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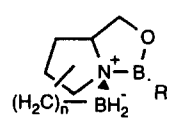
Chiral intramolecular amine–borane complexes as reducing agents for prochiral ketones

Jean-Brice Le Toumelin and Michel Baboulène *

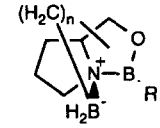
Laboratoire des IMRCP, UMR 5623 (CNRS), Université P. Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex 04, France

Abstract: A new family of chiral amine–borane complexes the N-spiroazaborolidines **4** is synthesized. These compounds are stable, convenient to use and have proved to be excellent reducing agents of prochiral ketones (yield$_{reduction}$ ≥95%). However, a poor enantioselectivity was obtained (ee≤38%). The configuration of these molecules (*cis* position between B$_{aza}$ and the substituent on the B$_{oxaza}$), unfavourable for a good approach of the ketone, is a possible explanation. Furthermore our results show the importance of the stereochemistry of the nitrogen atom in amine–borane complexes for asymmetric synthesis. © 1997 Elsevier Science Ltd

Intermolecular amine–borane complexes (R_3N–BH_3) are a convenient source of diborane. Although their stability is good, their lack of reactivity reduces their applicability.[1] However, the wide application of chiral alcohols has prompted considerable research on the reduction of prochiral ketones by chiral amine–borane derivatives.[2] The quest for a lower basicity of the nitrogen atom has led to the use of terpenic 1,2-azaboracyclohexane,[3] phosphoramidate derivatives,[4] oxazaphospholidine oxides,[5] aminoacids and esters,[6] and chiral amines in the presence of BF_3–OEt_2[7]; the best results to date have been obtained with chiral oxazaborolidines (CBS reductions).[8] Despite a large number of studies, the reaction mechanism is still not clear and the ideal catalyst has yet to be found.[9] From *ab initio* molecular orbital calculations (RHF method), Nevalainen[10] proposed amine–borane complexes bearing a semi-polar intramolecular bond (compounds **A** and **B**).

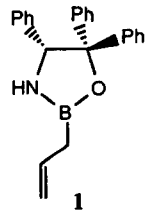


A

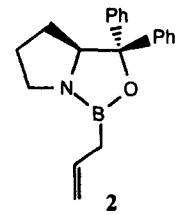


B

These molecules combine an amino-organoborane structure with an oxazaborolidine ring. To our knowledge, only Garcia *et al.*[11] have prepared oxazaborolidine analogs **3** (e.g. compound **3a**) by hydroboration of B-allyl 1,3,2-oxazaborolidines **1** and **2**.



1



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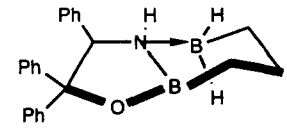


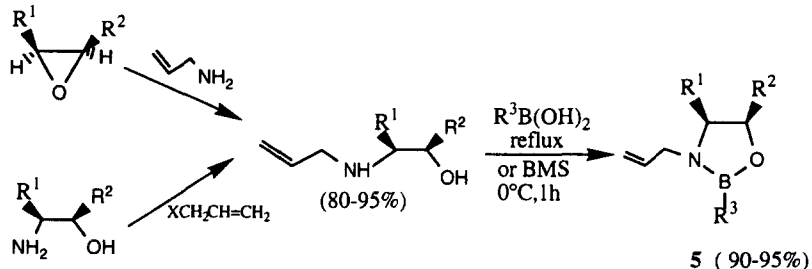
3 a

Although these derivatives are excellent reducing agents towards acetophenone, they have poor enantioselectivity.[11] In the course of our research on the synthesis and reactivity of semi-polar bonded N->B intramolecular complexes,[12] we prepared a new family of derivatives, the N-spiroazaborolidines

* Corresponding author. Email: mbab@ramses.ups-tlse.fr

4. The above-mentioned considerations prompted us to examine their reducing capacity for the enantioselective reduction of prochiral ketones.

The chiral N-allyl 1,3,2-oxazaborolidines **5** are readily obtained from chiral epoxides or chiral 1,2 amino-alcohols (Scheme 1).

