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Combining high pressure and catalysis: pinacol- or catecholborane hydroboration of functionalized olefins †

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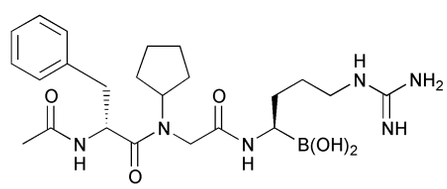
The hydroboration of three families of functionalized olefins (1-bromo- and 1,3-dibromopropenes, allylamines, 2,3-dihydrofuran) by pinacolborane and catecholborane has been studied under various experimental conditions. For 1-bromo- and 1,3-dibromopropenes, pinacolborane (PBH) is a poor reagent that requires the use of high pressure in ethereal solvents and provides only by-products, resulting from the undesired β-bromoboronate regioisomer. By contrast, catecholborane (CBH) affords mainly the expected α-bromoboronate at atmospheric pressure. With dibenzylallylamine, PBH yields a mixture of the two possible regioisomers (β- and γ-amino-boronates), whatever the pressure, while CBH affords selectively the expected γ-isomer in good yields under atmospheric thermal conditions. For 2,3-dihydrofuran, only PBH gives an efficient access, in THF, to a mixture of the corresponding α- and β-regioisomers when combining the effects of 0.5% Wilkinson's catalyst and high pressure.

Introduction

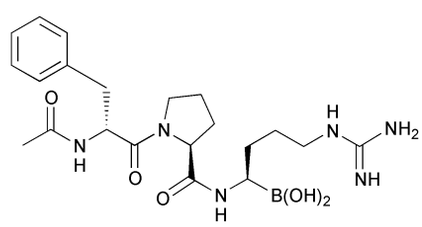
Organoboron compounds play a pivotal role in modern organic chemistry because of their functional versatility[1] and their implications in asymmetric synthesis.[2] Currently boronic esters and especially α-aminoboronates, are also of interest in medicinal chemistry since they can behave as extremely efficient enzyme inhibitors.[3] Their interaction with serine proteases has been particularly well studied. The importance of the tetrahedral ate-complex formed by the boron atom upon attack of the serine hydroxy group seems to be responsible for the inhibitory activity, thanks to its topological analogy with the transition state occurring during hydrolysis of the peptide amide function.[4] One of the major therapeutic challenges in this area is definitely the application of these compounds to the selective inhibition of thrombin, in an effort to prevent the transformation of fibrinogen into soluble fibrin, further converted into insoluble fibrin under the action of coagulation factor XIIIa. This fundamental event in the formation of fibrin clots alters the very last step of the coagulation cascade of which control is essential in the treatment of serious affections such as pulmonary embolism or cardiovascular diseases (*e.g*, unstable angina, deep vein thrombosis). Thus, several molecules such as S18326[5] and DuP714[6] (Fig. 1) have already been evaluated in the corresponding clinical tests.

One of the key-steps in the synthesis of these compounds is the chemo- and enantioselective access to the α-aminoboronic moiety. Approaches based on the hydroboration of functionalized olefins by dialkoxyboranes are of special interest. These reagents are indeed efficient and afford products bearing a boron atom directly at the appropriate oxidation state.

In this wide context, we have decided to evaluate and compare (i) the efficiency and selectivity of the hydroboration of variously functionalized olefins by catechol[7] (CBH) and pinacol[8] (PBH) boranes. The latter is indeed known for its selectivity and the increased stability of the boronic esters it provides. However, Knochel *et al*. underline it needs to be used in excess (2 eq.) and also note that its $RhCl(PPh_3)_3$ (Wilkinson) catalysed version can be troublesome;[8] and (ii) the influence of high pressures (>10 kbar) and/or catalysis[9] on the efficiency and selectivity of these same reactions. Although the effect of transition metal catalysis on the hydroboration reaction has indeed been the object of extensive work compiled recently in a very good review,[10] the influence of high pressure on this type of reaction has been scarcely studied.[11]



S18326



DuP714

Fig. 1

Results and discussion

Three different types of olefins have been considered, *viz*. two bromopropenes, three allylamines and 2,3-dihydrofuran. Various synthetic routes to transform the corresponding α-functionalized boronates into α-aminoboronic esters can be proposed and are summarised in Fig. 2. The PBH used in this work has been either prepared in CH_2Cl_2–dimethyl sulfide

† The IUPAC name for pinacolborane is 4,4,5,5-tetramethyl-1,3,2-dioxaborolane and for catecholborane is 1,3,2-benzodioxaborole.

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Table 1 Wilkinson catalyzed hydroboration of 1-bromopropene **1** by pinacol (PBH) and catechol (CBH) boranes

Entry	**1** isomer	Borane (eq.)	Cat. (%)	Pressure	*T*/°C	Solvent	Time/h	Product (% yield)
1[a]	*E* + *Z*	PBH (1)	1	1 bar	25	CH_2Cl_2	3	**5** (50)
2	*Z*	PBH (1)	0.5	12.5 kbar	20	THF	24	**6** (80)
3	*Z*	PBH (2)	0.5	12.5 kbar	20	Et_2O	24	**5** (82)
4[b]	*E* + *Z*	CBH (1.5)	0.1	1 bar	20	C_6H_6	8	**7** (82)
5	*E*	CBH (2)	0.5	1 bar	20	—	6	**7** (74)[c]
6	*Z*	CBH (2)	0.5	1 bar	20	—	3	**7** (75)[c]

[a] Results taken from ref. 12. [b] Results taken from ref. 14*b*. [c] As product **7** was difficult to purify, conversions are given instead of yields.

