HYDROBORATION OF HETEROCYCLIC OLEFINS - A VERSATILE ROUTE FOR THE SYNTHESIS OF BOTH RACEMIC AND OPTICALLY ACTIVE HETEROCYCLIC COMPOUNDS

Herbert C. Brown and J. V. N. Vara Prasad

Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907, U.S.A.

Abstract - The hydroboration of representative types of heterocyclic olefins with various hydroborating agents, viz., borane-methyl sulfide, 9-borabicyclo[3.3.1]nonane, dicyclohexylborane and disiamylborane, is described. The synthesis of heterocyclic derivatives of high enantiomeric purity via asymmetric hydroboration of heterocyclic olefins with chiral hydroborating agents is also reviewed. The preparation and isolation of heterocyclic boronates of essentially 100% ee is also discussed, as well as the probable range of utilization of these derivatives for the asymmetric synthesis of optically pure enantiomeric heterocyclic derivatives.

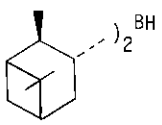
CONTENTS:

INTRODUCTION

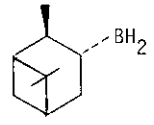
Since the discovery of the ether-catalyzed addition of diborane to carbon-carbon multiple bonds,[1] hydroboration has become a highly powerful and versatile reaction for organic synthesis.[2-4] The organoboranes thus prepared by hydroboration are among the most versatile organometallic intermediates, making possible a wide variety of carbon-carbon-forming reactions to afford almost all types of organic compounds.[5,6] Numerous reports of the hydroboration of cis-olefins, trans-olefins, trisubstituted olefins, dienes, acetylenic compounds and functionalized unsaturated substrates have appeared. To achieve the desired hydroboration in an appropriate and convenient manner, a wide variety of hydroborating agents, such as borane-methyl sulfide (BMS), 9-borabicyclo-[3.3.1]nonane (9-BBN), dicyclohexylborane (Chx_2BH), disiamylborane (Sia_2BH), thexylborane ($ThxBH_2$), catecholborane, and haloboranes, were developed and their hydroboration properties studied systematically.[7] These hydroborating characteristics often proved to be complementary, providing valuable procedures to the synthetic organic chemist to achieve the selective hydroboration of multi-functional compounds.

Recently intense interest has been aroused in the development of efficient methods for asymmetric synthesis.[8] Of these procedures, asymmetric hydroboration is an especially promising process for the synthesis of chiral compounds.[9] Various chiral hydroborating agents, using naturally abundant, low-cost terpenes, of various steric requirements, have been developed to hydroborate different classes of prochiral olefins.

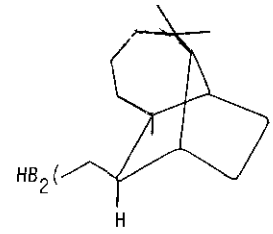
Diisopinocampheylborane (Ipc_2BH, 1) hydroborates cis-alkenes, resulting in asymmetric induction in the range of 60-80% ee.[10] Similarly, monoisopinocampheylborane ($IpcBH_2$, 2) hydroborates trans-alkenes and trisubstituted alkenes with optical induction ranging from 53% to 98% ee.[11]



1

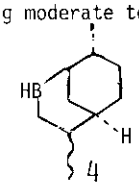


2



3

Both cis- and trisubstituted olefins have been hydroborated with dilongifolylborane (Lgf_2BH, 3) and limonylborane (LimBH, 4), realizing moderate to good asymmetric induction.[12,13]



