A Highly Diastereoselective $TiCl_4$-Mediated Reduction of β-Hydroxy Ketones with BH_3·py — A Very Efficient and General Synthesis of *syn*-1,3-Diols

Giuseppe Bartoli,*[a] Marcella Bosco,[a] Enrico Marcantoni,[b] Massimo Massaccesi,[a] Samuele Rinaldi,[a] and Letizia Sambri[a]

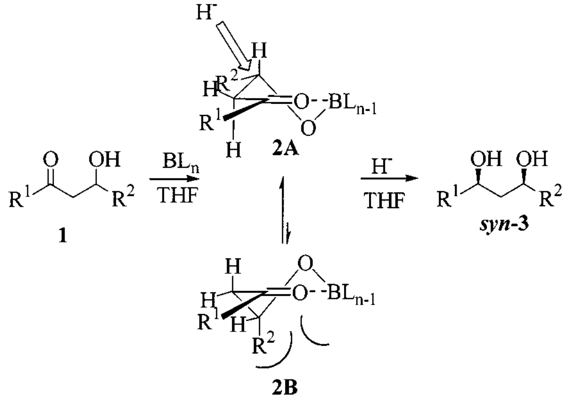
Keywords: Alcohols / Titanium / Reduction / Diastereoselectivity / Chemoselectivity

β-Hydroxy ketones can be reduced to the corresponding 1,3-diols in high yields and with excellent diastereoselectivity by carrying out the reaction with BH_3·pyridine in CH_2Cl_2 at −78 °C in the presence of $TiCl_4$. This protocol is general and chemoselective: excellent results are obtained when the substituents are primary, secondary, tertiary alkyl chains or aromatic moieties. The presence of reducible functionalities such as bromide, nitro and cyano groups is well tolerated.

Introduction

The reduction of β-hydroxy ketones in a predictable and stereoselective manner continues to be of considerable interest in organic synthesis as a straightforward approach to the construction of 1,3-diol units with stereodefined geometry.

From extensive studies carried out on systems with a stereogenic centre in the β-position,[1] it emerged that *syn* selectivity becomes prevalent when a chelate complex such as **2** (Scheme 1) is preformed from the interactions of the bidentate hydroxy ketone with an appropriate Lewis acid, followed by treatment with an external hydride source. The crucial point of this approach is the structural conformation of the chelate complex **2** in its stable form (see Scheme 1). In fact, in order to achieve a high selectivity, it is necessary that **2** assumes a half-chair conformation (like **2A**) with the R^2 substituent in a pseudo-equatorial position, so as to force the hydride ion to enter from the top of conformation **A** due to the steric hindrance exerted by the axial hydrogen in the α-position.



Scheme 1. Diastereoselective reduction of β-hydroxy ketones **1** via boron-bound intermediates

Generally, the most efficient methodologies require the use of Lewis acids carrying very encumbered substituents, in order to increase the steric interactions between the R^2 substituent and the metal ligands in conformation **2B**. In this context, methoxydiethyl borane,[2] catechol borane,[3] and terphenyl boronic acid[4] have been proved to be very efficient. Furthermore, it is necessary to firmly anchor the boron-centred Lewis acid to the hydroxy group through the formation of a covalent boron−oxygen bond. The use of a solvent of medium polarity, such as THF, is generally required.

However, simpler approaches are in principle possible. Recent studies on the reduction of β-ketophosphane oxides[5] and related systems[6,7] demonstrated that a six-membered chelate complex can assume a very rigid and conformationally stable half-chair structure when formed and allowed to react in noncoordinating solvents such as CH_2Cl_2 or toluene.

Given the importance of the target at issue, it seemed very useful to investigate the possibility of applying this concept to the reduction of β-hydroxy ketones in order to set up an operatively simple methodology.

Following these suggestions, we now report a very efficient and convenient protocol for the *syn*-reduction of β-hydroxy ketones like **1**, which has been proved to be general, chemoselective and highly diastereoselective.

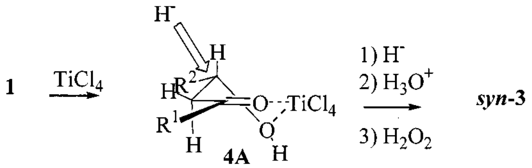
Results and Discussion

The methodology was based on the treatment at low temperature of a β-hydroxy ketone **1** with $TiCl_4$ in CH_2Cl_2 as the solvent, followed by the addition of BH_3·pyridine, (Scheme 2). After the reaction was complete, the usual acidic workup gave crude cyclic borates, which were decomposed to the desired *syn*-diol by treatment with H_2O_2 in a basic medium.

---

[a] Dipartimento di Chimica Organica “A. Mangini”,
V.le Risorgimento 4, 40136 Bologna, Italy
Fax: (internat.) + 39-051/209-3654
E-mail: bartoli@ms.fci.unibo.it
[b] Dipartimento Scienze Chimiche, Università di Camerino,
Via S.Agostino 1, 62032 Camerino, (Macerata), Italy

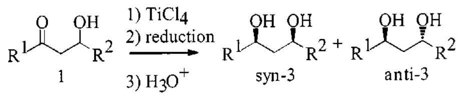
1434−193X/01/1224−4679 $ 17.50+.50/0



Scheme 2. Diastereoselective reduction of β-hydroxy ketones **1** via titanium-bound intermediate

The method shows general applicability. High yields and high *syn*-selectivity have always been observed independently of the nature of the R^1 and R^2 groups. In fact, the reaction works well when R^1 and R^2 are primary, secondary and tertiary carbon chains, or aromatic moieties, as shown in Table 1.

Table 1. $TiCl_4$-mediated reduction of β-hydroxy ketones **1a**−**o** with borane complexes