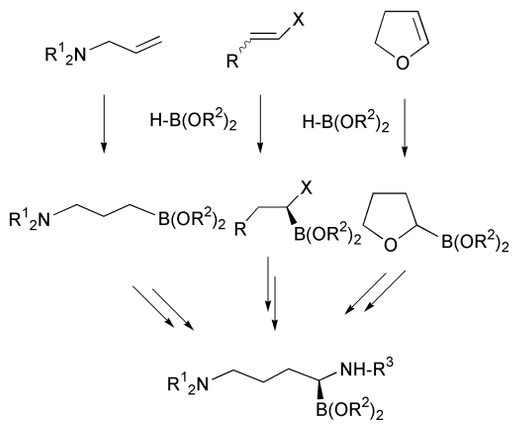
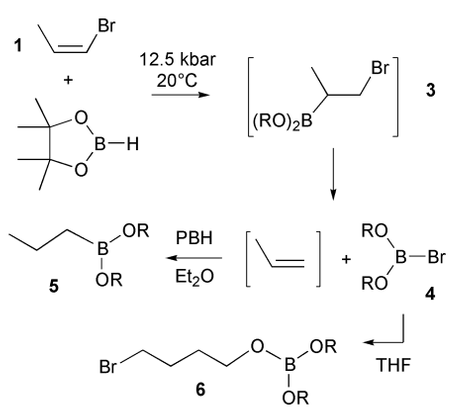


Fig. 2

(DMS) from BH_3–DMS and pinacol following the described procedure[8] or purchased neat or in solution in THF. The CBH has only been purchased neat and added as such to the reaction mixture.

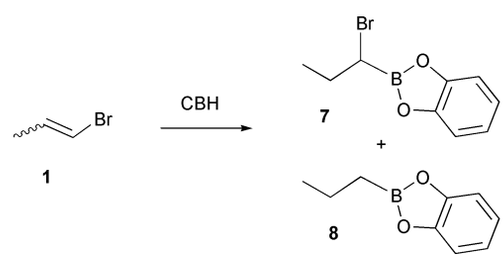
Let us first discuss the case of vinylic bromides such as 1-bromopropene **1** and 1,3-dibromopropene **2**. Srebnik and Pereira have already studied the reaction of PBH with vinyl bromide and a mixture of (*E*)- and (*Z*)-**1**.[12] These authors focused on the Wilkinson catalysed version of the reaction, since its thermal activation requires elevated temperatures or a large excess of PBH. Their results are presented in Table 1 (entry 1) with those we have obtained under high pressure, taken as an alternative to prolonged heating. In Scheme 1 are



Scheme 1

described the results of hyperbaric hydroboration of pure (*Z*)-**1** in the presence of Wilkinson's catalyst. In ether (entry 2), only pinacol-derived 1-propylboronate **5** is obtained, as observed by Srebnik under atmospheric pressure. Following previous observations,[13] these authors proposed that a rapid β-*syn*-elimination of bromoboronate **4** from primary hydroboration adduct **3** can explain the temporary formation of propene, a very good substrate for further hydroboration by a second equivalent of PBH, thus leading to **5**.[12] One could expect that the positive activation volume associated with such an elimination mechanism would disfavour this route under high pressure. The 82% yield we observe seems to indicate that it is not the case (entry 3). When switching from ether to THF, 4-bromobutoxyborane **6** is selectively obtained in the same conditions (entry 2). The occurrence of this four-carbon atom chain product can be explained by a THF ring fission, probably under the influence of the Lewis-acid bromoboronate **4**. It is indeed unlikely that PBH itself triggers this reaction since we will see below that hydroboration of 2,3-dihydrofuran by PBH in THF is chemically efficient.

It is worth noting that by resorting to CBH instead of PBH, Elgendy *et al.*[14] have observed the opposite regioselectivity in the hydroboration of **1**, and have recovered the corresponding α-bromoboronate **7** in high yield (entry 4). We therefore tried to use CBH in separate reactions with the (*E*)- and the (*Z*)-isomers of 1-bromopropene (Scheme 2 and Table 1, entry 5 and 6).



Scheme 2

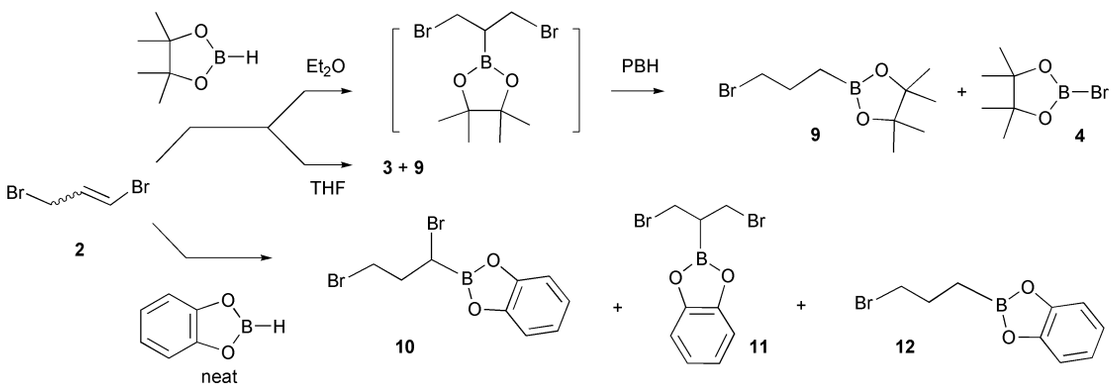
Despite slight experimental differences, such as the absence of solvent in our case or the amount of catalyst, our data are in fine agreement with those of Elgendy. For total conversion,[15] the propylboronate **8**, more than likely derived from the "central" boration of the olefin as described above, is the only side-product formed during this reaction. The efficiency associated with this transformation at atmospheric pressure and possible hazards in the use of CBH under high pressure (*vide infra*) discouraged us from considering a hyperbaric version of this reaction.

