addition an Aldehyde führt zu den *E/Z*-isomeren Homoallylalkoholen **13** und **14**. Die Ursachen für die bevorzugte Bildung der *Z*-Isomeren **14** werden diskutiert. Die so gewonnenen *Z*-Brom-Olefine **16** und **20** dienen als Ausgangspunkt für eine Kettenverlängerung oder für die Bildung von δ-Lactonen **21**.

Many allyl metal compounds add to aldehydes and ketones with "allyl inversion"[2]. Those allyl metal compounds having an α-alkyl branch should therefore lead to adducts **1** with a linear alkene chain. Accordingly, this reaction ought to be useful for assembling larger alkyl chains[3]. The same target could be reached by using α-heterosubstituted allyl metal compounds, which can be considered as multicoupling building blocks **3**[4], because in the resulting adducts **2** the heteroatom can be substituted by an alkyl chain using either the cuprate-[5] or the Ni^0-[6] and Pd^0[7]-catalyzed carbon carbon bond forming reactions.



Of course, such methodology requires that structurally defined η^1-allyl metal compounds are existant and available. Yet these compounds appear to be exceptional in view of the generally fluctional nature of the allyl compounds of electropositive metals.

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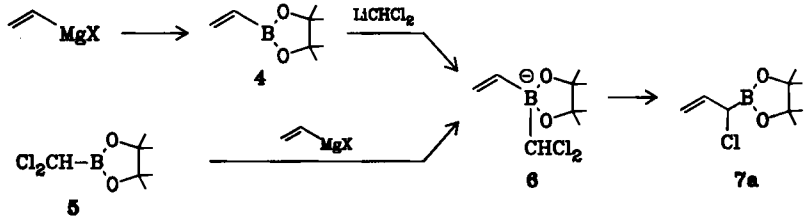
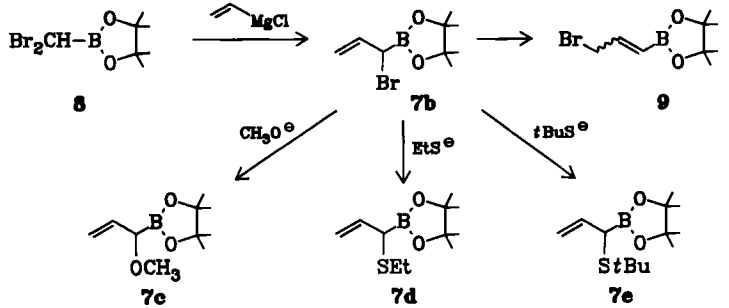
The possibility to implement the above methodology is therefore restricted to the use of the non-fluctional η^1-allyl derivatives of silicon, tin[8], and boron[2]. Extending our earlier investigation on the addition of α-methylallylboronates to aldehydes[9] we describe here our studies on the generation and reactions of α-heterosubstituted allylboronates **7**[10].

Preparation of α-Substituted Allylboronates

Matteson had described a route to **7a** by homologation of the vinylboronate **4** with dichloromethyllithium[11] via the ate-complex **6**. Since *Matteson* has shown[11-13] that the halogen in α-haloalkylboronates can be readily exchanged by other groups, we envisaged the α-chloroallylboronate **7a** as key intermediate for the preparation of a larger variety of α-substituted allylboronates.



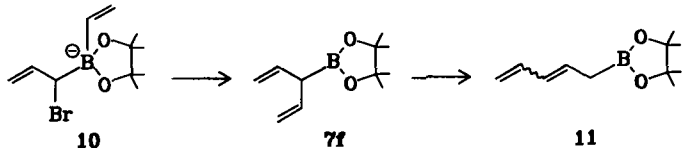
We wanted to avoid the handling of the easily polymerisable **4** in the preparation of **7a**. Therefore we persued a complementary generation of the ate-complex **6**. Addition of vinylmagnesium chloride to the dichloromethaneboronate **5**[14] at −78 °C generated **6** which rearranged at room temperature to give **7a** in 73% yield. Unfortunately we were unable to replace the chlorine in **7a** by nucleophiles such as ethanethiolate or methoxide. We therefore prepared the dibromomethaneboronate **8** from dibromomethyllithium[15] and converted it similarly to the α-bromoallylboronate **7b**.



This material had only limited stability, as it isomerized slowly to an *E/Z*-mixture of the vinylboronate **9** on distillation or on standing in a process that is completed quickly by heating of **7b** to 140 °C. This allyl isomerization[16] may well proceed via carbenium ions as a result of the cation stabilizing effect[13] of a dialkoxyboryl group. Substitution of the bromine in **7b** by methoxide could be achieved, but the resulting allylboronate

7c was understandably even less thermally stable than **7b**. On the other hand substitution of the bromine in **7b** by ethane- or 1,1-dimethylethanethiolate gave the stable α-thioallylboronates **7d** and **e**.

Addition of vinylmagnesium chloride to the bromo compound **7b** stopped at the ate-complex **10**, which rearranged to **7f** (51%) only upon addition of aluminium chloride (or zinc chloride).



10 **7f** **11**

Heating in the presence of Lewis acids resulted in rearrangement to the dienylboronate **11**[17].

Addition of the α-Substituted Allylboronates to Aldehydes

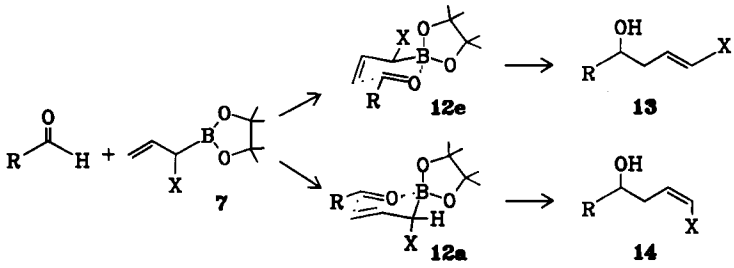
The α-heterosubstituted allylboronates **7a–e** added cleanly to representative aldehydes at 0–20°C (results in Table 1). Included are the data of the silyl compound **7g**[18] and the methyl compound **7h**[9]. The formation of *Z*-homoallyl alcohols **14** on reaction of alkoxy-substituted allylboronates related to **7c** has been noted previously[19].