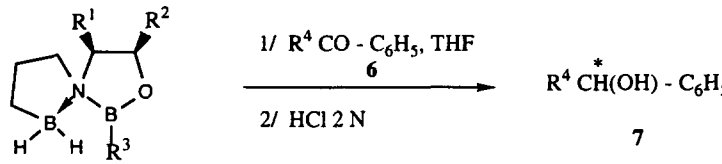


run	R^1	R^2	R^3
a	H	CH_3	CH_3
b	H	CH_3	C_6H_5
c	H	CH_3	H
d	H	C_6H_5	CH_3
e	H	C_6H_5	C_6H_5
f	H	C_6H_5	H
g	CH_3	C_6H_5	H
h	CH_3	C_6H_5	CH_3

Scheme 1. Synthesis of N-allyl-1,3,2-oxazaborolidines **5** and their boranes **4**

To prevent formation of unwanted by-products, the borane dimethylsulfide (BMS) must be added in successive stoichiometric amounts at different temperatures (Scheme 1). In contrast to hydroboration of dialkylallylamine,[13] the reaction is regioselective and quantitative at room temperature and above. The retro-coordination induced by the oxazaborolidine ring reduces the basicity of the nitrogen atom giving rise to a rapid hydroboration. IR and NMR (^1H, ^{13}C, ^{11}B) spectroscopic analysis confirmed the amine–borane structure in accord with literature data.[14] The oxazaborolidine ring confers high stability on borane azaborolidine (B_{aza}), and compounds **4** may be handled and stored without recourse to an inert atmosphere.

In contrast to other amine–boranes, compounds **4** are good reducers of prochiral ketones even at room temperature, although mild refluxing for 1 to 3 h speeds the reaction (Table 1). Compounds **4** (with R^3=H) were found to be the most reactive. In contrast to the amine–boranes **3**,[11] all the amine–boranes **4** are able to transfer both hydrogen atoms. Furthermore, they are also able to reduce aliphatic ketones. For example, 3-methyl 2-butanone was reduced by **4f** in 95% yield after refluxing for 1 h.



4

Unfortunately, the reductions are poorly enantioselective irrespective of the ketone, the amine–borane derivative or the ratio of the two reactants (Table 1). However, the presence of two

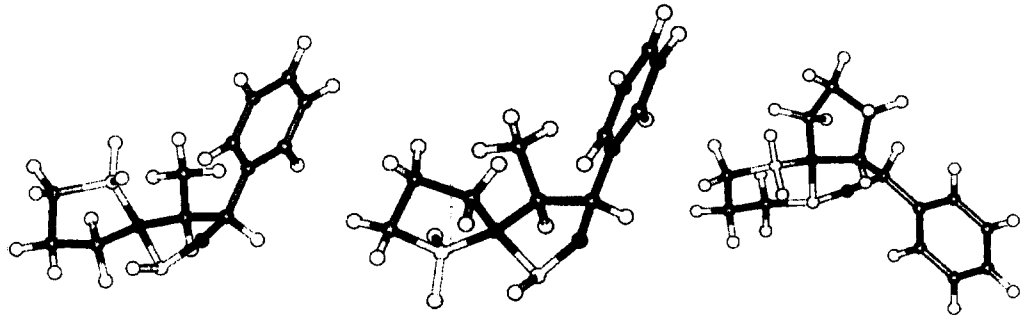
Table 1. Reduction of prochiral ketone **6**

Entry	borane **4**			ketone **6**	secondary alcohol[a] **7**			
	R^1	R^2	R^3	R^4	with 4 / 6 =1		with 4 / 6 =1/2	
					Yield %	ee % (config)	Yield %	ee % (config)
1	H	C_6H_5	H	CH_3	98	17 (R)	90	15 (R)
2	H	C_6H_5	H	C_2H_5	98	12 (R)	85	8 (R)
3	H	C_6H_5	H	$(CH_3)_2CH$	98	8 (R)	80	6 (R)
4	H	C_6H_5	CH_3	CH_3	98	7 (R)	85	3 (R)
5	H	C_6H_5	C_6H_5	CH_3	96	3 (R)	80	3 (R)
6	H	CH_3	H	CH_3	98	8 (R)	87	13 (R)
7	H	CH_3	CH_3	CH_3	98	5 (R)	87	nd
8	H	CH_3	CH_3	C_2H_5	95	5 (R)	86	nd
9	H	CH_3	C_6H_5	CH_3	97	5 (R)	80	nd
10	CH_3	C_6H_5	CH_3	CH_3	93	38 (S)	80	29 (S)
11	CH_3	C_6H_5	H	CH_3	95	38 (S)	87	26 (S)

[a] Yield were calculated before chromatography. The absolute configuration and enantiomeric excess were determined by comparison of the specific rotation with the literature values.

stereogenic centers in the oxazaborolidine ring markedly enhances the enantioselectivity (entries 10 and 11).