	Starting material	R^1	R^2	Reducing agent	Product	Yield (%)	***syn*-3/*anti*-3**
1	**1a**	Ph	Et	BH_3·py	**3a**	80	>99:1
2	**1b**	Ph	Ph	BH_3·py	**3b**	98	97:3
3	**1c**	*p*-CN-Ph	C_5H_{11}	BH_3·py	**3c**	77	98:2
4	**1d**	Et	Ph	BH_3·py	**3a**	92	91:9
5	**1d**	Et	Ph	BH_3·Me_2S	**3a**	93	91:9
6	**1e**	Et	*p*-Br-Ph	BH_3·py	**3e**	88	88:12
7	**1e**	Et	*p*-Br-Ph	BH_3·Me_2S	**3e**	86	80:20
8	**1f**	Et	*p*-NO_2-Ph	BH_3·py	**3f**	80	80:20
9	**1f**	Et	*p*-NO_2-Ph	BH_3·Me_2S	**3f**	85	77:23
10	**1g**	C_4H_9	*p*-MeO-Ph	BH_3·py	**3g**	87	95:5
11	**1g**	C_4H_9	*p*-MeO-Ph	BH_3·Me_2S	**3g**	85	72:28
12	**1h**	Et	*t*Bu	BH_3·py	**3h**	92	98:2
13	**1i**	C_4H_9	C_5H_{11}	BH_3·py	**3i**	92	99:1
14	**1l**	C_4H_9	*i*Pr	BH_3·py	**3l**	92	95:5
15	**1m**	*i*Pr	*i*Pr	BH_3·py	**3m**	90	99:1
16	**1n**	*i*Pr	C_5H_{11}	BH_3·py	**3n**	89	>99:1
17	**1o**	*t*Bu	*t*Bu	BH_3·py	**3o**	90	>99:1

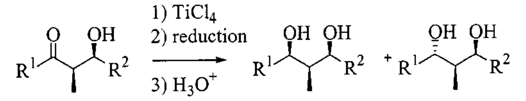
However, a decrease in selectivity is observed when the R^2 framework is a *p*-nitro-substituted phenyl group (*syn*/*anti* = 80:20, Table 1, entry 8). The presence of a strongly electron-withdrawing substituent probably causes a decrease in the electron density on the oxygen atom of the hydroxy group, weakening the interaction between the oxygen and Ti^{IV}; the cyclic complex **4A** becomes less rigid with a consequent decrease in the stereofacial discrimination. This interpretation is in good agreement with the substituent effect on the phenyl group: the *syn*-selectivity decreases in the order *p*-OMe (*syn*/*anti* = 95:5, entry 10), H (*syn*/*anti* = 91:9, entry 4), *p*-Br (*syn*/*anti* = 88:12, entry 6), *p*-NO_2 (*syn*/*anti* = 80:20, entry 8).

Some runs were carried out using BH_3·Me_2S as the reducing agent. However, the observed selectivities are generally slightly lower with respect to those with BH_3·py.

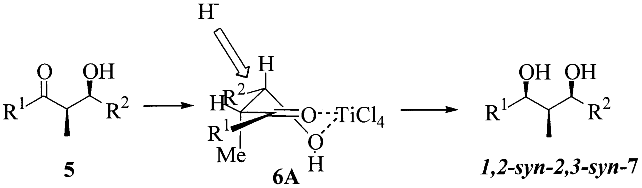
The present method shows good chemoselectivity; owing to the specific and mild conditions employed, easily reducible functionalities such as nitro, cyano and aromatic bromide groups remain unaffected.

The method was also applied to substrates with two stereogenic centres in the α- and β-positions. When the α- and β-substituents are in a *syn* relationship (**5a** and **5b**) the reduction is highly diastereoselective (Table 2). This is not surprising because in these cases the effects of the substituents are complementary in stabilising the **6A** structure due to the presence of an additional $A^{1,2}$ strain when the α-methyl group is equatorial,[7a] (Scheme 3). Therefore, since in these systems there are no apparent difficulties in *syn*-selectivity control, we limited our investigations to only two examples (see Table 2). Efficient and simple methodologies for the reduction of this kind of system have recently been reported in the literature.[7a]

Table 2. $TiCl_4$-mediated reduction of β-hydroxy ketones **5a**−**b** with borane complexes



	Starting material	R^1	R^2	Reducing agent	Product	Yield (%)	**1,2-*syn*-2,3-*syn*-7/ 1,2-*anti*-2,3-*syn*-7**
1	**5a**	Ph	Ph	BH_3·Me_2S	**7a**	92	>99:1
2	**5b**	Ph	Et	BH_3·Me_2S	**7b**	89	98:2



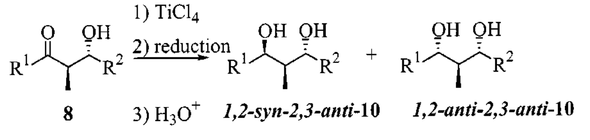
Scheme 3. Diastereoselective reduction of *syn*-α,β-disubstituted-β-hydroxy ketones **5** via a titanium-bound intermediate

When the α- and β-substituents are in an *anti*-relationship (**8a** and **8b**), however, the reaction is not stereoselective (Table 3). In these cases the effects of the substituents are opposite: while the R^2 group destabilises the **9B** conformation, the α-methyl group destabilises the **9A** conformation (Scheme 4). As a consequence the structure of the chelate complex can be depicted by an equilibrium between the almost equally populated **9A** and **9B** arrays. Thus, the low selectivity observed is not unexpected since it has been proved that the selectivity of attack of the borane complexes approximately reflects the conformational equilibrium of chelate complexes.[7a]

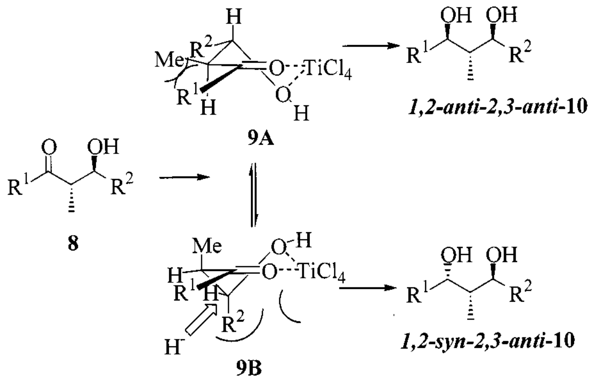
As far as the structure of the chelate complex is concerned, two hypotheses can be made: i) the interaction between the β-hydroxy ketone and $TiCl_4$ gives rise to the formation of a Ti-alcoholate with loss of HCl; ii) the loss of HCl does not occur and structures **4**, **6** and **9** are probable.

In systems with a stereocentre in the α-position this aspect has been investigated by Di Mare,[8] who reported convincing evidence supporting the second hypothesis. There-

Table 3. $TiCl_4$ mediated reduction of β-hydroxy ketones **8a−b** with borane complexes



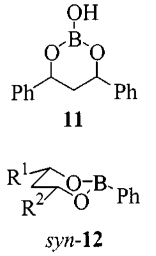
	Starting material	R^1	R^2	Reducing agent	Product	Yield (%)	*syn,anti*-**10**/*anti,anti*-**10**
1	**8a**	Ph	Ph	BH_3·py	**10a**	90	24:76
2	**8a**	Ph	Ph	BH_3·Me_2S	**10a**	90	52:48
3	**8b**	Et	Et	BH_3·py	**10b**	88	13:87



Scheme 4. Diastereoselective reduction of *anti*-α,β-disubstituted-β-hydroxy ketones **8** via a titanium-bound intermediate

fore we assumed that structures **4**, **6** and **9** are representative of the actual nature of the chelate complexes.