Table 1. Formation of homoallyl alcohols by the addition of α-substituted allylboronates **7** to aldehydes

Allylboronate	Aldehyde R =	Homoallyl Alcohols **13/14** % yield	*E*/*Z*-ratio
7a (X = Cl)	CH_3	63	7:93[a]
	CH_3CH_2	86	6:94[a]
	$(CH_3)_2CH$	83	4:96[a]
	C_6H_5	82	5:95[b]
7b (X = Br)	CH_3	78[d]	7:93[a]
	CH_3CH_2	82[d]	6:94[b]
	$(CH_3)_2CH$	83[d]	4:96[a]
	C_6H_5	80[d]	3:97[b]
	n-C_5H_{11}	69[d]	8:92[a]
	$CH_3CH_2CH=CHCH_2$	85[d]	8:92[a]
7c (X = OCH_3)	$(CH_3)_2CH$	55	<3:>97[a]
7d (X = SCH_2CH_3)	$(CH_3)_2CH$	84	15:85[a]
7e (X = $SC(CH_3)_3$)	$(CH_3)_2CH$	63	20:80[a]
7f (X = $CH=CH_2$)	$(CH_3)_2CH$	94	60:40[c]
7g (X = $Si(CH_3)_3$)	C_6H_5	89	12:88[e]
7h (X = CH_3)	$(CH_3)_2CH$	72	21:79[f]
15a	$(CH_3)_2CH$	68	34:66
15b	$(CH_3)_2CH$	78[d]	61:39
15c	$(CH_3)_2CH$	74[d]	82:18

[a] Determined by ^{13}C NMR spectroscopy. – [b] Determined by g.c. – [c] Determined by ^1H NMR spectroscopy. – [d] Reaction without isolation of **7** or **15**; yield refers to **8** or related compounds as starting material. – [e] Data from Ref.[18]. – [f] Data from Ref.[9].

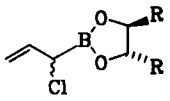
The addition probably proceeds via the chair-type transition states **12** and leads to the *E*- and *Z*-homoallyl alcohols **13** and **14**, depending on which diastereotopic face of the double bond in **7** is attacked. The data in Table 1 reveal that the isomer **14** with *Z*-substituted double bond predominates, which must derive from a transition state **12a** with an axial arrangement of the substituent X.



While the similarity of the transition states **12** to those of the Cope and Claisen rearrangement[20] would suggest that the homoallyl alcohols **13** with an *E*-configuration of the double bond should predominate, it should be noted that the Cope rearrangement leading to products with a polar substituent at the new sp^2-center is not necessarily *E*-selective[21].

On reactions of aldehydes with other α-substituted ally metal derivatives selectivities in favor of **13**[22,23] or **14**[23,24,25] have been recorded. While there is no consistent picture, at least in the majority of the cases non-polar substituents X lead to *E*-homoallyl alcohols **13**, whereas with polar substituents X the *Z*-isomer **14** is frequently preferred. Considering only those reactions which are likely to proceed via cyclic transition states similar to **12** the varying stereochemistry suggests that it is due to the interplay of several factors determining the relative energy of the transition states **12a** and **e**.

Steric Effects: These can best be evaluated as long as X is a non-polar methyl group as in **7h**. The cause of the observed *Z*-preference has been discussed previously[9] as involving two destabilizing *gauche* interactions in the transition state **12e** between the methyl group and the bulky glycol component of the boronate, whereas in transition state **12a** there is only one such interaction. The slimmer the group X the higher should be the fraction reacting via transition state **12e**. This may account partly for the preponderance of **13** in the reaction of the vinyl compound **7f**. The corollary is that diminishing the size of the groups on boron in the allylboronates **7** should also increase the fraction of the *E*-isomer **13** in the homoallyl alcohols formed. That this holds not only for **7h** in which X is methyl[9], but also for the α-chloroallylboronates is seen from the data on the reactions of **15a–c** in Table 1.



15

	a	**b**	**c**
R	C_6H_5	CH_2OCH_3	$CH_2OCH_2C_6H_4Cl$–(4)

Polar Effects: It is obvious from Table 1 that the underlying small preference for the formation of the *Z*-isomer **14** caused by steric effects is enhanced when the substituent X in the allylboronate becomes more and more electronegative. In view of the dipole moment of the boron-oxygen bond it seems plausible that such conformations are more stable in which the C – X dipole opposes at least one of the B – O dipoles or better their vectorial sum. This would be equivalent to a popular explanation of the anomeric effect[26], as molecules tend to assume the conformation with the smallest net dipole moment. While such a discussion would certainly apply to the ground state conformations of **7**, it remains a moot point to what extent it would be relevant to the transition states **12** in which the third boron-oxygen bond (to the aldehyde) is already formed to a considerable extent. This would give the vectorial sum of the three boron-oxygen bonds another direction.

Stereoelectronic Effects: Rather than invoking general polar effects it would be more convincing to attribute the noteworthy *Z*-preference to stereoelectronic effects operating in the transition states **12**. If the association of the aldehyde to boron were the product determining step, the transition state **12e** should be favored over **12a**, since in the former electron density could be delocalized into the σ^* orbital of the C – X bond. Since this prediction is at variance with the observed preferential formation of **14**, we conclude that the product determining step is the formation of the new carbon – carbon bond in a precomplexed aldehyde boron adduct. In such an adduct the electrophilicity of the aldehyde is increased. Hence, the formation of the carbon carbon bond occurs by electrophilic attack of the aldehyde group at the olefinic double bond. The ease of electrophilic attack on an allyl system depends on the dihedral angle between the C – X bond and the π-orbital. While clear experimental distinctions between the various models proposed[27] have not been achieved yet we base our discussion on the arguments presented by *Schreiber*[28], *Houk*[29], and *Danishefsky*[30]:

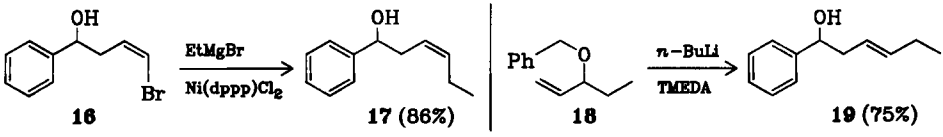
In the case of a polar C – X bond, equivalent to a low lying C – X σ^*-orbital, electron density is transferred from the π-orbital into the C – X bond, provided that these orbitals are parallel to allow overlap. In the transition state **12e** with an equatorial C – X bond such overlap would be possible diminishing the electron density at the C – C double bond. In contrast, in the transition state **12a** the C – X bond and the π-orbital of the double bond are essentially orthogonal precluding any delocalisation of electron density from the double bond. Hence, this conformation **12a** should be the more reactive conformation with respect to **12e**.

The observed *E*/*Z*-selectivities probably reflect composite steric and stereoelectronic effects: High *Z*-preference results when these effects cooperate as, e.g., in the cases of bromine and methoxide substituents. In the case of the trimethylsilyl group the stereoelectronic effect would prefer an equatorial placement as in **12e**, whereas the steric bulk of this group could be better accommodated on axial placement as in **12a**[24]. Hence, depending on which effect is more marked any *Z*/*E*-selectivity could have been justified.