Although the reducing action can be accounted for by retro-coordination of the oxazaborolidine ring reflected by an increase in acid character of B_{aza} relative to that of a normal intermolecular amine–borane complex, the reactivity of the additional hydrogen atom may impair enantioselectivity. However, the absence of any change in enantioselectivity following use of one or both hydrogens of B_{aza} appeared to rule out racemization as a function of chiral and achiral attack of these two hydrogen atoms.[16,9c] In a putative CBS reduction mechanism,[15,9c] the second transfer of hydrogen should pass through a cyclic spiro-azaborane intermediate, which may be assumed to be much less reactive than the cyclic N-alkylazaboranes described as a very poor reducing agents towards ketones.[3] It was thus concluded that, unlike the CBS reduction mechanism, the reduction took place without orientation of the ketone. Pyramidalization of the nitrogen atom may have occurred giving rise to a fixed spiro type structure inducing a *cis* or *trans* configuration between B_{aza} and the substituent of the B_{oxaza} ring.



4g (*cis* configuration) **4g** (*trans* configuration) **3b** (Garcia[11])

The *trans* configuration is comparable to the configuration adopted by the molecules **3** described by Garcia[11] and that obtained by X-ray analysis of the CBS reduction reagents.[17] It will be favourable at the enantioselective reductions. But, our results are more consistent with the *cis* configuration involving a reduction without the binding of the ketone with the B_{oxaza} and thus lacking enantioselectivity.

A preliminary study by ^{11}B-NMR confirmed this structure for compounds **4**. We did not observe any difference in the chemical shifts of B_{oxaza} between compounds **5** and **4**.[18] If the derivative was in the *trans* configuration, one would expect an alteration of the B_{oxaza} environment by interaction with a hydrogen of B_{aza} (four link chain). In an ^{11}B-NMR study of diboranes derived from N-alkyloxazaborolidines, Contreras *et al.*[14] observed such a difference. We were unable to obtain the X-ray structure of compounds **4**, which would have confirmed this hypothesis. But, by molecular simulation calculations,[20] we found the *cis* configuration was energetically favoured (29.5 kcal/mol for *cis* configuration; 35,14 kcal/mol for *trans* configuration). Futhermore, the values of the lengths of N–B bond (1.58 Å) and N->B bond (1.62 Å) were in accordance with the data of the literature for intermolecular amine–boranes derived of oxazaborolidines.[11,17,21]

In conclusion, we show that the lack of reactivity of intramolecular amine–borane complexes[12] can be overcome by linking an azaborolidine ring to an oxazaborolidine ring. The N-spiroazaborolidines prepared were stable, convenient and effective reducing agents towards ketones. The selectivity of the reducing agents is currently under investigation. These new compounds were thought to adopt a preferentially *cis* configuration (between B_{aza} and the substituent on the B_{oxaza} ring), which, in contrast to the required *trans* configuration of the CBS reduction catalysts, impaired the enantioselectivity of the reduction of prochiral ketones. Our results point to the rather neglected role of the stereochemistry of the nitrogen atom in amine–borane complexes for asymmetric synthesis. Formation of a stereogenic quaternary nitrogen represents a new synthetic challenge.

Experimental

All reagents were of commercial quality and were used without further purification. IR spectra were determined on a Perkin–Elmer 683 spectrophotometer. ^{1}H-, ^{13}C- and ^{11}B-spectra were recorded on a Bruker AC 80 or Bruker 200 instruments. Optical rotation values were measured with a Perkin–Elmer 241 polarimeter.

General procedure for the synthesis of N-allyl aminoethanol

From epoxide

A solution of (R) epoxide (0.1 mol) in ethyl alcohol was added to a solution of allylamine (0.2 mol) in ethyl alcohol. The mixture was stirred under reflux for 4 h and 10 h at room temperature, then concentrated and distilled in vacuo.

N-Allyl-1-aminopropan-2-ol

Yield: 86%; Bp $_{10\ Torr}$=75°C; ^{1}H-NMR ($CDCl_3$) δ (ppm): 5.72 (m, 1H), 5 (m, 2H), 3.8 (m, 1H), 3.15 (m, 2 H), 2.75 (br.s, 2H), 2.45 (dd, 2H) 1.03 (d, 3H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 136, 116, 65.3, 56.5, 52, 20.6; Anal. Calcd for $C_6H_{13}NO$ (115.18): C, 62.57; H, 11.38; N, 12.16. Found: C, 62.87; H, 11.25; N 12.32.