As previously mentioned, the reaction gives 1,3-diols as borate derivatives after a simple acidic quenching. In fact, we were able to isolate compound **11** (Figure 1) after the reduction of **1b** in >95% purity.[9]



12a: R^1 = Ph, R^2 = Et

12c: R^1 = p-NCC_6H_4, R^2 = C_5H_{11}

12e: R^1 = Et, R^2 = p-BrC_6H_4

12f: R^1 = Et, R^2 = p-$O_2NC_6H_4$

12g: R^1 = C_4H_9, R^2 = p-$MeOC_6H_4$

12h: R^1 = Et, R^2 = *t*Bu

12i: R^1 = C_4H_9, R^2 = C_5H_{11}

12n: R^1 = *i*Pr, R^2 = C_5H_{11}

Figure 1. Cyclic borate **11** and boronate derivatives *syn*-**12** for structural assignment of 1,3-diols **3**

These results confirm the stability of the cyclic borate intermediates to prolonged acidic treatment, and thus an oxidative decomposition with H_2O_2 in basic medium was required to obtain the corresponding 1,3-diol **3b**.[6c,7a,10]

Finally, particular attention was devoted to the reaction of **1m** with BH_3·py. It has been suggested previously[8] that the use of BCl_3 instead of $TiCl_4$ as the Lewis acid promoter is more productive for the reduction of β-hydroxy ketones with borane complexes in CH_2Cl_2, as the $TiCl_4$-mediated reduction has been found not to be stereoselective. We repeated this reaction several times according to our methodology and we found excellent yields and high diastereoselectivity in all cases (see Table 1, entry 15). At present there are no reasonable explanations for this discrepancy; however, our methodology differs from the previously reported one in the decomposition step of the borate intermediates.

Finally, for structure assignment, the unknown 1,3-diols were converted into the corresponding phenyl boronates **12** (Figure 1),[11] since the spectroscopic analysis of these derivatives is more straightforward than that of the parent diols owing to their well defined cyclic structure.

Conclusion

In conclusion, a simple, general and highly diastereoselective procedure for the reduction of β-hydroxy ketones, with a stereogenic centre in the β-position, to the corresponding *syn*-1,3-diols is now available. From the obtained results the present methodology seems to be competitive with, and in some cases superior to, more sophisticated methods available in the literature.

Moreover, the present work confirms that reductions proceeding via a chelate complex intermediate are more fruitful if the reaction is carried out in noncoordinating solvents with powerful coordinating agents such as $TiCl_4$. From literature reports, the use of $TiCl_4$ should not be considered the most appropriate choice since this reagent does not carry bulky ligands, and thus it is not able to exert a high steric repulsion towards the β-substituent in the chelate complex intermediate; however, the experimental results demonstrated that the $A^{1,3}$ strain between the chlorine ligand and the alkyl substituent is generally sufficient to completely shift the equilibrium towards conformation **4A**. This is the only strain present in the system. Moreover, the 1,3-interaction cannot be considered negligible because in the reduction of *anti*-β-hydroxy ketones **8** it competes with the 1,2-interaction between R^1 and the α-methyl substituent.

Experimental Section

General Remarks: Flash chromatography was performed on Merck silica gel (0.040−0.063 nm). All reactions were carried out in oven dried glassware under a dry argon atmosphere. ^1H NMR, NOE and decoupling experiments were recorded at 300 MHz with a Varian Gemini instrument. ^{13}C NMR and DEPT experiments were acquired at 75 MHz with a Varian Gemini instrument. The relative proportions between the two diastereoisomers were measured by integration of the ^1H peaks and of some ^{13}C peaks using appropriate long delay times. Chemical shifts are given in ppm from $SiMe_4$. Coupling constants are given in Hertz.

Typical Experimental Procedure: The starting β-hydroxy ketone (1 equiv.), dissolved in CH_2Cl_2, was treated with 1.2 equiv. of $TiCl_4$

(1 M solution in CH_2Cl_2) at −78 °C. After 10 min an excess of BH_3·py or BH_3·Me_2S (3−4 equiv.) was added at −78 °C. After 2 h the reaction was quenched with aqueous HCl (1 M). The mixture was extracted with CH_2Cl_2 and concentrated at reduced pressure to give a mixture of cyclic boron derivatives. In order to obtain pure 1,3-diols the mixture was treated with basic H_2O_2 (NaOH, 10%) in Et_2O/MeOH (1:1) for 48 h, extracted with CH_2Cl_2 and dried over $MgSO_4$. The solvent was removed under reduced pressure and the pure 1,3-diols isolated by column chromatography (petroleum ether/Et_2O,7:3).

β-Hydroxy ketones **1a−o, 5a−b, 8a−b** were synthesised by a standard procedure.[12] The spectroscopic data of the known compounds **1a**,[1f] **1b**,[1f] **1l**,[1e] **1m**,[13] **5a**,[14] **5b**,[15] **8a**,[16] **8b**,[17] **3b**,[18] **3l**,[1e] **3m**,[19] **3o**,[19] **1,2-*syn*-** and **2,3-*syn*-7a**,[7a] **1,2-*syn*-** and **2,3-*syn*-7b**,[7a] **1,2-*syn*-** and **2,3-*anti*-10a**,[7a] **1,2-*anti*-** and **2,3-*anti*-10a**,[7a] **1,2-*syn*-2** and ***3-anti*-10b**,[7a] and **1,2-*anti*-2** and ***3-anti*-10b**[7a] were identical to those reported in the literature.

The spectroscopic data of unknown compounds follow:

4-(3-Hydroxyoctanoyl)benzonitrile (1c): ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.91 (t, $J_{H,H}$ = 7.0, 3 H, CH_3), 1.25−1.70 (m, 8 H, 4 × CH_2), 3.0 (br. s, 1 H, OH), 3.10−3.15 (m, 2 H, CH_2), 4.20−4.30 (m, 1 H, CH), 7.75−7.80 (m, 2 H, Ph), 8.00−8.10 (m, 2 H, Ph). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 13.8 (CH_3), 22.4 (CH_2), 25.0 (CH_2), 31.5 (CH_2), 36.4 (CH_2), 45.4 (CH_2), 67.5 (CH), 117.6 (C), 128.4 (CH), 132.3 (CH), 139.6 (C), 151.3 (C), 199.2 (C). $C_{15}H_{19}NO_2$ (245.3): calcd. C 73.44, H 7.81; found C 73.43, H 7.82.