Chain Extensions of the Homoallyl Alcohols 14

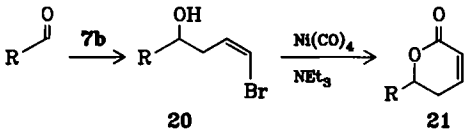
In order to use the vinylic heteroatom in **14** for further chain extension the compounds with X = Br[7] or SR[6] command special interest. Since only the bromo com-

pounds were accessible with a reasonable level of stereochemical purity (>90% *Z*) we surveyed their reactions briefly.



Thus, the vinyl bromide **16** (*E*:*Z* = 3:97) was reacted with excess ethylmagnesium bromide[31] to give the homoallyl alcohol **17** (*E*:*Z* = 8:92). To verify the stereochemical assignment of the double bond in **17** as *Z*, the corresponding *E*-isomer **19** was prepared by a Wittig rearrangement[32].

Another way to utilize the *Z*-configuration of the double bond in **14** is to carbonylate[33] these systems to α,β-unsaturated δ-lactones, a partial structure of several fragrant natural products such as massoia lactone **21b** or tubero lactone **21c**. Indeed, the vinyl bromides **20** could be reacted with $Ni(CO)_4$ and triethylamine to give the lactones **21** in fair to good yields.



a: R = $(CH_3)_2CH$ 90%
b: R = n-C_5H_{11} 81%
c: R = (*Z*)-$CH_3CH_2CH{=}CH{-}CH_2$ ≈ 50%

Thus, the use of the α-bromoallylboronates as "conjunctive reagents" or "multicoupling building blocks" allows the two-step conversion of aldehydes into the unsaturated δ-lactones **21**. This sequence complements other multistep methods[34] to achieve this conversion.

We are grateful to the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for supporting this investigation. We thank the *BASF Aktiengesellschaft* for supplying chemicals.

Experimental Part

All temperatures quoted are non-corrected. – ^1H NMR spectra: Varian T-60, Bruker WH-400. – ^{13}C NMR spectra: Varian XL-100, CFT-20, Jeol FX-100, and Bruker WH-400. – Preparative gas chromatography: Aerograph A-90-P3, 1.5 m × 0.6 cm column with 5% SE 30 on Chromosorb G, AW-DMCS (60–80 mesh), 130 ml He/min. – Analytical gas chromatography: a) Perkin-Elmer F-900, 3 m × 0.3 cm column with 3% Silar 10 C on Chromosorb G, AW-DMCS 100/120 mesh; b) Varian 2700 with glass capillary column 40 m × 0.3 mm with SE 52, 1.4 bar He.

Preparation of the Allylboronates

1. *2-(1-Chloro-2-propenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**7a**): To a solution of 3.16 g (15 mmol) of 2-(dichloromethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5**)[14] in 50 ml of dry THF was added over 5 min at –78 °C 7.25 ml (15 mmol) of a 2.07 M solution of vinylmagnesium chloride in THF. The mixture was allowed to reach room temperature. After 15 h it was poured

on 50 ml of water and was extracted three times with 40 ml each of petroleum ether (40–60°C). The combined extracts were dried over Na_2SO_4. The solvents were removed and the residue was distilled to give 2.20 g (73%) of **7a** as colourless liquid, b.p. 89–91°C/14 Torr. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (s, 12H), 3.97 (d, *J* = 8.2 Hz, 1H), 5.17 (dt, *J* = 10.1 and 1.1 Hz, 1H), 5.34 (dt, *J* = 16.8 and 1.2 Hz, 1H), 5.99 (ddd, *J* = 16.8, 10.1 and 8.1 Hz, 1H); cf. Lit.[11]. – ^{13}C NMR ($CDCl_3$): δ = 24.4, 84.4, 116.8, 134.9.

2. *2-(Dibromomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**8**): A solution of 0.10 mol of lithium diisopropylamide was prepared from 10.4 g of diisopropylamine in 100 ml of dry ether and *n*-butyllithium in *n*-hexane at 0°C. After additon of 70 ml of dry THF the mixture was cooled to –100°C. A solution of 8.0 ml (0.11 mol) of dibromomethane in 50 ml of dry THF was added under stirring over 1 h and was kept for further 30 min at this temperature. 12.5 ml (0.11 mol) of trimethyl borate was added at once. After 40 min at –100°C 23.5 ml (0.207 mol) of 48% hydrobromic acid was added at once and the mixture was allowed to reach room temperature. The amine hydrobromide was filtered and washed with ether. The filtrates were concentrated and the residue was taken up in 100 ml of ether. Addition of 10.0 g (85 mmol) of 2,3-dimethyl-2,3-butanediol was followed by addition of 100 ml of petroleum ether (40–60°C). After stirring for 1 h the organic phase was separated and washed 4 times with 10 ml each of water. After drying over Na_2SO_4 the solution was concentrated and the solid residue (27.4 g) bulb to bulb distilled at 0.5 Torr from a bath of 100–110°C: 23.0 g (77%) of colourless **8**, m.p. 51.5–54°C. For analysis a sample was resublimed twice at 0.01 Torr, m.p. 53–54°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31 (s, 12H), 5.09 (s, 1H).

$C_7H_{13}BBr_2O_2$ (299.8) Calcd. C 28.04 H 4.37 Br 53.31 Found C 28.18 H 4.35 Br 53.33

3. *2-(1-Bromo-2-propenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**7b**): 3.0 g (10 mmol) of **8** was reacted as described under 1. After reaching room temp. the reaction mixture was processed after 2 h as described under 1. to give 1.63 g (66%) of **7b** as colourless liquid, b.p. 34°C/0.5 Torr. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27 (s, 12H), 3.90 (d, *J* = 9.8 Hz, 1H), 5.13 (d, *J* = 9.9 Hz, 1H), 5.32 (dt, *J* = 16.8 and 1.0 Hz, 1H), 6.07 (dt, *J* = 16.8 and 9.9 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 24.3, 84.3, 118.1, 135.3. – The substance readily decomposes upon standing.

4. *2-(3-Bromo-1-propenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**9**): 4.9 g (20 mmol) of **7b** was heated over 1 h at 140°C. Distillation at 110°C/14 Torr gave 1.20 g (24%) as light tan oil. *Z*/*E*-ratio ca. 3:1 by ^{1}H NMR. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (s, 9H), 1.27 (s, 3H), 3.96 (dd, *J* = 7.1 and 1.2 Hz, 1.5H), 4.32 (d, *J* = 8.0 Hz, 0.5H), 5.46 (d, *J* = 13.2 Hz, 0.25H), 5.66 (dt, *J* = 17.6 and 1.1 Hz, 0.75H), 6.56–6.62 (m, 0.25H), 6.66 (dt, *J* = 17.6 and 7.1 Hz, 0.75H). – ^{13}C NMR ($CDCl_3$): *E*-**9**: δ = 24.7, 33.5, 83.4, 146.6; *Z*-**9**: δ = 30.6, 83.3, 147.7, one signal obscured.