4

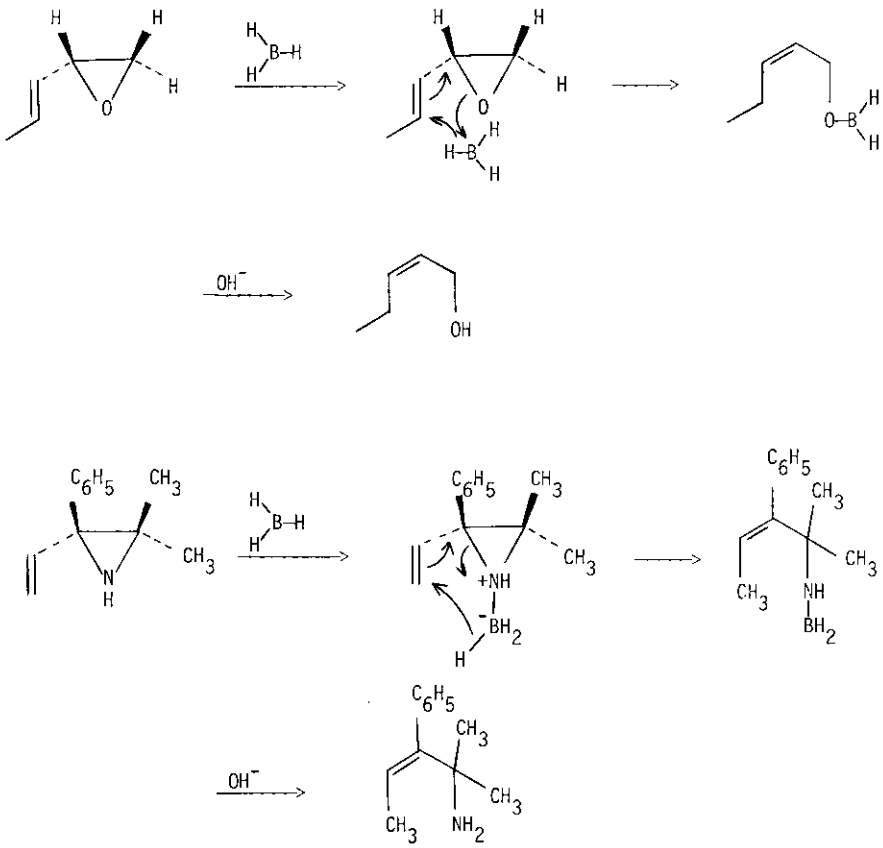
This article presents a brief review of recent developments in the hydroboration of heterocyclic olefins using both achiral and chiral hydroborating agents.

1. Hydroboration of Vinyl Heterocyclic Olefins

1.1 Vinyl epoxides and vinyl aziridines

The hydroboration of vinyl epoxides and vinyl aziridines with borane in tetrahydrofuran (BH_3·THF) yields stereochemically pure allylic alcohols and amines.[14,15] It is assumed that the reaction proceeds via a cyclic transition state involving complexation of borane to the corresponding hetero atoms, followed by an intramolecular conjugate reduction (Scheme 1).

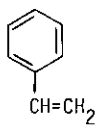
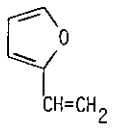
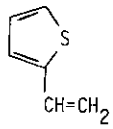
Scheme 1



1.2 Vinyl furan, vinyl thiophene and vinyl pyridines

We have studied the hydroboration of representative vinyl heterocycles with BMS, 9-BBN, Chx_2BH and Sia_2BH to establish directive effects in the hydroboration.[16] The directive effects observed for 2-vinylfuran and 2-vinylthiophene are similar to those realized in styrene (Chart I).

Chart I[a]

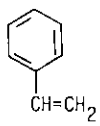
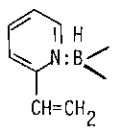
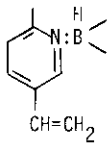
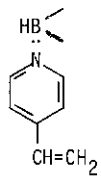




	↑	↑	↑	↑	↑	↑
$BH_3 \cdot SMe_2$	19	81	16	84	12	88
9-BBN	2	98	3	97	2	98
Chx_2BH			0	100	0	100
Sia_2BH	2	98	0	100	0	100

[a]The values given indicate relative distribution of boron in hydroboration.

The hydroboration of vinylpyridines required an excess of hydroborating agent to compensate for the molar equivalent of borane coordinating with the base. When the vinyl group is ortho or para to the nitrogen, α-organoboranes are the major products in the hydroboration. However when the vinyl group is meta to the pyridine-nitrogen, β-organoboranes are formed preferentially (Chart II).

Chart II[a]

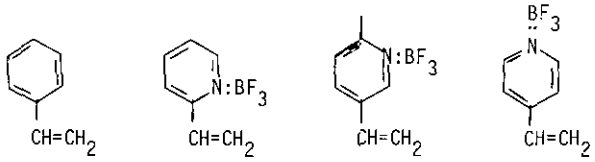





	↑	↑	↑	↑	↑	↑	↑	↑
$BH_3 \cdot SMe_2$	19	81	67	33	50	50	100	0
9-BBN	2	98	37	63	8	92	69	31
Chx_2BH			83	17	23	77	42	58
Sia_2BH	2	98	85	15	17	83	57	43

[a]The values given indicate relative distribution of boron in the hydroboration.