N-Allyl-1-phenyl-2-aminoethan-1-ol

Yield: 90%; Bp $_{3\ Torr}$=118°C; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.3 (m, 5H), 5.8 (m, 1H), 5.15 (m, 2H), 4.7 (td, 1H), 3.6 (br.s, 2H), 3 (dd, 2H), 2.7 (d, 2H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 141, 136, 128, 127, 126, 116.7, 73.3, 55.8, 50.8; Anal. Calcd for $C_{11}H_{15}NO$ (177.25): C, 74.54; H, 8.53; N, 7.9. Found: C, 74.68; H, 8.48; N, 8.14.

From aminoalcohol

To a mixture of (S,R) aminoalcohol (0.1 mol), K_2CO_3 (0.1 mol) and ethyl alcohol (60 ml) was added, at room temperature, allyl bromide (0.1 mol). This mixture was refluxed for 8 h and then left to rise to room temperature. After filtration, the solution was concentrated in vacuo, dissolved in distilled water (20 ml) and extrated with methylene chloride (3×20 ml). The organic layer was

dried over $MgSO_4$ and evaporated in vacuo. The residue was chromatographed on silica gel (ethyl acetate/cyclohexane 1/1).

N-Allyl-1-phenyl-2-aminopropan-1-ol-(1R,2S)

Yield: 65%; Rf=0.32 (ethyl acetate/cyclohexane 1/1); $[\alpha]_D^{20}=-0.84$ (c=2.4, MeOH); ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.28 (m, 5H), 5.82 (m, 1H), 5.2 (m, 2H), 4.72 (d, 1H), 3.3 (d, 2H), 2.9 (m, 1H), 2.65 (br.s, 2H), 0.9 (d, 3H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 141.5, 136, 128, 127, 126, 116.5, 73.3, 57.8, 49.5, 14.3; Anal. Calcd for $C_{12}H_{17}NO$ (191.28): C, 75.35; H, 8.96; N, 7.32. Found: C, 75.83; H, 8.84; N, 7.28.

General procedure for the preparation of oxazaborolidines 5

These oxazaborolidines were synthesized from trimethylboroxine (R^3=Me) or phenyl boronic acid ($R^3=C_6H_5$) according a previously reported procedure.[11,19] The oxazaborolidines (R^3=H) were not isolated. These compounds were characterized by ^{1}H-, ^{13}C- and ^{11}B-NMR spectroscopy and used without purification.

N-Allyl-B-methyl-5-methyl-1,3,2-oxazaborolidine ***5a***

Yield (crude): 95%; ^{1}H-NMR ($CDCl_3$) δ (ppm): 5.72 (m, 1H), 5.38 (m, 2H), 4.18 (m, 1H), 3.48 (m, 4H), 1.21 (d, 3H), 0.16 (br.s, 3H); ^{11}B-NMR ($CDCl_3$) δ (ppm, BF_3–OEt_2): 34.8; Anal. Calcd for $C_7H_{14}BNO$ (139.01): C, 60.48; H, 10.15; N, 10.08. Found: C, 61.20; H, 9.91.; N, 10.36.

N-Allyl-B-phenyl-5-methyl-1,3,2-oxazaborolidine ***5b***

Yield (crude): 92%; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.37 (m, 5H), 5.81 (m, 1H), 5.28 (m, 2H), 4.68 (m, 1H), 3.83 (d, 2H), 3.42 (m, 2H), 1.39 (d, 3H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 138, 135.2, 133.6, 132, 128.3, 127, 125.2, 115.5, 72.6, 56.6, 48.5, 23.3; ^{11}B-NMR ($CDCl_3$) δ (ppm, BF_3–OEt_2): 32.09; Anal. Calcd for $C_{12}H_{16}BNO$ (201.08): C, 71.68; H, 8.02; N, 6.97. Found: C, 72.11; H, 8.48; N, 6.88.

N-Allyl-B-methyl-5-phenyl-1,3,2-oxazaborolidine ***5d***

Yield (crude): 96%; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.27 (m, 5H), 5.68 (m, 1H), 5.17 (m, 2H), 4.48 (t, 1H), 3.62 (m, 2H), 3.12 (d, 2H), 0.4 (br.s, 3H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 143.7, 142.3, 135.8, 128.7, 127.7, 126.2, 115.8, 77.9, 56.17, 48.05; ^{11}B-NMR ($CDCl_3$) δ (ppm, BF_3–OEt_2): 34.9; Anal. Calcd for $C_{12}H_{16}BNO$ (201.08): C, 71.68; H, 8.02; N, 6.97. Found: C, 71.08; H, 8.32; N, 7.22.