We next considered the case of 1,3-dibromopropene **2**, a difunctionalized substrate much more suited to our synthetic plan, and that is commercially available as a mixture of (*E*)- and (*Z*)-isomers (*E*:*Z* ≈ 60:40). Both the thermal and catalytic hydroboration of this olefin by catecholborane have also been studied by Elgendy and co-workers[14] who report the recovery of the expected α,γ-dibromoboronate **10** in good yields. The results we have obtained are summarised in Scheme 3 and Table 2. Our first set of experiments was conducted with PBH in the absence of solvent and at atmospheric pressure. With 2 eq. of PBH, the reaction is slow under thermal as well as catalytic conditions, a low 40% yield in **9** being obtained after 5 h at 90 °C. This result could not be improved, even after 17 h, by the addition of 0.5% Wilkinson catalyst (entry 1). In ether, it takes the combination of 0.5% Wilkinson's catalyst and a 13 kbar pressure to increase the yield to 75% (entry 2). In THF, and still under high pressure, the solvent ring-fission side-reaction described above takes place, leading mainly to borate **6** (entries 3 and 4). Therefore, for the two bromoolefins studied

Table 2 Wilkinson catalyzed hydroboration of (*E*/*Z*)-1,3-dibromopropene **2** by pinacol (PBH) and catechol (CBG) boranes

Entry	Borane (eq.)	Cat. (%)	Pressure	*T*/°C	Solvent	Time/h	Product (% yield)[a]
1	PBH (2)	0.5	1 bar	90	—	17	**9** (40)
2	PBH (2)	0.5	13 kbar	20	Et_2O	72	**9** (75)
3	PBH (2)	—	13 kbar	20	THF	96	**9** (17) + **6** (50)
4	PBH (2)	0.5	13 kbar	20	THF	72	**9** (26) + **6** (74)
5	CBH (2)	—	1 bar	90	—	2	**10** (59)[b]
6	CBH (2)	0.5	1 bar	20	—	24	**10** (70)[b]

[a] As compounds **10**–**12** were difficult to purify, conversions are given instead of yields. [b] Accompanied by various amounts of by-products **11** and **12** (see text).



Scheme 3

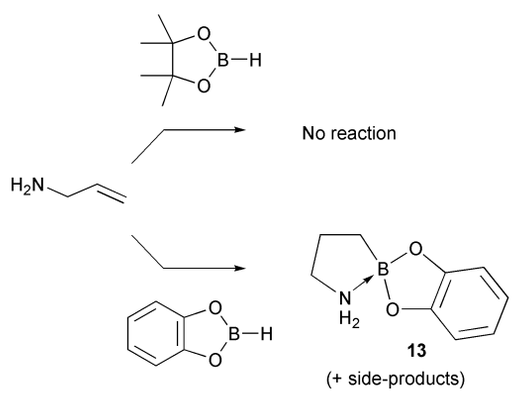
here, PBH does not yield, under our experimental conditions, the expected α-bromoboronates but only by-products derived from the regioselective boration of the central carbon atom instead of the terminal one as obtained with catecholborane. The CBH hydroboration of 1,3-dibromopropene has been performed only at atmospheric pressure (Scheme 3 and Table 2, entries 5 and 6). Our results are in overall agreement with those by Elgendy, but significant amounts of the "wrong" regioisomer **11** (8 for entry 5, 15% for entry 6) and of its β-elimination–hydroboration derivative **12** (33% for entry 5, 15% for entry 6) have been identified beside the expected dibromoboronate **10**.

In conclusion, catecholborane affords, in the cases of the two bromoolefins considered here and whatever the experimental conditions employed, a much higher regioselectivity in favour of the expected α-bromoboronates than pinacolborane.

We next considered the hydroborations of allylamines. The reaction between primary, secondary and tertiary allylamines and boranes such as BH_3, 9-BBN or CBH has been previously studied in literature.[16] In fact, the complexation between the boron and nitrogen atoms is known to lead first to a primary amine–borane complex; upon warming, this later triggers the hydroboration of the double bond. Baboulène and co-workers have shown [16c,e,f] that the regioselectivity of this step depends on the nature of the amino group and on that of the borane employed. The interaction between the nitrogen and the boron can also take place after the hydroboration has occurred,[12b] eventually leading to cyclic structures called 1,2-azaborolidine.

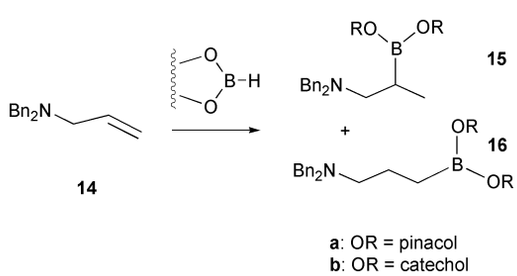
We began this part of the study with allylamine itself that had been first reacted with PBH. In the CH_2Cl_2–Me_2S mixture (resulting from the synthesis of PBH itself)[8] no reaction was observed, even after 7 days at room temperature under 11 kbar. With CBH, the reaction was performed in the absence of any solvent and led mainly to the expected terminal hydroboration product **13**, together with several contaminants that could not be identified (Scheme 4). In addition, this reaction turned out to be extremely exothermic and was once even explosive. We thus decided not to further explore this system.

Protecting the amino group in the 1-allyl-2,2,5,5-tetramethyl-1,2,5-azadisilolidine form and exposing it to CBH led to a



Scheme 4

partial hydroboration, but also to rather extensive desilylation. We then turned to a more robust protecting group for the amino group and envisaged *N*,*N*-(dibenzyl)allylamine **14** as a well-suited candidate. Reacting **14** with 2 eq. PBH under thermal conditions in a mixture of solvents induces a total conversion (Scheme 5) after 16 h but as a 50 : 50 mixture of the two regio-



Scheme 5

isomers **15a** and **16a** (Table 3, entry 1). Adding 1% Wilkinson's catalyst to the mixture left the starting materials unaltered after 1 h at room temperature and we had to warm the medium for 1 h to 100 °C to obtain results comparable to those in entry 1. Use of 5% catalyst improves the kinetics such that the completion is

Table 3 Wilkinson catalyzed hydroboration of *N*,*N*-dibenzylallylamine **14** by pinacol (PBH) and catechol (CBH) boranes

Entry	Borane (eq.)	Cat. (%)	Pressure	*T*/°C	Solvent	Time/h	Product (% conv.)
1	PBH (2.0)	—	1 bar	110	Xylene[a]	16	**15a** (50) + **16a** (50)
2	PBH (2.0)	5	1 bar	25	—[a]	16	**15a** (60) + **16a** (40)
3	PBH (2.0)	—	9 kbar	25	THF[a]	168	**14**
4	PBH (2.0)	—	11 kbar	25	—[a]	48	**15a** (50) + **16a** (50)
5	CBH (1.1)	1	1 bar	25	THF	16	**14**
6	CBH (1.1)	—	1 bar	95	—	8	**14** (50) + **16b** (50)
7	CBH (1.1)	1	1 bar	100	—	8	**15b** (45) + **16b** (55)
8	CBH (2.0)	—	1 bar	95	—	4	**16b** (100)

[a] The medium contains also CH_2Cl_2 and dimethyl sulfide since PBH is prepared in this mixture.