5. *2-(1-Methoxy-2-propenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**7c**): A solution of 3.38 g (13.7 mmol) of **7b** in 20 ml of dry methanol was stirred over 4 h at 20°C with 12.1 mmol of sodium methoxide in methanol (30%). The mixture was partitioned between 40 ml of water and 40 ml of petroleum ether (40–60°C). The aqueous phase was washed twice with 50 ml of petroleum ether and the combined extracts were washed twice with 25 ml of saturated NaCl solution. After drying over Na_2SO_4 the solution was concentrated i. vac. at room temp. to give 2.04 g (75%) of crude **7c** as colourless oil. – ^{1}H NMR (60 MHz, $CDCl_3$, TMS external): δ = 1.2 (s, 12H), 3.3 (s, 3H), 3.7 (d, *J* = 8 Hz, 1H), 5.0–6.3 (m, 3H). – The product readily decomposed upon standing.

6. *2-[1-(Ethylthio)-2-propenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**7d**): To a solution of 0.93 g (15 mmol) of ethanethiol in 40 ml of dry THF was added at 0°C 8.3 ml (13.3 mmol) of a

1.6 M solution of *n*-butyllithium in *n*-hexane. To the resulting suspension was added 3.21 g (13.0 mmol) of **7b** in 5 ml of THF. The resulting homogeneous solution was stirred for 2 h at room temp. and partitioned between 30 ml of water and 30 ml of petroleum ether (40–60 °C). The aqueous phase was extracted twice with 30 ml of petroleum ether. The combined extracts were dried over Na_2SO_4 and concentrated. Distillation at 94–98 °C/1 Torr gave 1.60 g (54%) of **7d** as colourless oil. A small sample was purified by gas chromatography (130 °C). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.19 (t, *J* = 7.4 Hz, 3H), 1.25 (s, 12H), 2.48 (q, *J* = 7.4 Hz, 2H), 2.96 (d, *J* = 9.6 Hz, 1H), 5.01–5.06 (m, 2H), 5.76 (dt, *J* = 17.3 and 9.6 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 14.0, 24.5, 83.9, 115.3, 135.6.

$C_{11}H_{21}BO_2S$ (228.2) Calcd. C 57.91 H 9.28 S 14.05 Found C 57.91 H 9.30 S 14.17

7. *2-[1-(1,1-Dimethylethylthio)-2-propenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**7e**): 1.35 g (15.0 mmol) of 2-methyl-2-propanethiol was reacted with **7b** as described under 6. to give 1.49 g (44%) of **7e** as light tan oil of b.p. 75–80 °C/0.5 Torr. – ^{1}H NMR (60 MHz, $CDCl_3$, TMS external): δ = 1.27 and 1.35 (2 s, 21H), 3.1 (d, 9 Hz, 1H), 4.9–6.3 (m, 3H). – The product was reacted with isobutyraldehyde without further characterisation.

8. *2-(1-Ethenyl-2-propenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**7f**): To a solution of 3.32 g (13.4 mmol) of **7b** in 50 ml of dry THF was added at –78 °C 6.1 ml (12.8 mmol) of a 2.1 M solution of vinylmagnesium chloride in THF. The mixture was allowed to reach 0 °C and was transferred via canula onto 3.41 g (25.6 mmol) of $AlCl_3$ at –78 °C. The mixture was allowed to reach room temp. under stirring and was filtered after 15 min. The filtrate was concentrated to a volume of 10 ml, diluted with 40 ml of dry petroleum ether (40–60 °C) and filtered again. The filtrate was concentrated i. vac. at room temp. and the residue was bulb to bulb distilled at 0.01 Torr from a bath of 50 °C to give 1.32 g (51%) of **7f** as colourless oil. A sample was purified by gas chromatography (90 °C). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (s, 12H), 2.71 (t, *J* = 8 Hz, 1H), 5.00–5.06 (m, 4H), 5.92 (ddd, *J* = 17.2, 10.3, and 7.8 Hz, 2H). – ^{13}C NMR ($CDCl_3$): δ = 24.5, 83.3, 114.1, 137.0.

$C_{11}H_{19}BO_2$ (194.1) Calcd. C 68.08 H 9.87 Found C 68.05 H 10.00

In another experiment the solution of the ate-complex (0 °C) was transferred via canula onto 1.9 g (14 mmol) of anhydrous $ZnCl_2$ at room temp., resulting in a strongly exothermic reaction. After stirring for 2 d the mixture was filtered under nitrogen and the filtrate was concentrated *in vacuo*. The residue was taken up in 20 ml of petroleum ether (40–60 °C), filtered, and concentrated again. The residue was bulb to bulb distilled at 0.01 Torr from a bath of 50 °C to give 1.73 g of crude **11** (*E*/*Z*-mixture) as colourless oil. A sample was purified by gas chromatography (90 °C) to give material of ca. 90% purity. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (s, 12H), 1.75 and 1.84 (2 d, *J* = 7.3 Hz, together 2H), 4.8–6.7 (several m, 5H).

9. *(4R*,5R*)-2-[(R,S)-1-Chloro-2-propenyl]-4,5-diphenyl-1,3,2-dioxaborolane* (**15a**): 4.29 g (20 mmol) (*R*,R**)-1,2-diphenyl-1,2-ethanediol[35] and 4.26 g (20 mmol) of (dichloromethyl)diisopropoxyborane[14] were dissolved in 30 ml of benzene. The benzene/isopropyl alcohol azeotrope was slowly distilled over a 25 cm column. Distillation was continued after addition of 30 ml of benzene. The solvents were removed i. vac. from a bath of 80 °C to leave 6.14 g of (*4R*,5R**)-2-(dichloromethyl)-4,5-diphenyl-1,3,2-dioxaborolane as tan oil. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.37 (s, 2H), 5.60 (s, 1H), 7.30–7.44 (m, 10H). – ^{13}C NMR ($CDCl_3$): δ = 87.5, 125.6, 128.7, 128.8, 138.8.

For analysis the material was converted to the pyridine adduct: 0.70 g (2.3 mmol) were dissolved in 4 ml of dry ether and treated with 0.19 g (2.4 mmol) of pyridine. The crystalline

adduct was filtered, washed with a small amount of ether and dried i. vac.: 0.76 g (86%) colourless crystals of dec. p. 144–145.5°C.