1-Hydroxy-1-phenyl-3-pentanone (1d): ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.06 (t, $J_{H,H}$ = 7.4, 3 H, CH_3), 2.45 (q, $J_{H,H}$ = 7.4, 2 H, CH_2), 2.70−2.90 (m, 2 H, CH_2), 3.3 (br. s, 1 H, OH), 5.10−5.20 (m, 1 H, CH), 7.25−7.40 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 7.3 (CH_3), 36.7 (CH_2), 50.6 (CH_2), 69.8 (CH), 125.5 (CH), 127.4 (CH), 128.3 (CH), 142.9 (C), 211.5 (C). $C_{11}H_{14}O_2$ (178.2): calcd. C 74.13, H 7.92; found C 74.15, H 7.92.

1-(4-Bromophenyl)-1-hydroxy-3-pentanone (1e): ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.97 (t, $J_{H,H}$ = 7.3, 3 H, CH_3), 2.36 (q, $J_{H,H}$ = 7.3, 2 H, CH_2), 2.65−2.85 (m, 2 H, CH_2), 3.6 (br. d, $J_{H,H}$ = 3.1, 1 H, OH), 4.90−5.10 (m, 1 H, CH), 7.05−7.20 (m, 2 H, Ph), 7.30−7.45 (m, 2 H, Ph). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 7.3 (CH_3), 36.7 (CH_2), 50.4 (CH_2), 69.2 (CH), 121.2 (C), 127.3 (CH), 131.4 (CH), 141.9 (C), 211.5 (C). $C_{11}H_{13}BrO_2$ (257.1): calcd. C 51.56, H 5.12; found C 51.55, H 5.13.

1-Hydroxy-1-(4-nitrophenyl)-3-pentanone (1f): ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.08 (t, $J_{H,H}$ = 7.3, 3 H, CH_3), 2.48 (q, $J_{H,H}$ = 7.3, 2 H, CH_2), 2.75−2.85 (m, 2 H, CH_2), 3.6 (br. s, 1 H, OH), 5.20−5.30 (m, 1 H, CH), 7.50−7.60 (m, 2 H, Ph), 8.15−8.25 (m, 2 H, Ph). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 7.2 (CH_3), 36.6 (CH_2), 50.1 (CH_2), 68.8 (CH), 123.4 (CH), 126.3 (CH), 146.9(C), 150.3 (C), 211.1 (C). $C_{11}H_{13}NO_4$ (223.2): calcd. C 59.17, H 5.87; found C 59.18, H 5.86.

1-Hydroxy-1-(4-methoxyphenyl)-3-heptanone (1g): ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.89 (t, $J_{H,H}$ = 7.5, 3 H, CH_3), 1.25−1.35 (m, 2 H, CH_2), 1.45−1.60 (m, 2 H, CH_2), 2.35−2.45 (m, 2 H, CH_2), 2.73 (dd, $J_{H,H}$ = 3.6, $J_{H,H}$ = 17.1, 1 H, CH_2), 2.84 (dd, $J_{H,H}$ = 8.9, $J_{H,H}$ = 17.1, 1 H, CH_2), 3.4 (br. s, 1 H, OH), 3.78 (s, 3 H, CH_3), 5.00−5.10 (m, $J_{H,H}$ = 8.9, $J_{H,H}$ = 3.6, 1 H, CH), 6.80−6.90 (m, 2 H, Ph), 7.20−7.30 (m, 2 H, Ph). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 13.7 (CH_3), 22.1 (CH_2), 25.5 (CH_2), 43.3 (CH_2), 50.9 (CH_2), 55.1 (CH_3), 69.5 (CH), 113.7 (CH), 126.8 (CH), 135.0 (C), 158.9 (C), 211.5 (C). $C_{14}H_{20}O_3$ (236.3): calcd. C 71.16, H 8.53; found C 71.14, H 8.53.

5-Hydroxy-6,6-dimethyl-3-heptanone (1h): ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.86 (s, 9 H, 3 × CH_3), 1.02 (t, $J_{H,H}$ = 7.3, 3 H, CH_3), 2.35−2.60 (m, 4 H, 2 × CH_2), 3.0 (d, $J_{H,H}$ = 3.1, 1 H, OH), 3.71 (dt, $J_{H,H}$ = 9.9, $J_{H,H}$ = 3.1, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 7.5 (CH_3), 25.6 (CH_3), 34.1 (C), 36.8 (CH_2), 43.7 (CH_2), 74.9 (CH), 213.1 (C). $C_9H_{18}O_2$ (158.2): calcd. C 68.31, H 11.47; found C 68.31, H 11.46.

7-Hydroxy-5-dodecanone (1i): ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.85−1.00 (m, 6 H, 2 × CH_3), 1.25−1.70 (m, 12 H, 6 × CH_2), 2.40−2.65 (m, 4 H, 2 × CH_2), 3.1 (br. s, 1 H, OH), 4.00−4.10 (m, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 13.8 (CH_3), 14.0 (CH_3), 22.2 (CH_2), 22.5 (CH_2), 25.1 (CH_2), 25.6 (CH_2), 31.7 (CH_2), 36.4 (CH_2), 43.3 (CH_2), 48.9 (CH_2), 67.6 (CH), 212.5 (C). $C_{12}H_{24}O_2$ (200.3): calcd. C 71.95, H 12.08; found C 71.97, H 12.07.

5-Hydroxy-2-methyl-3-decanone (1n): ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.97 (t, $J_{H,H}$ = 7.3, 3 H, CH_3), 1.12 (d, $J_{H,H}$ = 7.4, 6 H, 2 × CH_3), 1.25−1.55 (m, 8 H, 4 × CH_2), 2.45−2.70 (m, 3 H, CH and CH_2), 3.1 (br. s, 1 H, OH), 3.95−4.05 (m, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.0 (CH_3), 17.9 (CH_3), 22.6 (CH_2), 25.1 (CH_2), 31.7 (CH_2), 36.4 (CH_2), 41.4 (CH), 46.6 (CH_2), 67.6 (CH), 216.0 (C). $C_{11}H_{22}O_2$ (186.3): calcd. C 70.92, H 11.90; found C 70.94, H 11.90.