Alternatively, these vinylpyridines could be hydroborated by protecting the nitrogen atom of the pyridine ring by prior complexing the nitrogen atom with boron trifluoride. Hydroboration of the vinylpyridine-BF_3 complexes results in modest increases in the formation of α-organoboranes as compared to β-organoboranes in some of the cases (Chart III). Polymerization of the 4-vinylpyridine derivatives is a serious side reaction, possibly influencing the directive effects observed (Charts II and III).

Chart III[a]



	↑	↑	↑	↑	↑	↑	↑	↑
$BH_3 \cdot SMe_2$	19	81	83	17	40	60	85	15
9-BBN	2	98	44	56	14	86	74	26
Chx_2BH			84	16	29	71	59	41
Sia_2BH	2	98	88	12	13	87	53	47

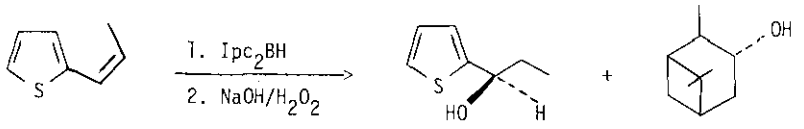
[a]The values given indicate relative distribution of boron in the hydroboration.

2. Hydroboration of Heterocyclic Disubstituted Olefins

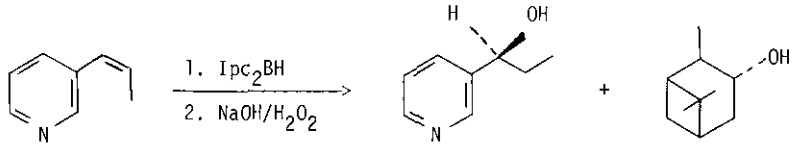
2.1 Heterocycles Containing Double-Bond Outside the Ring

2.1.a Heterocyclic cis-1-Propenyl Olefins

cis-2-(1-Propenyl)thiophene and cis-3-(1-Propenyl)pyridine, hydroborated with diisopinocampheylborane (derived from (+)-α-pinene) at -25°C, followed by oxidation, furnished (2-thienyl)propan-1-ol and (3-pyridyl)propan-1-ol of 59% and 40% respectively in good yields (eqs 1 and 2).[17]



59% ee (1)

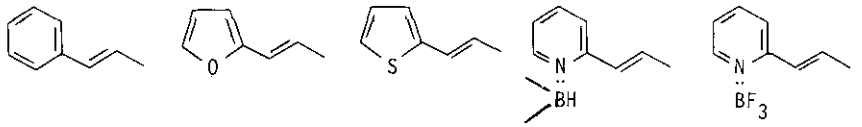


40% ee (2)

2.1.b Heterocyclic trans-1-Propenyl Olefins

A systematic study of the hydroboration of trans-(1-Propenyl)heterocycles with BMS, 9-BBN, Chx_2BH and Sia_2BH shows the formation of α-organoboranes as major products.[16] A comparison of the behavior of trans-(1-propenyl)heterocycles with that of trans-(1-propenyl)benzene in the hydroboration reveals that the effect of heterocycles is pronounced in directing the boron atom more strongly to the α-carbon atom of the side-chain (Chart IV).

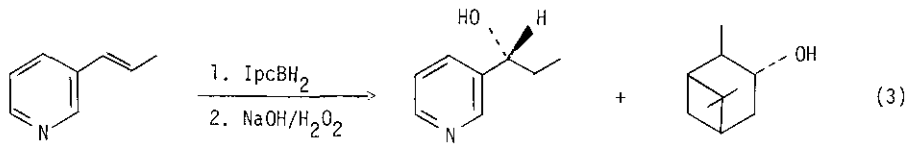
Chart IV[a]



	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑
$BH_3 \cdot SMe_2$	85	15	91	9	89	11	96	4	99	1
9-BBN	97	3	96	4	94	6	93	7	99	1
Chx_2BH			98	2	95	5	95	5	99	1
Sia_2BH			95	5	96	4	99	1	100	0

[a]The values given indicate relative distribution of boron in the hydroboration.

trans-3-(1-propenyl)pyridine, on hydroboration with monoisopinocampheylborane (derived from (+)-α-pinene), followed by oxidation, yields trans-(3-pyridyl)propan-1-ol in 45% enantiomeric purity (eq 3).[17]

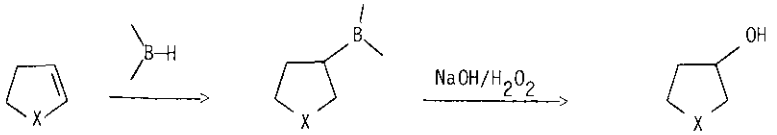


(3)