$C_{20}H_{18}BCl_2NO_2$ (386.1) Calcd. C 62.22 H 4.70 Cl 18.37 N 3.63
Found C 62.04 H 4.65 Cl 18.25 N 3.59

To a solution of 4.85 g (15.8 mmol) of (*4R*,5R**)-2-(dichloromethyl)-4,5-diphenyl-1,3,2-dioxaborolane in 50 ml of dry THF was added at −78°C over 4 min 7.6 ml (15.7 mmol) of a 2.07 M solution of vinylmagnesium chloride in THF. The mixture was allowed to reach room temperature. After 14 h the solvents were removed i. vac. and the residue was triturated with 50 ml of petroleum ether (40–60°C) over 1 h. The mixture was filtered and the filtrate was freed of solvent i. vac. from a bath of 100°C. A sample of the remaining **15a** was bulb to bulb distilled i. vac. at 150°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.26 (d, *J* = 8.2 Hz, 1H), 5.28 (s, 2H), 5.28–5.31 (m, 1H), 5.49 (d, *J* = 16.8 Hz, 1H), 6.18 (ddd, *J* = 16.8, 10.1 and 8.2 Hz, 1H), 7.29–7.43 (m, 10H). – ^{13}C NMR ($CDCl_3$): δ = 87.1, 117.7, 125.6, 128.5, 128.8, 134.7, 139.5 (the diastereomers were not resolved in the spectra).

$C_{17}H_{16}BClO_2$ Calcd. mass 298.0932 Found 298.0941

10. *(4S,5S)-2-[(RS)-1-Chloro-2-propenyl]-4,5-bis(methoxymethyl)-1,3,2-dioxaborolane* (**15b**): 4.51 g (30 mmol) of (2*S*,3*S*)-1,4-dimethoxy-2,3-butanediol[36] and 6.44 g (30.2 mmol) of (dichloromethyl)diisopropoxyborane[14] were converted into (4*S*,5*S*)-2-(dichloromethyl)-4,5-bis(methoxymethyl)-1,3,2-dioxaborolane as described under 9.: 6.61 g (91%) as colourless oil, b.p. 82–84°C/0.5 Torr. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.42 (s, 6H), 3.48–3.56 (m, 4H), 4.49–4.53 (m, 2H), 5.42 (s, 1H). – ^{13}C NMR ($CDCl_3$): δ = 59.4, 73.3, 79.2.

Pyridine Adduct: As under 9. 84%, m.p. 99–100.5°C.

$C_{12}H_{18}BCl_2NO_4$ (322.0) Calcd. C 44.76 H 5.63 Cl 22.02 N 4.35
Found C 44.72 H 5.54 Cl 21.98 N 4.42

A solution of 3.46 g (14.2 mmol) of (4*S*,5*S*)-2-(dichloromethyl)-4,5-bis(methoxymethyl)-1,3,2-dioxaborolane in 30 ml of dry THF were reacted at −78°C with 6.8 ml (14.3 mmol) of a 2.1 M solution of vinylmagnesium chloride in THF. After reaching room temp., the resulting solution of **15b** was reacted immediately with 1.18 g (16.4 mmol) of 2-methylpropanal over 15 h at 20°C. The solvents were removed i. vac. and the residue was hydrolysed with 15 ml of saturated NH_4Cl solution. The mixture was extracted three times with 20 ml each of CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated. The residue was filtered over 200 g of basic alumina with CH_2Cl_2 to give 1.66 g (78%) of *6-chloro-2-methyl-5-hexene-3-ol.*

11. *(4S,5S)-4,5-Bis[(4-chlorobenzyloxy)methyl]-2-[(RS)-1-chloro-2-propenyl]-1,3,2-dioxaborolane* (**15c**): ca. 10 mmol of crude dichloromethaneboronic acid[14] and 3.71 g (10 mmol) of (2*S*,3*S*)-1,4-bis(4-chlorobenzyloxy)-2,3-butanediol[37] were esterified in 50 ml of benzene as described under 9. to give 4.39 g (95%) of (4*S*,5*S*)-4,5-bis[(4-chlorobenzyloxy)methyl]-2-(dichloromethyl)-1,3,2-dioxaborolane as tan oil. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.56–3.65 (m, 4H), 4.51–4.57 (m, 6H), 5.41 (s, 1H), 7.24 and 7.31 (AB, *J* = 8.5 Hz, 8H).

Pyridine Adduct: As under 9.: 85%, m.p. 89–90°C.

$C_{24}H_{24}BCl_4NO_4$ (543.1) Calcd. C 53.08 H 4.45 Cl 26.11 N 2.58
Found C 53.19 H 4.46 Cl 26.10 N 2.60

4.26 g (9.2 mmol) of (4*S*,5*S*)-4,5-bis[(4-chlorobenzyloxy)methyl]-2-(dichloromethyl)-1,3,2-dioxaborolane were reacted with vinylmagnesium chloride as under 9. After reaching room temp. the solvent was removed i. vac. and the residue taken up in 25 ml of dry CH_2Cl_2. The mixture was filtered and the filtrate was concentrated to give 4.11 g of crude **15c**. – ^{1}H NMR (60 MHz,

$CDCl_3$, TMS external): δ = 3.4–3.8 (m, 4H), 4.1 (d, *J* = 8 Hz, 1H), 4.3–4.7 (m, 2H), 4.5 (s, 4H), 5.0–6.4 (m, 3H), 7.1–7.5 (m, 8H). – ^{13}C NMR ($CDCl_3$): δ = 71.2, 72.6, 78.7, 117.2, 128.4, 128.7, 133.3, 134.6, 136.2. – The crude product was immediately reacted with 2-methylpropanal.

Addition of the Allylboronates 7 and 15 to Aldehydes

General Procedure: 5–15 mmol of the (crude) α-substituted allylboronate **7** or **15** and generally 1.15 equivalents of the aldehyde were allowed to react for 15 h at 0°C. After dilution with 10–15 ml of ether 1 equivalent of triethanolamine was added. The resulting suspension was stirred for 2–4 h and filtered. The filtrate was concentrated i. vac. and the residue was chromatographed with CH_2Cl_2 over 100–200 g of basic alumina. The eluate was concentrated i. vac. to give the crude product in the yields given in Table 1. Samples for combustion analysis were purified by preparative g.c. The *E*/*Z*-ratios were determined either by ^{13}C NMR spectroscopy, or by analytical g.c. (conditions b) or ^1H NMR spectroscopy.

(Z)-5-Chloro-4-penten-2-ol: g.c. purification at 70°C. – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.22 (d, *J* = 6.2 Hz, 3H), 1.61 (s, 1H), 2.38–2.42 (m, 2H), 3.93 (sextett, *J* = 6.2 Hz, 1H), 5.85 (q, *J* = 7.2 Hz, 1H), 6.14 (dt, *J* = 7.2 and 1.5 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 23.0, 36.6, 66.9, 120.0, 127.7.