5-Hydroxy-2,2,6,6-tetramethyl-3-heptanone (1o): ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.89 (s, 9 H, 3 × CH_3), 1.12 (s, 9 H, 3 × CH_3), 2.40 (dd, $J_{H,H}$ = 10.2, $J_{H,H}$ = 17.3, 1 H, CH_2), 2.70 (dd, $J_{H,H}$ = 1.7, $J_{H,H}$ = 17.3, 1 H, CH_2), 3.2 (br. s, 1 H, OH), 3.63 (dd, $J_{H,H}$ = 1.7, $J_{H,H}$ = 10.2, 1 H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 25.7 (CH_3), 26.3 (CH_3), 34.2 (C), 37.9 (CH_2), 44.6 (C), 75.0 (CH), 218.2 (C). $C_{11}H_{22}O_2$ (186.3): calcd. C 70.92, H 11.90; found C 70.91, H 11.89.

(1*R,3*R**)-1-phenyl-1,3-pentanediol (3a):** Yield 144 mg (80%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.93 (t, $J_{H,H}$ = 7.5, 3 H, CH_3), 1.45−1.60 (m, 2 H, CH_2), 1.70−1.90 (m, 2 H, CH_2), 3.2 (br. s, 1 H, OH), 3.5 (br. s, 1 H, OH), 3.80−3.95 (m, 1 H, CH), 4.90−5.00 (m, 1 H, CH), 7.25−7.40 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 9.5 (CH_3), 30.7 (CH_2), 44.7 (CH_2), 74.0 (CH), 75.2 (CH), 125.6 (CH), 127.4 (CH), 128.4 (CH), 144.5 (C). $C_{11}H_{16}O_2$ (180.2): calcd. C 73.30, H 8.95; found C 73.31, H 8.94.

4-[(1*R,3*R**)-1,3-dihydroxyoctyl]benzonitrile (3c):** Yield 190 mg (77%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.88 (t, $J_{H,H}$ = 7.2, 3 H, CH_3), 1.20−1.60 (m, 9 H, 4 × CH_2 and 1 H CH_2), 1.70−1.80 (m, 1 H, CH_2), 2.5 (br. s, 2 H, OH), 3.95−4.05 (m, 1 H, CH), 4.95−5.05 (dd, $J_{H,H}$ = 7.4, $J_{H,H}$ = 5.8, 1 H, CH), 7.40−7.50 (m, 2 H, Ph), 7.55−7.65 (m, 2 H, Ph). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 13.8 (CH_3), 22.4 (CH_2), 24.7 (CH_2), 31.5 (CH_2), 37.9 (CH_2), 44.8 (CH_2), 73.0 (CH), 74.1 (CH), 110.6 (C), 118.7 (C), 126.2 (CH), 132.0 (CH), 149.7(C). $C_{15}H_{21}NO_2$ (247.3): calcd. C 72.84, H 8.56; found C 72.86, H 8.57.

(1*R,3*R**)-1-(4-bromophenyl)-1,3-pentanediol (3e):** Yield 228 mg (88%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.88 (t, $J_{H,H}$ = 7.4, 3 H, CH_3), 1.45−1.60 (m, 2 H, CH_2), 1.70−1.80 (m, 2 H, CH_2), 3.2 (br. s, 2 H, OH), 3.80−3.95 (m, 1 H, CH), 4.80−4.90 (m, 1 H, CH), 7.15−7.25 (m, 2 H, Ph), 7.40−7.50 (m, 2 H, Ph). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 9.4 (CH_3), 30.6 (CH_2), 44.4 (CH_2), 73.7 (CH), 74.3 (CH), 121.0 (C), 127.3 (CH), 131.3 (CH), 143.4 (C). $C_{11}H_{15}BrO_2$ (259.1): calcd. C 50.98, H 5.83; found C 51.00, H 5.84.

(1*R,3*R**)-1-(4-nitrophenyl)-1,3-pentanediol (3f):** Yield 180 mg (80%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.96 (t, $J_{H,H}$ = 7.5, 3 H, CH_3), 1.45−1.60 (m, 2 H, CH_2), 1.70−1.85 (m, 2 H, CH_2), 2.3 (br.

s, 1 H, OH), 3.90−4.05 (m, 1 H, CH), 4.1 (br. s, 1 H, OH), 5.05−5.15 (m, 1 H, CH), 7.50−7.65 (m, 2 H, Ph), 8.15−8.30 (m, 2 H, Ph). ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 9.4 (CH$_3$), 31.0 (CH$_2$), 44.6 (CH$_2$), 74.2 (CH), 74.3 (CH), 123.6 (CH), 126.4 (CH), 147.1 (C), 152.2 (C). $C_{11}H_{15}NO_4$ (225.2): calcd. C 58.66, H 6.71; found C 58.64, H 6.70.

(1*R,3*R**)-1-(4-methoxyphenyl)-1,3-heptanediol (3g):** Yield 207 mg (87%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 0.90 (t, $J_{H,H}$ = 7.2, 3 H, CH$_3$), 1.25−1.55 (m, 6 H, 3 × CH$_2$), 1.70−1.90 (m, 2 H, CH$_2$), 2.9 (br. s, 1 H, OH), 3.1 (br. s, 1 H, OH), 3.80 (s, 3 H, CH$_3$), 3.90−4.00 (m, 1 H, CH), 4.90 (dd, $J_{H,H}$ = 3.7, $J_{H,H}$ = 9.5, 1 H, CH), 6.85−6.95 (m, 2 H, Ph), 7.25−7.35 (m, 2 H, Ph). ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 14.0 (CH$_3$), 22.7 (CH$_2$), 27.5 (CH$_2$), 37.8 (CH$_2$), 45.2 (CH$_2$), 55.3 (CH$_3$), 72.7 (CH), 75.0 (CH), 113.8 (CH), 126.8 (CH), 136.8 (C), 159.0 (C). $C_{14}H_{22}O_3$ (238.3): calcd. C 70.56, H 9.30; found C 70.54, H 9.31.

(3*R,5*R**)-2,2-dimethyl-3,5-heptanediol (3h):** Yield 147 mg (92%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 0.91 (s, 9 H, 3 × CH$_3$), 0.95 (t, $J_{H,H}$ = 7.4, 3 H, CH$_3$), 1.25−1.70 (m, 4 H, 2 × CH$_2$), 2.8 (br. s, 2 H, OH), 3.50 (dd, $J_{H,H}$ = 10.6, $J_{H,H}$ = 1.8, 1 H, CH), 3.70−3.80 (m, 1 H, CH). ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 9.7 (CH$_3$), 25.5 (CH$_3$), 30.9 (CH$_2$), 34.8 (C), 36.4 (CH$_2$), 74.8 (CH), 81.2 (CH). $C_9H_{20}O_2$ (160.3): calcd. C 67.45, H 12.58; found C 67.46, H 12.59.