Table 4 Wilkinson catalyzed hydroboration of 3,4-dihydrofuran **17** by pinacolborane (PBH)

Entry	PBH (eq.)	Cat. (%)	Pressure	*T*/°C	Solvent	Time/h	Product (Sel. %)	Yield (%)[a]
1	1	0.5	1 bar	25	THF	8	**18** (41) + **19** (24)	45
2	1	—	12.5 kbar	25	THF	48	**19** (25)[b]	46
3	2	0.5	12.5 kbar	25	THF	72	**18** (61) + **19** (39)	84
4	1	5	12.5 kbar	25	THF	48	**18** (44) + **19** (56)	80
5	1	0.5[c]	12.5 kbar	25	THF	48	**18** (11) + **19** (22)[b]	38
6	1	—	12.5 kbar	25	Et_2O	24	**19** (36)[b]	70
7	2	0.5	12.5 kbar	25	Et_2O	48	**20** (50) + **21** (50)	75

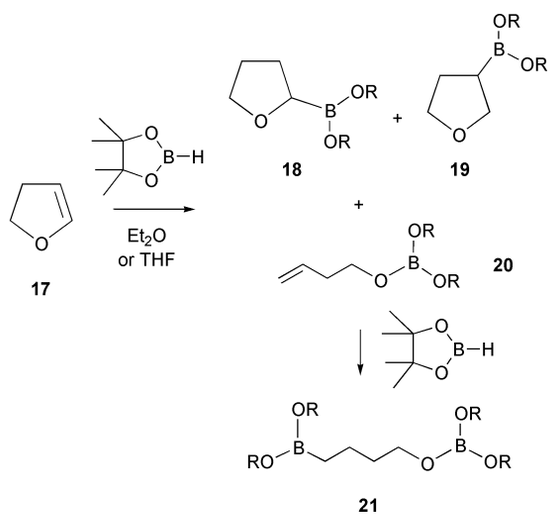
[a] Calculated on the basis of all products recovered. [b] Accompanied by various amounts of by-products **20** and/or **21** (see text). [c] $[RhCl(COD)_2]$ used instead of Wilkinson's catalyst.

reached after 16 h at room temperature (entry 2). Replacing the high temperature and the catalyst by high pressure affords disappointing results since no reaction is observed in THF, while a 50 : 50 mixture of the regioisomers is obtained in CH_2Cl_2–DMS (entries 3 and 4). We therefore switched to CBH. Entry 5 indicates that this reagent is ineffective toward dibenzylallylamine **14** when in solution in THF or toluene, even upon warming or in the presence of Wilkinson's catalyst. By contrast entry 6 shows a partial conversion using neat reagents in 8 h at 95 °C. Adding 1% catalyst speeds up the reaction such that a total conversion is observed after the same time at the same temperature, but an almost 50 : 50 mixture of regioisomers **15b** and **16b** is recovered (entry 7). Using two equivalents of CBH finally offers a total conversion in 4 h and provides selectively the expected isomer **16b** in the absence of catalyst (entry 8).

To conclude with the hydroboration of dibenzylallylamine, it appears that the expected terminal boration product can be obtained in excellent yields in the absence of any catalyst and at atmospheric pressure, provided two equivalents of neat catecholborane are used and the reaction mixture with the amine (neat) is warmed to 95 °C for 4 h.

Finally, we considered the case of 2,3-dihydrofuran (DHF). Its hydroboration has been the object of at least three important studies in the literature. Zweifel and Plamondon[17] first showed that the action of BH_3 and other boranes leads to a clean, efficient and regioselective hydroboration of the double bond, providing, after oxidation, 3-hydroxytetrahydrofuran in good yields. These results were confirmed later by Brown and co-workers who improved the yields and conditions[18] and proposed an asymmetric version of this reaction.[19] The regioselectivity is in fine agreement with other results on enol ethers hydroborations,[20] although it does not fit the synthetic pathway presented in Fig. 2 that requires the opposite regioisomer.

The reaction of DHF with pinacolborane has been performed in THF or ether (Scheme 6). At atmospheric pressure and room temperature, pinacolborane is totally unreactive after 8 h; the addition of 0.5% Wilkinson's catalyst to the medium increases the yield to 45%, the main product being the unexpected (but desired) alkoxyborane **18** resulting from α-boration (entry 1, Table 4), together with 24% **19** and 35% **21**. It therefore appeared that the catalyst could advantageously reverse, at least partially, the regioselectivity of this reaction.