C_5H_9ClO (120.6) Calcd. C 49.81 H 7.52 Cl 29.40 Found C 49.85 H 7.56 Cl 29.52

(Z)-6-Chloro-5-hexen-3-ol: g.c. purification at 85°C. – ^1H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 7.4 Hz, 3H), 1.44–1.57 (m, 2H), 1.65 (s, 1H), 2.32–2.47 (m, 2H), 3.61–3.67 (m, 1H), 5.86 (q, *J* = 7.2 Hz, 1H), 6.13 (dt, *J* = 7.1 and 1.5 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 9.7, 29.6, 34.3, 72.0, 119.6, 127.9.

$C_6H_{11}ClO$ (134.6) Calcd. C 53.54 H 8.24 Cl 26.34 Found C 53.43 H 8.22 Cl 26.35

(Z)-6-Chloro-2-methyl-5-hexen-3-ol: g.c. purification at 80°C. – ^1H NMR (400 MHz, $CDCl_3$): δ = 0.936 (d, *J* = 6.8 Hz, 3H), 0.944 (d, *J* = 6.8 Hz, 3H), 1.49 (d, *J* = 4.9 Hz, 1H), 1.64–1.73 (m, 1H), 2.31–2.47 (m, 2H), 3.43–3.49 (m, 1H), 5.89 (q, *J* = 7.1 Hz, 1H), 6.13 (dt, *J* = 7.1 and 1.6 Hz, 1H), cf. Lit.[38]. – ^{13}C NMR ($CDCl_3$): δ = 17.3, 18.6, 31.9, 33.3, 75.5, 119.3, 128.5.

$C_7H_{13}ClO$ (148.6) Calcd. C 56.57 H 8.82 Cl 23.85 Found C 56.73 H 8.84 Cl 23.67

(E)-6-Chloro-2-methyl-5-hexen-3-ol: Data from the reaction of **15a**: ^1H NMR (400 MHz, $CDCl_3$): δ = 0.909 (d, *J* = 6.8 Hz, 3H), 0.917 (d, *J* = 6.8 Hz, 3H), 1.59 (s, 1H), 1.62–1.72 (m, 1H), 2.09–2.29 (m, 2H), 3.36–3.40 (m, 1H), 5.90–5.97 (m, 1H), 6.03 (dt, *J* = 13.3 and 1.1 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 17.2, 18.6, 33.0, 35.6, 75.4, 118.8, 130.6.

(Z)-4-Chloro-1-phenyl-3-buten-1-ol: g.c. purification at 150°C. – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.95 (s, 1H), 2.66–2.76 (m, 2H), 4.79–4.82 (m, 1H), 5.82 (q, *J* = 7.1 Hz, 1H), 6.13 (dt, *J* = 7.2 and 1.5 Hz, 1H), 7.26–7.41 (m, 5H), cf. Lit.[38]. – ^{13}C NMR ($CDCl_3$): δ = 36.5, 73.0, 120.1, 125.7, 127.4, 127.7, 128.4, 143.6.

$C_{10}H_{11}ClO$ (182.6) Calcd. C 65.76 H 6.07 Cl 19.41 Found C 65.95 H 5.98 Cl 19.67

(Z)-5-Bromo-4-penten-2-ol: g.c. purification at 70°C. – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.23 (d, *J* = 6.2 Hz, 3H), 1.58 (s, 1H), 2.36–2.39 (m, 2H), 3.95 (sextett, *J* = 6.2 Hz, 1H), 6.19 (q, *J* = 6.9 Hz, 1H), 6.29 (dt, *J* = 7.1 and 1.4 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 22.7, 39.0, 66.4, 109.4, 130.9.

C_5H_9BrO (165.0) Calcd. C 36.39 H 5.50 Br 48.42 Found C 36.58 H 5.61 Br 48.14

(Z)-6-Bromo-5-hexen-3-ol: g.c. purification at 80°C. – ^1H NMR (400 MHz, $CDCl_3$): δ = 0.96 (t, *J* = 7.5 Hz, 3H), 1.43–1.60 (m, 3H), 2.30–2.45 (m, 2H), 3.64–3.70 (m, 1H),

6.21 (q, J = 6.9 Hz, 1H), 6.27 (dt, J = 7.1 and 1.3 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 9.8, 29.6, 37.0, 71.8, 109.3, 131.2.

$C_6H_{11}BrO$ (179.1) Calcd. C 40.25 H 6.19 Br 44.63 Found C 40.48 H 6.29 Br 44.38

(Z)-6-Bromo-2-methyl-5-hexen-3-ol: g.c. purification at 85°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (d, J = 6.8 Hz, 3H), 0.95 (d, J = 6.8 Hz, 3H), 1.48 (s, 1H), 1.65 – 1.73 (m, 1H), 2.29 – 2.45 (m, 2H), 3.46 – 3.51 (m, 1H), 6.21 – 6.28 (m, 2H). – ^{13}C NMR ($CDCl_3$): δ = 17.3, 18.6, 33.3, 34.6, 75.4, 109.2, 131.8.

$C_7H_{13}BrO$ (193.1) Calcd. C 43.54 H 6.79 Br 41.38 Found C 43.70 H 6.86 Br 41.20

(Z)-4-Bromo-1-phenyl-3-buten-1-ol: g.c. purification at 145°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.99 (d, J = 3.5 Hz, 1H), 2.61 – 2.74 (m, 2H), 4.81 – 4.84 (m, 1H), 6.17 (q, J = 6.9 Hz, 1H), 6.27 (dt, J = 7.1 and 1.4 Hz, 1H), 7.27 – 7.39 (m, 5H). – ^{13}C NMR ($CDCl_3$): δ = 39.1, 72.8, 109.8, 125.7, 127.6, 128.3, 130.7, 143.4.

$C_{10}H_{11}BrO$ (227.1) Calcd. C 52.89 H 4.88 Br 35.19 Found C 53.02 H 4.89 Br 35.13

(Z)-1-Bromo-1-nonen-4-ol: g.c. purification at 135°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 3H), 1.26 – 1.62 (m, 9H), 2.31 – 2.45 (m, 2H), 3.71 – 3.77 (m, 1H), 6.21 (q, J = 6.9 Hz, 1H), 6.28 (dt, J = 7.1 and 1.3 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 13.9, 22.5, 25.2, 31.7, 36.9, 37.5, 70.6, 109.5, 131.2.

$C_9H_{17}BrO$ (221.1) Calcd. C 48.88 H 7.75 Br 36.13 Found C 49.01 H 7.76 Br 35.81

(1Z,6Z)-1-Bromo-1,6-nonadien-4-ol: g.c. purification at 130°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.97 (t, J = 7.5 Hz, 3H), 1.66 (s, 1H), 2.03 – 2.11 (m, 2H), 2.20 – 2.30 (m, 2H), 2.33 – 2.46 (m, 2H), 3.74 – 3.78 (m, 1H), 5.33 – 5.40 (m, 1H), 5.56 – 5.62 (m, 1H), 6.23 (q, J = 6.8 Hz, 1H), 6.28 (dt, J = 7.0 and 1.3 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 14.1, 20.6, 34.8, 36.9, 70.2, 109.6, 123.8, 131.1, 135.3.