(5*R,7*S**)-5,7-dodecanediol (3i):** Yield 186 mg (92%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 0.85−1.00 (m, 6 H, 2 × CH$_3$), 1.25−1.70 (m, 16 H, 8 × CH$_2$), 3.2 (br. s, 2 H, OH), 3.75−3.90 (m, 2 H, CH). ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 14.0 (CH$_3$), 22.6 (CH$_2$), 22.7 (CH$_2$), 25.0 (CH$_2$), 27.5 (CH$_2$), 31.8 (CH$_2$), 37.9 (CH$_2$), 38.2 (CH$_2$), 42.8 (CH$_2$), 73.2 (CH). $C_{12}H_{26}O_2$ (202.3): calcd. C 71.23, H 12.95; found C 71.24, H 12.94.

(3*R,5*R**)-2-methyl-3,5-decanediol (3n):** Yield 168 mg (89%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 0.85−1.00 (m, 9 H, 3 × CH$_3$), 1.15−1.75 (m, 11 H, 5 × CH$_2$ and CH), 3.1 (br. s, 2 H, OH), 3.64 (ddd, $J_{H,H}$ = 2.2, $J_{H,H}$ = 5.1, $J_{H,H}$ = 10.0, 1 H, CH), 3.75−3.90 (m, 1 H, CH). ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 14.0 (CH$_3$), 17.4 (CH$_3$), 18.2 (CH$_3$), 22.6 (CH$_2$), 25.0 (CH$_2$), 31.8 (CH$_2$), 34.2 (CH), 38.2 (CH$_2$), 39.3 (CH$_2$), 73.3 (CH), 78.0 (CH). $C_{11}H_{24}O_2$: calcd. C 70.16, H 12.85; found C 70.18, H 12.84.

Cyclisation of 1,3-Diols into the Corresponding Phenylboronate Derivatives 12: The 1,3-diols were converted into the corresponding phenylboronates **12** according to a previously reported procedure.[10] In all cases almost quantitative yields were obtained (>98%).

When a detectable amount of the *anti*-isomer was present, a comparison of the (δ_CC-1 + δ_CC-3) values[11] of the *syn*- and *anti*-isomers (Hoffmann rules)[20] allowed an unequivocal assignment. In all other cases the structure was assigned by NOE NMR experiments.

Spectroscopic data and (δ_CC-1 + δ_CC-3) *syn* and (δ_CC-1 + δ_CC-3) *anti* values of boronates **12** follow:

(4*R,6*R**)-4-ethyl-2,6-diphenyl-1,3,2-dioxaborinane (12a):** ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 0.97 (t, $J_{H,H}$ = 7.3, 3 H, CH$_3$), 1.50−1.70 (m, 3 H, 1 × CH$_2$ and 1H CH$_2$), 2.12 (dt, $J_{H,H}$ = 2.8, $J_{H,H}$ = 14.0, 1 H, CH$_2$), 4.10−4.20 (m, 1 H, CH), 5.10 (dd, $J_{H,H}$ = 2.8, $J_{H,H}$ = 11.5, 1 H, CH), 7.15−7.40 (m, 8 H, Ph), 7.80−7.90 (m, 2 H, Ph). ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 9.4 (CH$_3$), 30.0 (CH$_2$), 41.4 (CH$_2$), 73.1 (CH), 73.4 (CH), 125.2 (CH), 127.4 (CH), 127.5 (CH), 128.4 (CH), 130.6 (CH), 133.9 (CH), 143.0 (C); (δ_CC-1 + δ_CC-3) *syn* = 146.5, (δ_CC-1 + δ_CC-3) *anti* = 140.1. $C_{17}H_{19}BO_2$ (266.1): calcd. C 76.72, H 7.20; found C 76.73, H 7.20.

4-[(4*R,6*R**)-6-pentyl-2-phenyl-1,3,2-dioxaborinan-4-yl]benzonitrile (12c):** ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 0.91 (t, $J_{H,H}$ = 7.2, 3 H, CH$_3$), 1.25−1.40 (m, 4 H, 2 × CH$_2$), 1.40−1.50 (m, 1 H, CH$_2$), 1.50−1.75 (m, 4 H, 2 × CH$_2$), 2.25 (dt, $J_{H,H}$ = 2.8, $J_{H,H}$ = 14.1, 1 H, CH$_2$), 4.20−4.35 (m, 1 H, CH), 5.23 (dd, $J_{H,H}$ = 2.8, $J_{H,H}$ = 11.5, 1 H, CH), 7.60−7.75 (m, 3 H, Ph), 7.75−7.85 (m, 2 H, Ph), 7.90−8.00 (m, 2 H, Ph), 8.15−8.25 (m, 2 H, Ph). ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 14.0 (CH$_3$), 22.6 (CH$_2$), 24.6 (CH$_2$), 31.7 (CH$_2$), 37.0 (CH$_2$), 41.4 (CH$_2$), 71.8 (CH), 72.8 (CH), 111.3 (C), 118.8 (C), 125.9 (CH), 127.6 (CH), 130.9 (CH), 132.4 (CH), 133.9 (CH), 148.2 (C); (δ_CC-1 + δ_CC-3) *syn* = 144.6, (δ_CC-1 + δ_CC-3) *anti* = 134.1. $C_{20}H_{24}BNO_2$ (321.2): calcd. C 74.78, H 7.53; found C 74.80, H 7.54.

(4*R,6*R**)-4-(4-bromophenyl)-6-ethyl-2-phenyl-1,3,2-dioxaborinane (12e):** ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 1.07 (t, $J_{H,H}$ = 7.5, 3 H, CH$_3$), 1.45−1.80 (m, 3 H, CH$_2$ and 1 H CH$_2$), 2.21 (dt, $J_{H,H}$ = 2.7, $J_{H,H}$ = 13.9, 1 H, CH$_2$), 4.15−4.25 (m, 1 H, CH), 5.17 (dd, $J_{H,H}$ = 2.0, $J_{H,H}$ = 7.8, 1 H, CH), 7.15−7.60 (m, 7 H, Ph), 7.80−7.95 (m, 2 H, Ph). ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 9.3 (CH$_3$), 30.0 (CH$_2$), 41.1 (CH$_2$), 72.8 (CH), 72.9 (CH), 121.2 (C), 126.9 (CH), 127.5 (CH), 130.7 (CH), 131.5 (CH), 133.9 (CH), 141.9 (C); (δ_CC-1 + δ_CC-3) *syn* = 145.7, (δ_CC-1 + δ_CC-3) *anti* = 139.4. $C_{17}H_{18}BBrO_2$ (345.0): calcd. C 59.18, H 5.26; found C 59.16, H 5.28.