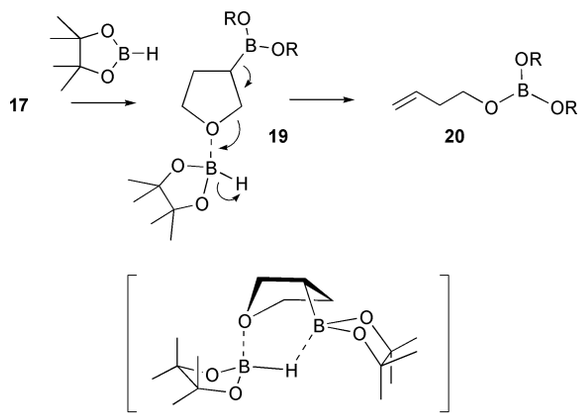


Scheme 6

Resorting to high pressure did not improve either the efficiency or the selectivity (entry 2). A mixture of the direct hydroboration product **19** was obtained together with but-3-enyloxyborane **20** (50%) and its hydroboration product **21** (25%). The combination of high pressure and Wilkinson's catalyst improves both the reactivity and the selectivity, as can be seen from entry 3 where both PBH and catalyst quantities have been optimised. Such a low amount as 0.5% of the rhodium complex indeed raises the yield significantly and gives access to a mixture of the two regioisomers **18** and **19**, in absence of any rearrangement product, while higher catalyst loadings decrease the selectivity (entry 4). In one case Wilkinson's catalyst was replaced by the rhodium(I) chloride–cyclooctadienyl complex (entry 5) in an attempt to take advantage of a ligand effect on the selectivity, as reported in many circumstances.[10,21] The results are disappointing considering the presence of side-products (22% **20** + 45% **21**) and a mediocre 38% overall yield.[22] A strong solvent effect can be noticed in the two last entries of Table 4, since working in ether rather than in THF yields a mixture of the undesired regioisomer **19** and ring-fission derivatives **20** (36%) and **21** (28%) in the absence

of catalyst (entry 6), while 0.5% Wilkinson's catalyst gives exclusively the two latter side-products (in a 50 : 50 ratio) as noted in entry 7.

The recovering of but-3-enylborate **20** has been rationalised by Zweifel and Plamondon[17] on one hand, and Brown *et al.*[18] on the other. These authors have indeed shown that the cyclic ethers resulting from the hydroboration of DHF and dihydropyran (DHP) undergo ring opening induced by inter- or intramolecular borane complexation on the oxygen followed by a β-elimination. A more-or-less concerted six-membered transition state, such as that depicted in Scheme 7, could be imagined



Scheme 7

for the intramolecular pathway. The resulting double bond can, in turn, be hydroborated by an excess of reagent (Scheme 7), giving access, in our case, to compound **21**.

The extension of this work to catecholborane is not reported here since we have been unable to characterise the product(s) obtained in the reaction mixture. The $CDCl_3$ and C_6D_6 NMR spectra seemed to correspond to the formation of oligomeric mixtures of the borated adduct(s) in solution.

To conclude this part of the study, it is clear that the combination of catalysis and high pressure induces a partial inversion of the "classical" regioselectivity of the hydroboration of DHF. Up to 60% of the desired α-regioisomer can be obtained using PBH in THF under these conditions.

Conclusion

Our two objectives in this study have led to the following conclusions.

(i) Regarding selectivities, both catecholborane and pinacolborane can effect regioselective hydroboration of functionalized olefins. Interestingly, these two reagents tend to provide the opposite regioisomers. The hydroborations by CBH have been found to be efficient under thermal or catalytic conditions, while the reactions with PBH seem to require high pressure and catalysis together. However, strong solvent effects are to be expected.

(ii) Regarding the relative interest of catalysis and high pressure for hydroboration reactions, both modes of activation can be efficient (separately) for hydroborations with dialkoxyboranes, as already known for other boranes. However, the conjunction of these two techniques can bring significant improvements to the reactivity and selectivity of these reactions, as recently underlined by Reiser for palladium-catalysed reactions.[9f]

Further studies of the utility of this combination of activation modes are certainly worth pursuing and should include essential factors that have not been taken into consideration here, such as variation of the catalyst (many transition metal complexes have been successfully used for hydroborations)[10] and of the nature of the hydroborating reagent. We believe the data presented here show that significant synthetic gains are at stake. Extensions to asymmetric versions[23] of these results will also be disclosed in due course.[24]

Experimental

General

Solvents were purified by conventional methods prior to use. Reagents were purchased from common commercial suppliers. High-pressure hydroboration reactions were performed in a Unipress piston-cylinder apparatus for pressures up to 14 kbar. TLC was performed on Kieselgel 60F-254–0.25 mm silica gel plates and column chromatography over silica gel SI 60 (230–400 mesh). Gas chromatography was performed on a Hewlett Packard 5890 apparatus equipped with a 30 m, 0.25 mm ID, 0.25 μm J & W column. Gas chromatography coupled to a mass spectrometer were realised on a ATI Unicam Automass spectrometer equipped with the same column. Elemental microanalyses were carried out on a Carlo Erba EA 1110 analyser. NMR spectra were recorded in $CDCl_3$ (unless precised) on a Bruker AC-200 (200 MHz) or Advance DMX 400 (400 MHz); chemical shifts (δ) are expressed in ppm relative to TMS for ^1H and ^{13}C, BF_3–Et_2O for ^{11}B; constants coupling (J) are given in Hz; coupling multiplicities are reported using conventional abbreviations. The infrared spectra were recorded on a Perkin-Elmer 16PC FT-IR instrument. The hydroboration reactions were carried out in an atmosphere of argon. The high-pressure hydroboration flasks were usually 2 or 4 mL reactors.

Hydroboration of 1-bromoprop-1-ene by pinacolborane

1-Bromoprop-1-ene (0.34 g, 2.8 mmol) and $RhCl(PPh_3)_3$ (13.0 mg, 0.014 mmol) were dissolved in ether or THF (4.6 mL) and pure pinacolborane (410 μL, 2.8 mmol) was added slowly at 20 °C. The reaction mixture was then placed under 12.5 kbar for 24 hours. After release of the pressure, the excess ether or THF was evaporated under vacuum. The product was then purified by flash chromatography on silica gel with heptane–AcOEt (80 : 20) as eluent, to yield 82% 2-propyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (colourless oil), when the reaction was performed in ether, and 80% 2-(4-bromobutoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (colourless oil) when in THF.

2-(4-Bromobutoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 6. δ_H (200 MHz) 3.84 (t, 2H, J = 6.7 Hz), 3.40 (t, 2H, J = 6.7 Hz), 1.92 (quintet, 2H, J = 6.7 Hz), 1.70 (quintet, 2H, J = 6.7 Hz); δ_C (50 MHz) 83.1, 63.7, 33.5, 29.8, 28.9, 24.5; *m*/*z* (EI, 70 eV) (rel. int.): 279 (M, 15%), 199 (100), 137 (48).