$C_9H_{15}BrO$ (219.1) Calcd. C 49.33 H 6.90 Br 36.47 Found C 49.42 H 7.06 Br 35.03

(Z)-6-Methoxy-2-methyl-5-hexen-3-ol: g.c. purification at 90°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (d, J = 6.8 Hz, 3H), 0.93 (d, J = 6.8 Hz, 3H), 1.64 – 1.69 (m, 1H), 1.81 (s, 1H), 2.19 – 2.24 (m, 2H), 3.20 – 3.37 (m, 1H), 3.58 (s, 3H), 4.38 – 4.44 (m, 1H), 6.03 (dt, J = 6.2 and 1.3 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 17.5, 18.7, 28.9, 33.1, 59.4, 76.4, 102.5, 148.0.

$C_8H_{16}O_2$ (144.2) Calcd. C 66.63 H 11.18 Found C 66.58 H 11.16

6-(Ethylthio)-2-methyl-5-hexen-3-ol: g.c. purification at 120°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93 (d, J = 6.8 Hz, 3H), 0.94 (d, J = 6.8 Hz, 3H), 1.28 (t, J = 7.4 Hz, 3H), 1.51 (d, J = 4.7 Hz, 1H), 1.64 – 1.71 (m, 1H), 2.23 – 2.34 (m, 2H), 2.68 (q, J = 7.4 Hz, 2H), 3.42 – 3.45 (m, 1H), 5.64 (dt, J = 9.4 and 7.3 Hz, 1H), 6.08 (d, J = 9.5 Hz, 1H). – ^{13}C NMR ($CDCl_3$): *Z*: δ = 15.3, 17.2, 18.6, 27.6, 33.1, 34.0, 75.9, 125.5, 127.0. – *E*: δ = 14.4, 26.3, 32.8, 38.0, 75.5, 125.7, 125.9, the remaining signals are obscured.

$C_9H_{18}OS$ (174.3) Calcd. C 62.02 H 10.41 S 18.40 Found C 62.03 H 10.30 S 18.01

6-(1,1-Dimethylethylthio)-2-methyl-5-hexen-3-ol: g.c. purification at 125°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (d, J = 6.8 Hz, 3H), 0.93 (d, J = 6.8 Hz, 3H), 1.34 (s, 9H), 1.58 (s, 1H), 1.62 – 1.72 (m, 1H), 2.16 – 2.38 (m, 2H), 3.40 – 3.45 (m, 1H), 5.72 (dt, J = 9.7 and 7.3 Hz, 1H), 6.26 (dt, J = 9.7 and 1.3 Hz, 1H). – ^{13}C NMR ($CDCl_3$): *Z*: δ = 17.3, 18.7, 30.8, 33.1, 34.0, 43.4, 76.0, 123.4, 127.1. *E*: δ = 17.2, 30.6, 32.8, 38.2, 43.4, 75.4, 123.0, 132.5. One signal is obscured.

$C_{11}H_{22}OS$ (202.4) Calcd. C 65.29 H 10.96 S 15.84 Found C 65.15 H 10.87 S 14.73

2-Methyl-5,7-octadien-3-ol: g.c. purification at 85°C. – *Z*: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93–0.97 (6H), 1.52 (s, 1H), 1.64–1.76 (m, 1H), 2.34–2.38 (m, 2H), 3.38–3.45 (m, 1H), 5.15 (d, *J* = 10 Hz, 1H), 5.24 (d, *J* = 16.7 Hz, 1H), 5.51–5.56 (m, 1H), 6.12–6.20 (m, 1H), 6.65 (dt, *J* = 16.9 and 10.6 Hz, 1H).

E: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93–0.97 (6H), 1.52 (s, 1H), 1.64–1.76 (m, 1H), 2.13–2.38 (m, 2H), 3.38–3.45 (m, 1H), 5.02 (d, *J* = 10.3 Hz, 1H), 5.14 (d, *J* = 17 Hz, 1H), 5.69–5.77 (m, 1H), 6.12–6.20 (m, 1H), 6.34 (dt, *J* = 16.9 and 10.1 Hz, 1H).

$C_9H_{16}O$ (140.2) Calcd. C 77.09 H 11.50 Found C 77.15 H 11.31

Chain Extensions

(Z)-1-Phenyl-3-hexen-1-ol (**17**): To a solution of 10 mg (18 μmol) of Ni(dppp)Cl_2[39] and 0.36 g (1.6 mmol) of (*Z*)-4-bromo-1-phenyl-3-buten-1-ol in 3 ml of dry ether was added at 0°C 1.3 ml (4.2 mmol) of a 3.2 M solution of ethylmagnesium bromide in ether. After refluxing for 3 h hydrolysis was effected at 0°C by addition of 1.3 ml of 3 M HCl. After phase separation the aqueous phase was extracted two times with 5 ml each of ether. The combined organic phases were washed with 5 ml each of saturated aqueous $NaHCO_3$ and aqueous NaCl solution. After drying over Na_2SO_4 the solution was concentrated and the residue was filtered over 30 g of silica gel with CH_2Cl_2 to give 0.24 g (86%) of **17** as colourless liquid. A small sample was purified by preparative g.c. at 130°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.5 Hz, 3H), 1.99–2.10 (m, 3H), 2.43–2.59 (m, 2H), 4.68–4.71 (m, 1H), 5.32–5.39 (m, 1H), 5.52–5.59 (m, 1H), 7.26–7.39 (m, 5H). – ^{13}C NMR ($CDCl_3$): δ = 14.0, 20.5, 36.9, 73.7, 124.0, 125.8, 127.2, 128.1, 134.8, 144.0.

$C_{12}H_{16}O$ (176.3) Calcd. C 81.77 H 9.15 Found C 81.93 H 9.25

3-(Benzyloxy)-1-pentene (**18**): 0.60 g (20 mmol) of sodium hydride was washed free of oil by petroleum ether (40–60°C). To its suspension in 5 ml of dry THF was added dropwise a solution of 1.92 g (22.3 mmol) of 1-pentene-3-ol[40] in 5 ml of THF. After stirring for 1 h the mixture was refluxed for 2 h with 3.33 g (19.5 mmol) of benzyl bromide. Hydrolysis was effected under cooling by careful addition of 20 ml of water and 10 ml of saturated NH_4Cl solution. After extracting three times with 20 ml each of petroleum ether (40–60°C) the extracts were washed with 30 ml of saturated aqueous NaCl solution and dried over Na_2SO_4. After concentration the residue gave on distillation 2.70 g (69%) of **18** of b.p. 47–48°C/0.5 Torr. A small sample was purified by g.c. at 100°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.4 Hz, 3H), 1.50–1.71 (m, 2H), 3.62–3.67 (m, 1H), 4.38 and 4.60 (AB, *J* = 11.9 Hz, 2H), 5.18–5.25 (m, 2H), 5.73 (ddd, *J* = 17.1, 10.4, and 7.8 Hz, 1H), 7.25–7.38 (m, 5H). – ^{13}C NMR ($CDCl_3$): δ = 9.7, 28.3, 70.0, 82.0, 117.1, 127.3, 127.7, 128.3, 138.9, 139.0.