(4*R,6*R**)-4-ethyl-6-(4-nitrophenyl)-2-phenyl-1,3,2-dioxaborinane (12f):** ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 1.09 (t, $J_{H,H}$ = 7.4, 3 H, CH$_3$), 1.55−1.75 (m, 3 H, CH$_2$ and 1 H CH$_2$), 2.29 (dt, $J_{H,H}$ = 2.8, $J_{H,H}$ = 14.0, 1 H, CH$_2$), 4.20−4.30 (m, 1 H, CH), 5.33 (dd, $J_{H,H}$ = 2.8, $J_{H,H}$ = 11.4, 1 H, CH), 7.35−7.50 (m, 3 H, Ph), 7.60−7.65 (m, 2 H, Ph), 7.85−7.95 (m, 2 H, Ph), 8.10−8.20 (m, 2 H, Ph). ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 9.3 (CH$_3$), 30.0 (CH$_2$), 40.9 (CH$_2$), 72.6 (CH), 72.9 (CH), 123.8 (CH), 126.0 (CH), 127.6 (CH), 130.9 (CH), 133.9 (CH), 147.3 (C), 150.1 (C); (δ_CC-1 + δ_CC-3) *syn* = 145.5, (δ_CC-1 + δ_CC-3) *anti* = 138.7. $C_{17}H_{18}BNO_4$ (311.1): calcd. C 65.62, H 5.83; found C 65.63, H 5.81.

(4*R,6*R**)-4-butyl-6-(4-methoxyphenyl)-2-phenyl-1,3,2-dioxaborinane (12g):** ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 0.95 (t, $J_{H,H}$ = 7.3, 3 H, CH$_3$), 1.35−1.45 (m, 2 H, CH$_2$), 1.45−1.65 (m, 4 H, 2 × CH$_2$), 1.65−1.75 (m, 1 H, CH$_2$), 2.19 (dt, $J_{H,H}$ = 2.8, $J_{H,H}$ = 14.0, 1 H, CH$_2$), 3.80 (s, 3 H, CH$_3$), 4.20−4.30 (m, 1 H, CH), 5.15 (dd, $J_{H,H}$ = 2.8, $J_{H,H}$ = 11.5, 1 H, CH), 6.85−6.95 (m, 2 H, Ph), 7.30−7.45 (m, 5 H, Ph), 7.80−7.95 (m, 2 H, Ph). ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 14.1 (CH$_3$), 22.7 (CH$_2$), 27.2 (CH$_2$), 36.9 (CH$_2$), 41.9 (CH$_2$), 55.3 (CH$_3$), 71.9 (CH), 73.2 (CH), 113.8 (CH), 126.5 (CH), 127.5 (CH), 130.6 (CH), 133.9 (CH), 135.2 (C), 159.0 (C); (δ_CC-1 + δ_CC-3) *syn* = 144.1, (δ_CC-1 + δ_CC-3) *anti* = 139.7. $C_{20}H_{25}BO_3$ (324.2): calcd. C 74.09, H 7.77; found C 74.11, H 7.78.

(4*R,6*R**)-4-(*tert*-butyl)-6-ethyl-2-phenyl-1,3,2-dioxaborinane (12h):** ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 1.00 (s, 9 H, 3 × CH$_3$), 1.08 (t, $J_{H,H}$ = 7.3, 3 H, CH$_3$), 1.30−1.55 (m, 1 H, CH$_2$), 1.55−1.70 (m, 2 H, CH$_2$), 1.93 (dt, $J_{H,H}$ = 13.6, $J_{H,H}$ = 2.7, 1 H, CH$_2$), 3.79 (dd, $J_{H,H}$ = 11.5, $J_{H,H}$ = 2.7, 1 H, CH), 3.95−4.10 (m, $J_{H,H}$ = 8.7, $J_{H,H}$ = 2.7, 1 H, CH), 7.30−7.45 (m, 3 H, Ph), 7.80−7.90 (m, 2 H, Ph). ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 9.6 (CH$_3$), 25.4 (CH$_3$), 30.4 (CH$_2$), 32.9 (CH$_2$), 34.6 (C), 73.2 (CH), 79.3 (CH), 127.4 (CH), 130.4 (CH), 133.8 (CH). $C_{15}H_{23}BO_2$ (246.2): calcd. C 73.19, H 9.42; found C 73.22, H 9.40.

(4*R,6*S**)-4-butyl-6-pentyl-2-phenyl-1,3,2-dioxaborinane (12i):** ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 0.85−1.05 (m, 6 H, 2 × CH$_3$), 1.25−1.80 (m, 15 H, 7 × CH_2 and 1H CH_2), 1.97 (dt, $J_{H,H}$ = 2.7, $J_{H,H}$ = 13.8, 1 H, CH_2), 4.05−4.20 (m, 2 H, CH), 7.20−7.45 (m, 3 H, Ph), 7.80−7.90 (m, 2 H, Ph). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.0 (CH_3), 14.1 (CH_3), 22.7 (CH_2), 24.8 (CH_2), 27.3 (CH_2), 31.9 (CH_2), 37.1 (CH_2), 37.4 (CH_2), 39.1 (CH_2), 71.8 (CH); (δ_CC-1 + δ_CC-3) *syn* = 143.6, (δ_CC-1 + δ_CC-3) *anti* = 137.6. $C_{18}H_{29}BO_2$ (288.2): calcd. C 75.01, H 10.14; found C 75.03, H 10.15.

(4*R,6*R**)-4-isopropyl-6-pentyl-2-phenyl-1,3,2-dioxaborinane (12n):** ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.92 (t, $J_{H,H}$ = 7.4, 3 H, CH_3), 0.98 (d, $J_{H,H}$ = 6.9, 3 H, CH_3), 1.05 (d, $J_{H,H}$ = 6.8, 3 H, CH_3), 1.30−1.40 (m, 6 H, 3 × CH_2), 1.40−1.55 (m, 1 H, CH_2), 1.55−1.65 (m, 2 H, CH_2), 1.70−1.85 (m, 1 H, CH), 1.94 (dt, $J_{H,H}$ = 2.8, $J_{H,H}$ = 13.7, 1 H, CH_2), 3.84 (ddd, $J_{H,H}$ = 2.8, $J_{H,H}$ = 6.0, $J_{H,H}$ = 8.9, 1 H, CH), 4.00−4.10 (m, 1 H, CH), 7.30−7.45 (m, 3 H, Ph), 7.75−7.90 (m, 2 H, Ph). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.1 (CH_3), 17.8 (CH_3), 18.1 (CH_3), 22.7 (CH_2), 24.8 (CH_2), 31.9 (CH_2), 33.9 (CH), 35.8 (CH_2), 37.4 (CH_2), 71.9 (CH), 76.6 (CH), 127.4 (CH), 130.4 (CH), 133.8 (CH). $C_{17}H_{27}BO_2$ (274.2): calcd. C 74.46, H 9.92; found C 74.47, H 9.90.