2-Propyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5. δ_H (200 MHz) 1.40 (sextet, 2H, J = 6.7 Hz), 1.24 (s, 12H), 0.90 (t, 3H, J = 6.7 Hz), 0.75 (t, 2H, J = 6.7 Hz); δ_C (50 MHz) 83.0, 24.7, 17.4, 17.1; *m*/*z* (CI, CH_4) (rel. int.): 171 (M + 1, 100%), 155 (39), 129 (20), 101 (88), 85 (46), 71 (18), 57 (15).

Hydroboration of 1,3-dibromopropene

1,3-Dibromopropene (0.15 g, 0.75 mmol) and $RhCl(PPh_3)_3$ (3.47 mg, 0.004 mmol) were dissolved in ether (1.6 mL) and pure pinacolborane (110 μL, 0.75 mmol) was added slowly at 20 °C. The reaction mixture was then placed under 12.5 kbar for 3 days. After release of the pressure, excess ether was evaporated under vacuum. The product was then purified by flash chromatography on silica gel with heptane–AcOEt (80 : 20) as eluent, to yield 70% 2-(3-bromopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **9**, as a colourless oil. δ_H (200 MHz) 3.40 (t, 2H, J = 6.7 Hz), 1.94 (quintet, 2H, J = 6.7 Hz), 1.24 (s, 12H), 0.90 (t, 2H, J = 6.7 Hz); δ_C (50 MHz) 83.1, 36.2, 27.4, 24.7; *m*/*z* (EI, 70 eV) (rel. int.): 249 (M, 70%), 169 (100), 125 (35), 101 (75), 57 (45).

Hydroboration of (dibenzyl)allylamine by pinacolborane

A solution of pinacolborane in CH_2Cl_2 (10.4 mmol; 2 eq.), prepared according to the literature,[8] was added to (dibenzyl)allylamine (5.2 mmol, 1 eq.) in the presence of Wilkinson's catalyst (1% mol, 0.052 mmol). The reaction mixture was warmed to 100 °C for one hour. The NMR spectrum of the crude mixture corresponded to 40% 2-(1-dibenzylaminopropan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **15a** and 60% 2-(3-dibenzylaminopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **16a**.

2-(1-Dibenzylaminopropan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 15a. δ_H (200 MHz, C_6D_6) 7.53–7.08 (m, 10H, H), 4.20 (s, 4H), 2.60 (m, 2H), 2.05 (m, 1H), 1.18 (s, 12H), 0.75 (m, 3H); δ_C (50 MHz, C_6D_6) 140.1, 132.9, 128.9, 128.7, 128.2, 126.6, 82.4, 58.2, 53.1, 24.5, 11.5; *m*/*z* (EI, 70 eV) (rel. int.): 365 (M, 10%), 274 (10), 211 (100), 181 (40), 91 (100).

2-(3-Dibenzylaminopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 16a. δ_H (200 MHz, C_6D_6) 7.53–7.08 (m, 10H), 3.57 (s, 4H), 2.48 (t, 2H, J = 7.1 Hz), 1.79 (qt, 2H, J = 7.1 Hz), 1.16 (s, 12H), 1.01 (t, 2H, J = 7.1 Hz); δ_C (50 MHz, C_6D_6) 140.1, 132.9, 128.9, 128.6, 128.2, 126.6, 82.5, 58.2, 55.5, 24.5, 21.5; *m*/*z* (EI, 70 eV) (rel. int.): 365 (M, 3%), 350 (5), 210 (100), 91 (89).

Hydroboration of 2,3-dihydrofuran by pinacolborane

In THF. 2,3-Dihydrofuran (0.30 g, 4.3 mmol) and $RhCl(PPh_3)_3$ (19.8 mg, 0.0215 mmol) were dissolved in THF (3.4 mL) and pure pinacolborane (0.55 g, 4.3 mmol) was added slowly at 20 °C. The reaction mixture was then placed under 12.5 kbar for 2 days. After release of the pressure, the excess THF was evaporated under vacuum. The two products were then purified by flash chromatography on silica gel with heptane–AcOEt (50 : 50) as eluent, but their 50 : 50 mixture could not be fully separated. An authentic sample of pinacol-1-tetrahydrofuranyl-2-boronate **19** was prepared by hydroboration of DHF by BH_3-DMS, according to Brown's procedure,[18] followed by an overnight treatment by pinacol in THF at room temperature. This product was purified by flash column chromatography in the same conditions as above (75% yield). Its spectra were identical to that of the less polar product in the previous mixture.

2-(Tetrahydrofuran-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 18. δ_H (200 MHz) 3.83 (m, 2H), 3.37 (dd, 1H, J = 6.7, 2.2 Hz), 2.05 (m, 2H), 1.50 (m, 2H), 1.20 (s, 12H); δ_C (50 MHz) 82.4, 64.6, 33.9, 24.6, 19.9; *m*/*z* (CI, CH_4) (rel. int.): 199 (M + 1, 15%), 141 (48), 101 (53), 71 (100); $C_{10}H_{19}BO_3$ requires C, 60.64; H, 9.67; O, 24.23. Found: C, 60.43; H, 9.88.

2-(Tetrahydrofuran-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 19. δ_H (200 MHz) 3.92 (t, 1H, J = 8.2 Hz), 3.75 (dt, 1H, J = 8.2, 4.1 Hz), 3.65 (dd, 1H, J = 8.2, 4.1 Hz), 3.55 (t, 1H, J = 8.2 Hz), 1.97 (m, 1H), 1.76 (m, 1H), 1.53 (m, 1H), 1.19 (s, 12H); δ_C (50 MHz) 83.3, 70.2, 68.4, 28.6, 24.6; *m*/*z* (CI, CH_4) (rel. int.): 199 (M + 1, 70%), 183 (10), 145 (12), 101 (38), 85 (58), 71 (45), 55 (100); $C_{10}H_{19}BO_3$ requires C, 60.64; H, 9.67; O, 24.23. Found: C, 60.52; H, 10.02.