N-Allyl-B-phenyl-5-phenyl-1,3,2-oxazaborolidine ***5e***

Yield (crude): 90%; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.32 (m, 10H), 5.52 (m, 1H), 5.15 (m, 2H), 4.48 (t, 1H), 3.58 (m, 2H), 3.21 (d, 2H); ^{11}B-NMR ($CDCl_3$) δ (ppm, BF_3–OEt_2): 33.21; Anal. Calcd for $C_{17}H_{18}BNO$ (263.15): C, 77.59; H, 6.89; N, 5.32. Found: C, 76.98; H, 7.03; N, 5.09.

N-Allyl-B-methyl-4-methyl-5-phenyl-1,3,2-oxazaborolidine ***5h***

Yield: 92%; $[\alpha]_D^{20}=+27.5$ (c=2.5, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.30 (m, 5H), 5.80 (m, 1H), 5.20 (m, 2H), 4.68 (d, 1H), 3.75 (d, 1H), 3.20 (m, 2H), 0.90 (d, 3H), 0.33 (br.s, 3H); ^{11}B-NMR ($CDCl_3$) δ (ppm, BF_3–OEt_2): 35.3; Anal. Calcd for $C_{13}H_{18}BNO$ (215.11): C, 72.59; H, 8.43; N, 6.51. Found: C, 72.94; H, 8.36; N, 6.48.

General procedure for the preparation of N-spiroazaborolidine 4

These compounds are prepared in situ and used directly for the reduction of ketones. Only N-spiroazaborolidines with R^3=methyl or phenyl are been isolated. To a solution of perfomed oxazaborolidines **5** (10 mmol) was slowly added BMS solution (10 mmol), at room temperature and under argon. The reaction mixture was stirred for 30 min and then concentrated. 20 ml of anhydrous THF were added. The mixture was stirred and again evaporated in vacuo. The crude powder was

washed with anhydrous pentane. It was recuperated by filtration and desiccated in vacuo. These compounds are characterized without purification (presence of 5 to 10% of unknown by-products). A best purification has been unsuccessful.

*N-Spiroazaborolidine **4a***

White solid yield: 98%; IR (KBr): disappearance of ν allyl, ν BH_2=2367 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 4.38 (m, 1H), 3.61 to 2.50 (m, 4H), 1.60 to 0.92 (m, 7H), 0.32 (br.s, 3H); ^{11}B-NMR ($CDCl_3$) δ (ppm, BF_3–OEt_2): 33.6 and 5.15.

*N-Spiroazaborolidine **4b***

White solid yield: 95%; IR (KBr): disappearance of ν allyl, ν BH_2=2380 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.49 (m, 5H), 4.58 (m, 1H), 3.32 to 2.54 (m, 4H), 1.41 to 0.92 (m, 7H); ^{11}B-NMR ($CDCl_3$) δ (ppm, BF_3–OEt_2): 33.4 and 5.19.

*N-Spiroazaborolidine **4d***

White solid yield: 96%; IR (KBr): disappearance of ν allyl, ν BH_2=2380 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.43 (m, 5H), 4.59 (m, 1H), 3.58 to 2.47 (m, 4H), 1.58 to 0.95 (m, 4H), 0.34 (br.s, 3H); ^{11}B-NMR ($CDCl_3$) δ (ppm, BF_3–OEt_2): 34.8 and 6.09.

*N-Spiroazaborolidine **4h***

White solid yield: 96%; IR (KBr): disappearance of ν allyl, ν BH_2=2385 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.2 (m, 5H), 4.50 (m, 1H), 3.56 to 2.52 (m, 3H), 1.72 to 0.87 (m, 7H), 0.34 (br.s, 3H); ^{11}B-NMR ($CDCl_3$) δ (ppm, BF_3–OEt_2): 34.5 and 5.62.

General procedure for the reduction of prochiral ketones

To a solution of performed oxazaborolidines (10 mmol) was slowly added, at room temperature and under argon, BMS solution (10 mmol). The reaction mixture was stirred for 30 min and then concentrated. 20 ml of THF anhydrous were added and the solution was then evaporated. 20 ml of anhydrous THF were added again and prochiral ketones (10 or 20 mmol) added dropwise. The mixture was refluxed during 3 h. After cooling at 0°C, addition of HCl solution (2 N) was made. The mixture was stirred at room temperature for 1 h and then extracted with pentane. The organic layer was washed with distilled water and dried over $MgSO_4$ and evaporated in vacuo. The residue was chromatographed on silica gel (pentane/ethyl acetate 9/1). The chiral secondary alcohols were characterized by spectral analysis and by comparison with authentic secondary alcohols (yields and ee's are reported in Table 1).

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