Acknowledgments

This work was carried out in the framework of the National Project "Stereoselezione in Sintesi Organica. Metodologie e Applicazioni" supported by MURST, Rome, and by the University of Bologna, and in the framework of "Progetto di Finanziamento Triennale, Ateneo di Bologna 1999−2001".

---

[1] [1a] T. Hiyama G. B. Reddy, T. Minami, T. Hanamoto, *Bull. Soc. Chem. Jap.* **1995**, *68*, 350−363. [1b] I. Paterson, R. D. Norcross, R. A. Ward, P. Romea, M. A. Lister, *J. Am. Chem. Soc.* **1994**, *116*, 11287−11314. [1c] M. Sletzinger, T. R. Verhoeven, R. P. Volante, J. M. McNamara, T. M. H. Liu, *Tetrahedron Lett.* **1985**, *26*, 2951−2954. [1d] K. Narasaka, F. C. Pai, *Tetrahedron* **1984**, *40*, 2233−2238. [1e] C. Bonini, A. Bianco, R. Di Fabio, S. Mecozzi, A. Proposito, G. Righi, *Gazz. Chim. It.* **1991**, *121*, 75−80. [1f] K. S. Ravikumar, S. Sinha, S. Chandrasekaran, *J. Org. Chem.* **1999**, *64*, 5841−5844.

[2] K.-H. Chen, G. E. Hardtmann, K. Prasad, O. Repic, M. J. Shapiro, *Tetrahedron Lett.* **1987**, *28*, 155−158.

[3] D. A. Evans, H. A. Hoveyda, *J. Org. Chem.* **1990**, *55*, 5190−5192.

[4] H. Hamashita, K. Narasaka, *Chem. Lett.* **1996**, 539−540.

[5] [5a] G. Bartoli, M. Bosco, L. Sambri, E. Marcantoni, *Tetrahedron Lett.* **1996**, *37*, 7421−7424. [5b] G. Bartoli, M. Bosco, L. Sambri, E. Marcantoni, R. Dalpozzo, *Chem. Eur. J.* **1997**, *3*, 1941−1950.

[6] [6a] G. Bartoli, M. Bosco, S. Cingolani, E. Marcantoni, L. Sambri, *J. Org. Chem.* **1998**, *63*, 3624−3630. [6b] G. Bartoli, M. C. Bellucci, S. Alessandrini, M. Malavolta, E. Marcantoni, L. Sambri, R. Dalpozzo, *J. Org. Chem.* **1999**, *64*, 1986−1992. [6c] G. Bartoli, M. Bosco, M. C. Bellucci, R. Dalpozzo, E. Marcantoni, L. Sambri, *Org. Lett.* **2000**, *2*, 45−47. [6d] R. Ballini, G. Bosica, E. Marcantoni, P. Vita, G. Bartoli, *J. Org. Chem.* **2000**, *65*, 5854−5857. [6e] C. R. Sarko, I. C. Guch, M. DiMare, *J. Org. Chem.* **1994**, *59*, 705−706.

[7] [7a] G. Bartoli, M. Bosco, M. C. Bellucci, R. Dalpozzo, E. Marcantoni, L. Sambri, *Chem. Eur. J.* **2000**, *6*, 2590−2598. [7b] J. L. Vicario, D. Badia, E. Dominguez, M. Rodriguez, L. Carrillo, *J. Org. Chem.* **2000**, *65*, 3754−3760.

[8] C. R. Sarko, S. E. Collibee, A. L. Knorr, M. DiMare, *J. Org. Chem.* **1996**, *61*, 868−873.

[9] For this purpose the reaction of **1b** with BH_3·py was treated with aqueous HCl for 1 hour and then extracted with CH_2Cl_2. The crude reaction mixture was submitted to chromatographic purification on a silica gel column; compound **11**, accompanied with trace amounts (<5%) of unidentified products, was recovered and characterised by NMR spectroscopy and MS spectrometry. **(4*R**,6*S**)-diphenyl-1,3,2-dioxaborinan-2-ol (11)**: ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.90 (dt, $J_{H,H}$ = 14.4, $J_{H,H}$ = 11.5, 1 H, CH_2), 2.38 (dt, $J_{H,H}$ = 2.7, $J_{H,H}$ = 14.4, 1 H, CH_2), 2.4 (br. s, 1 H, OH), 4.90−5.00 (dd, $J_{H,H}$ = 2.7, $J_{H,H}$ = 11.5, 2 H, CH), 7.25−7.40 (m, 10 H, Ph). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 43.7 (CH_2), 74.3 (CH), 125.2 (CH), 127.7 (CH), 128.4 (CH), 141.7 (C). MS: *m/z*: 254 (8) [$M^+ - 1$], 193 (23) [$M^+ - B(OH)_3$], 104 (100).

[10] G. Bartoli, M. Bosco, M. C. Bellucci, R. Dalpozzo, E. Marcantoni, L. Sambri, *Tetrahedron Lett.* **1999**, *40*, 2845−2848.

[11] A. Pelter, G. F. Vaughan-Williams, R. M. Rosser, *Tetrahedron* **1993**, *49*, 3007−3034.

[12] G. Stork, G. A. Kraus, G. A. Garcia, *J. Org. Chem.* **1974**, *39*, 3459−3460.

[13] D. A. Evans, R. T. Chapman, E. M. Carreira, *J. Am. Chem. Soc.* **1988**, *110*, 3560−3578.

[14] D. A. Evans, J. V. Nelson, E. Vogel, T. R. Traber, *J. Am. Chem. Soc.* **1981**, *103*, 3099−3111.

[15] A. B. Smith, P. A. Levenberg, *Synthesis* **1981**, 567−570.

[16] S. S. Labadie, J. K. Stille, *Tetrahedron* **1984**, *40*, 2329−2336.

[17] A. Fauve, H. Veschambre, *Tetrahedron Lett.* **1987**, *28*, 5037−5040.

[18] J. P. Depres, C. Morat, *J. Chem. Educ.* **1992**, *69*, A232−A239.

[19] A. Guijarro, M. Yus, *Tetrahedron* **1996**, *52*, 1797−1810.

[20] R. W. Hoffmann, U. Weidman, *Chem. Ber.* **1985**, *118*, 3980−3992.

Received July 9, 2001
[O01340]