In ether. 2,3-Dihydrofuran (0.40 g, 5.7 mmol) and $RhCl(PPh_3)_3$ (26.4 mg, 0.0285 mmol, 0.5% mol) were dissolved in ether (3.4 mL) and pure pinacolborane (0.73 g, 5.7 mmol) was added slowly at 20 °C. The reaction mixture was then placed under 12.5 kbar for 2 days. After release of the pressure, excess ether was evaporated under vacuum. The two products were then purified by flash chromatography on silica gel with heptane–AcOEt (50 : 50) as eluent, but their 50 : 50 mixture could not be fully separated.

2-(But-3-enyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 20. δ_H (200 MHz) 5.90–5.65 (m, 1H), 5.15–4.92 (m, 2H), 3.85 (t, 2H, J = 6.8 Hz), 2.28 (m, 2H), 1.19 (s, 12H); δ_C (50 MHz) 134.6, 116.8, 82.9, 64.0, 35.9, 24.5; *m*/*z* (CI, CH_4) (rel. int.): 199 (M + 1, 5%), 183 (18), 101 (100).

2-[4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)butoxy]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 21. δ_H (200 MHz) 3.78 (t, 2H, J = 6.8 Hz), 1.50 (m, 4H), 0.80 (m, 2H), 1.19 (s, 12H); δ_C (50 MHz) 82.9, 64.7, 33.8, 24.7, 19.8; *m*/*z* (CI, CH_4) (rel. int.): 327 (M + 1, 2%), 227 (47), 183 (18), 101 (100).

General procedure for hydroboration of 1-haloalk-1-enes by catecholborane

Catecholborane (5.0 mmol, 2 eq.) was added dropwise to 1-haloalk-1-ene (2.5 mmol, 1 eq.) in the presence of Wilkinson's catalyst (0.5% mol, 0.0125 mmol). The reaction mixture was stirred at room temperature and monitored by ^1H NMR, following the disappearance of the olefinic protons, until the reaction was complete. The desired product was purified after transesterification with commercial (1*S*,2*S*,3*R*,5*S*)-(+)-pinane-2,3-diol according to the literature procedure.[14a]

2-(1-Bromopropyl)-1,3,2-benzodioxaborole 7. δ_H (200 MHz) 7.40–6.95 (m, 4H), 3.75 (t, 1H, J = 6.9 Hz), 2.16 (m, 2H), 1.14 (t, 3H, J = 6.9 Hz); *m*/*z* (EI, 70 eV) (rel. int.): 241 (M, 5%), 214 (22), 199 (35), 173 (30), 158 (24), 145 (71), 118 (30), 55 (100). (1*S*,2*S*,3*R*,5*S*)-(+)-Pinanediol derivative (overall yield = 60%): δ_H (200 MHz) 4.41–4.20 (m, 2H), 3.38–3.24 (m, 2H), 2.44–2.30 (m, 2H), 2.30–2.13 (m, 2H), 2.04 (t, 2H, J = 4.7 Hz), 2.04–1.85 (m, 6H), 1.82–1.80 (m, 2H), 1.80–1.60 (m, 2H), 1.38 (s, 6H), 1.27 (s, 6H), 1.23–1.15 (m, 2H), 1.03 (t, 6H, J = 4.7 Hz), 0.84 (s, 6H); δ_C (50 MHz) 87.0, 86.9, 78.6, 78.5, 51.3, 51.2, 39.4, 38.2, 35.5, 28.6, 27.6, 27.0, 26.4, 23.9, 13.4; *m*/*z* (CI, CH_4) (rel. int.): 302 (M + 1, 5%), 217 (38), 189 (64), 134 (42), 83 (38), 55 (100).

2-Propyl-1,3,2-benzodioxaborole 8. δ_H (200 MHz) 7.40–6.95 (m, 4H), 1.60 (m, 2H), 1.05 (t, 3H, J = 6.8 Hz), 0.95 (t, 2H, J = 6.9 Hz); *m*/*z* (EI, 70 eV) (rel. int.): 162 (M, 19%), 134 (5), 120 (100), 92 (8), 63 (17). (1*S*,2*S*,3*R*,5*S*)-(+)-Pinanediol derivative (overall yield = 20%): δ_H (200 MHz) 4.41–4.20 (m, 1H), 2.44–2.30 (m, 1H), 2.30–2.13 (m, 1H), 2.04–1.85 (m, 1H), 1.82–1.80 (m, 1H), 1.80–1.60 (m, 1H), 1.45 (m, 2H), 1.38 (s, 3H), 1.27 (s, 3H), 1.23–1.15 (m, 1H), 0.95 (t, 3H, J = 6.7 Hz), 0.84 (s, 3H), 0.80 (t, 2H, J = 6.7 Hz); δ_C (50 MHz) 85.2, 78.3, 51.4, 39.2, 38.2, 35.2, 28.3, 27.0, 26.4, 23.9, 17.5, 16.9; *m*/*z* (CI, CH_4) (rel. int.): 222 (M, 22%), 207 (72), 153 (95), 126 (58), 55 (100).

2-(1,3-Dibromopropyl)-1,3,2-benzodioxaborole 10. δ_H (200 MHz) 7.36–6.96 (m, 4H), 4.05 (t, 1H, J = 6.4 Hz), 3.68 (t, 2H, J = 6.4 Hz), 2.61 (q, 2H, J = 6.4 Hz); δ_C (50 MHz) 147.7, 122.9, 112.8, 36.3, 31.6; *m*/*z* (EI, 70 eV) (rel. int.): 320 (M, 5%), 252 (8), 200 (100), 159 (22), 136 (78), 120 (56), 92 (31), 77 (15), 54 (38). (1*S*,2*S*,3*R*,5*S*)-(+)-Pinanediol derivative (overall yield = 60%): δ_H (200 MHz) 4.38–4.21 (m, 2H), 3.78–3.73 (m, 4H), 3.45 (t, 2H, J = 6.9 Hz), 2.40–2.32 (m, 4H), 2.32–2.25 (m, 4H), 2.25–2.15 (m, 2H), 2.15–1.95 (m, 2H, J = 6.9 Hz), 1.95 (m, 2H), 1.95–1.75 (m, 2H), 1.39 (s, 6H), 1.27 (s, 6H), 1.25–1.00 (m, 2H), 0.85 (s, 6H); δ_C (50 MHz) 87.0, 86.9, 78.6, 78.5, 51.3, 51.2, 39.4, 38.2, 36.3, 35.2, 31.6, 28.4, 27.0, 26.5, 24.0; δ_B 30.7; *m*/*z* (EI, 70 eV) (rel. int.): 380 (M, 4%), 365 (5), 284 (8), 262 (12), 189 (22), 135 (82), 93 (100).