$C_{12}H_{16}O$ (176.3) Calcd. C 81.77 H 9.15 Found C 81.53 H 9.18

(E)-1-Phenyl-3-hexen-1-ol (**19**): 1.23 g (10.6 mmol) of tetramethylethylenediamine, 10 ml of dry petroleum ether (40–60°C), and 6.2 ml (9.9 mmol) of a 1.6 M solution of *n*-butyllithium in *n*-hexane were combined at 0°C. After 1 h at room temp. the mixture was cooled to –78°C. After addition of a solution of 1.77 g (10.0 mmol) of **18** the mixture was kept 5 h at –78°C and was allowed to reach room temperature. The mixture was poured on 30 ml of water, neutralized by addition of 10 ml of 3 N HCl, and extracted three times with 30 ml each of petroleum ether (40–60°C). The organic extracts were washed with few ml of saturated aqueous $NaHCO_3$ solution and 20 ml of saturated NaCl solution. After drying over Na_2SO_4 the solvents were removed and the residue was filtered over 190 g of silica gel with CH_2Cl_2 to give 1.32 g (75%) of **19** as colourless oil. A small sample was purified by g.c., 130°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.97 (t, *J* = 7.5 Hz, 3H), 2.00–2.07 (m, 2H), 2.07 (d, *J* = 3.1 Hz, 1H), 2.35–2.48 (m, 2H), 4.65–4.69 (m, 1H), 5.36–5.44 (m, 1H), 5.58–5.66 (m, 1H), 7.21–7.37 (m, 5H). –

^{13}C NMR ($CDCl_3$): δ = 13.5, 25.4, 42.4, 73.5, 124.4, 125.7, 127.0, 128.0, 135.7, 144.0. The *Z*/*E*-ratio was determined from the ^{13}C NMR spectrum to 4:96.

$C_{12}H_{16}O$ (176.3) Calcd. C 81.77 H 9.15 Found C 81.57 H 9.01

5,6-Dihydro-6-(1-methylethyl)-2H-pyran-2-one (**21a**): To a solution of 0.55 g (2.8 mmol) of (*Z*)-6-bromo-2-methyl-5-hexen-3-ol (**20a**) in 50 ml of dry benzene 0.65 g (6.4 mmol) of triethylamine and 2.1 ml (16 mmol) of tetracarbonylnickel were added under argon. After heating 2 h to 60 °C the solvent and excess tetracarbonylnickel were condensed into a cold trap. The remaining crude product was taken up in few ml of benzene and the solution was shaken twice with 200 ml each of 1 M HCl until the black precipitate was dissolved. The aqueous phase was extracted four times with 40 ml each of ether. The combined organic extracts were washed with 10 ml of saturated aqueous $NaHCO_3$ solution and three times with 10 ml each of saturated aqueous NaCl solution. After drying over Na_2SO_4 the solvents were removed and the residue bulb to bulb distilled at 0.1 Torr to give 0.36 g (90%) of **21a** as colourless oil. A small sample was purified by g.c. at 120 °C. – ^1H NMR (400 MHz, $CDCl_3$): δ = 0.98 (d, *J* = 6.9 Hz, 3H), 1.02 (d, *J* = 6.8 Hz, 3H), 1.91 – 1.99 (m, 1H), 2.29 – 2.34 (m, 2H), 4.13 – 4.19 (m, 1H), 6.00 (ddd, *J* = 9.7, 2.5, and 1.3 Hz, 1H), 6.87 – 6.91 (m, 1H). – ^{13}C NMR ($CDCl_3$): δ = 17.3, 17.4, 26.0, 31.5, 82.2, 120.6, 145.3, 164.4.

$C_8H_{12}O_2$ (140.2) Calcd. C 68.55 H 8.63 Found C 68.73 H 8.76

5,6-Dihydro-6-pentyl-2H-pyran-2-one (**21b**): 0.68 g (3.1 mmol) of (*Z*)-1-bromo-1-nonen-4-ol were reacted as above to give 0.42 g (81%) of **21b** as light tan liquid. A small sample was purified by g.c. at 145 °C. – ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.0 Hz, 3H), 1.22 – 1.83 (m, 8H), 2.25 – 2.38 (m, 2H), 4.37 – 4.44 (m, 1H), 6.00 (ddd, *J* = 9.7, 2.2, and 1.4 Hz, 1H), 6.84 – 6.89 (m, 1H). – ^{13}C NMR ($CDCl_3$): δ = 13.7, 22.2, 24.2, 29.1, 31.3, 34.6, 77.8, 121.0, 145.1, 164.4, cf. Lit.[41]).

$C_{10}H_{16}O_2$ (168.2) Calcd. C 71.39 H 9.59 Found C 71.37 H 9.58

5,6-Dihydro-6-[(Z)-2-pentenyl]-2H-pyran-2-one (**21c**): 0.67 g (3.1 mmol) of (1*Z*,6*Z*)-1-bromo-1,6-nonadien-4-ol were reacted as described above to give 0.34 g of a colourless oil. The ^{13}C NMR spectrum of the crude product revealed a major (77%) and two minor components. The main product was separated by preparative g.c. at 160 °C. – ^1H NMR (400 MHz, $CDCl_3$): δ = 0.96 (t, *J* = 7.5 Hz, 3H), 2.01 – 2.08 (m, 2H), 2.30 – 2.37 (m, 2H), 2.37 – 2.57 (m, 2H), 4.40 – 4.47 (m, 1H), 5.32 – 5.39 (m, 1H), 5.52 – 5.59 (m, 1H), 6.01 (ddd, *J* = 9.7, 2.3, and 1.4 Hz, 1H), 6.84 – 6.88 (m, 1H), cf. Lit.[42]). – ^{13}C NMR ($CDCl_3$): δ = 13.5, 20.1, 28.1, 31.8, 77.0, 120.5, 121.6, 134.7, 144.8, 163.7.

$C_{10}H_{14}O_2$ (166.2) Calcd. C 72.26 H 8.49 Found C 72.36 H 8.73

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