2-(1,3-Dibromopropan-2-yl)-1,3,2-benzodioxaborole 11. δ_H (200 MHz) 3.90 (m, 4H), 1.92 (m, 1H).

2-(3-Bromopropyl)-1,3,2-benzodioxaborole 12. δ_H (200 MHz) 7.21–6.95 (m, 4H), 3.51 (t, 2H, J = 6.7 Hz), 2.19 (qt, 2H, J = 6.7 Hz), 1.48 (t, 2H, J = 6.7 Hz); δ_C (50 MHz) 147.6, 122.6, 112.8,

30.2, 27.3; *m*/*z* (EI, 70 eV) (rel. int.): 240 (M − 1, 22%), 200 (100), 84 (86).

General procedure for hydroboration of allylamines by catecholborane

Catecholborane (10.5 mmol, 2 or 3 eq.) was added very slowly to the allylamine (3.5 mmol, 1 eq.). The reaction mixture was heated at 100–110 °C under argon and monitored by the disappearance of the olefinic protons in the proton NMR. The desired product was purified after transesterification with commercial (1*S*,2*S*,3*R*,5*S*)-(+)-pinanediol.[14a] **CAUTION**: the reaction of allylamine with catecholborane is strongly exothermic and can become explosive!

2-(3-Aminopropyl)-1,3,2-benzodioxaborole 13. δ_H (200 MHz) 7.24–6.85 (m, 4H), 3.65 (t, 2H, J = 7.0 Hz), 2.09 (qt, 2H, J = 7.0 Hz), 1.39 (t, 2H, J = 7.0 Hz); δ_B (128 MHz) 22.1; IR 3154, 1472, 1236, 1074, 912, 738 cm^{-1}; *m*/*z* (CI, CH_4) (rel. int.): 178 (M + 1, 100%), 111 (21), 76 (50). (1*S*,2*S*,3*R*,5*S*)-Pinanediol aminopropylboronate derivative (overall yield = 50%): δ_H (200 MHz) 4.45–4.05 (m, 1H), 3.65 (m, 2H), 2.41–2.32 (m, 1H), 2.32–2.25 (m, 2H), 2.25–2.20 (m, 1H), 2.10 (m, 1H), 2.00–1.91 (m, 1H), 1.91–1.88 (m, 1H), 1.40 (s, 3H), 1.30 (s, 3H), 1.25–1.04 (m, 1H), 1.03 (m, 3H), 0.80 (s, 3H); δ_B (128 MHz) 22.3; IR 3214, 1486, 1234, 1064, 908, 738, 650 cm^{-1}.

2-(1,1-Dibenzylaminopropan-2-yl)-1,3,2-benzodioxaborole 15b. δ_H (200 MHz) 7.46–6.90 (m, 14H), 4.25 (s, 4H), 3.00 (m, 2H), 2.10 (m, 1H), 0.75 (m, 3H).

2-(3,3-Dibenzylaminopropyl)-1,3,2-benzodioxaborole 16b. Bp (0.7 mmHg) = 250 °C; δ_H (200 MHz, $CDCl_3$) 7.40–6.90 (m, 14H), 3.80 (s, 4H), 2.68 (t, 2H, J = 7.0 Hz), 1.73 (qt, 2H, J = 7.0 Hz), 1.04 (t, 2H, J = 7.0 Hz); δ_H (200 MHz, C_6D_6) 7.42–6.90 (m, 14H), 3.66 (s, 4H), 2.53 (t, 2H, J = 7.0 Hz), 1.72 (qt, 2H, J = 7.0 Hz), 1.03 (t, 2H, J = 7.0 Hz); δ_C (50 MHz, $CDCl_3$) 150.5, 131.0, 129.4, 127.5, 122.9, 118.8, 112.3, 56.5, 51.8, 25.4; δ_B (128 MHz, $CDCl_3$) 14.3; IR 3050, 1493, 1240, 1065, 913 (br), 738 cm^{-1}; *m*/*z* (EI, 70 eV) (rel. int.): 357 (M, 6%), 210 (99), 181 (23), 151 (22), 91 (100). (1*S*,2*S*,3*R*,5*S*)-(+)-Pinanediol derivative (overall yield = 87%): δ_H (400 MHz, $CDCl_3$) 7.38–7.19 (m, 10H), 4.19 (dd, 1H, J = 8.7, 1.9 Hz), 3.58 (s, 4H), 2.43 (t, 2H, J = 7.4 Hz), 2.27–2.07 (m, 2H), 1.99 (t, 1H, J = 5.5 Hz), 1.91–1.81 (m, 2H), 1.79–1.75 (m, 1H), 1.72–1.61 (m, 1H), 1.38 (s, 3H), 1.26 (s, 3H), 1.00 (m, 1H), 1.03 (t, 2H), 0.84 (s, 3H); δ_C (50 MHz, $CDCl_3$) 144.1, 129.0, 128.1, 126.9, 85.4, 57.9, 55.1, 51.1, 39.4, 38.2, 35.2, 28.5, 27.0, 26.5, 23.9, 21.1; δ_B (128 MHz, $CDCl_3$) 12.3; IR 2930, 1486, 1368, 1234, 1068, 908, 734 cm^{-1}; *m*/*z* (EI, 70 eV) (rel. int.): 417 (M, 5%), 210 (98), 91 (100).

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