45% ee

2.2 Heterocycles Containing the Double-Bond Inside the Ring

The hydroboration of representative heterocycles bearing endocyclic double-bonds with BMS, 9-BBN, Chx_2BH and Sia_2BH was investigated systematically and the optimum conditions for clean, quantitative hydroboration established.[18,19] In the case of those heterocycles containing the double-bond adjacent to the heteroatom, the hydroboration is regioselective, furnishing β-organoboranes exclusively (eq 4). Thus, hydroboration-oxidation of these heterocyclic olefins constitutes a valuable



(4)

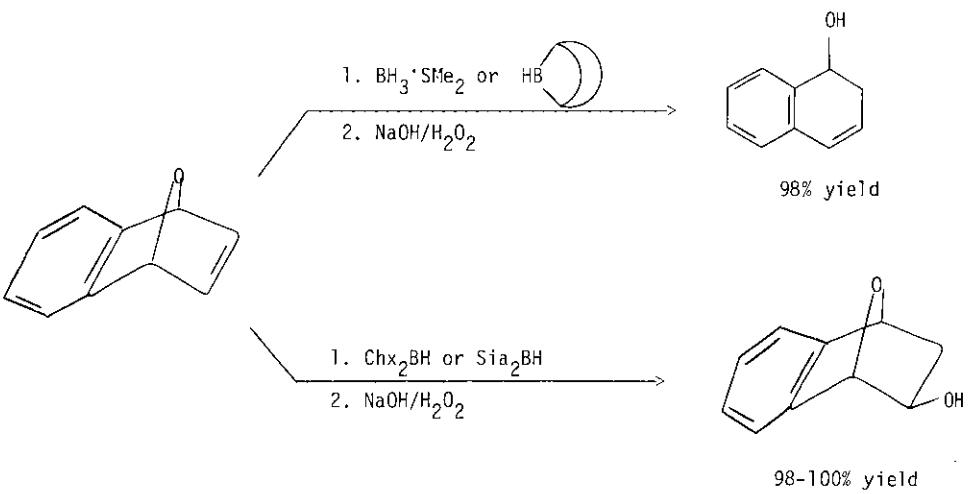
X = O or S

means for the synthesis of such heterocyclic derivatives.

Excess hydride and prolonged reaction times can cause cleavage of the intermediate alkylborane to yield first unsaturated and then the further hydroborated products. 1,4-Epoxy-1,4-dihydronaphtha-

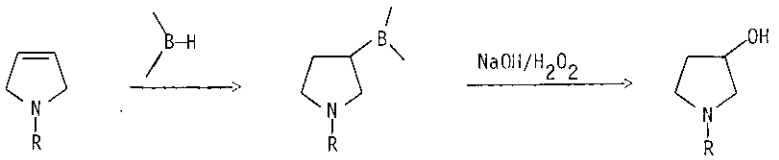
lene, an unusual heterocycle, was hydroborated with BMS, 9-BBN, Chx_2BH and Sia_2BH.[20] It was discovered that the organoboranes derived from BMS and 9-BBN are very unstable, yielding on oxidation 1-hydroxy-1,2-dihydronaphthalene in quantitative yield. On the other hand, organoboranes derived from Chx_2BH and Sia_2BH are stable, yielding on oxidation the new compound, 7-oxa-exo-2-benzonorborneol, in quantitative yield (Scheme 2). Thus, this example demonstrates the complementary

Scheme 2



nature of these hydroborating agents.

Hydroboration of nitrogen heterocycles with BMS could not be achieved with the unprotected nitrogen atom. Such hydroborations could be accomplished by protecting the nitrogen atom with the alkyl, the benzyl[17,21] and the carbobenzyloxy group. The intermediate trialkylboranes were readily converted to their corresponding alcohols (eq 5).

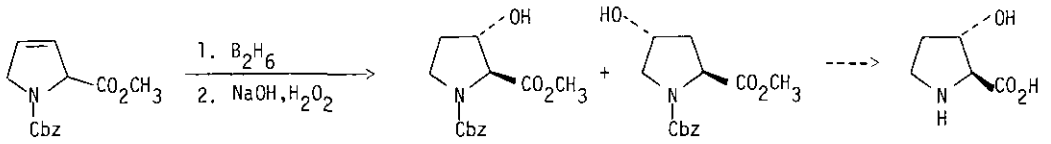


(5)

R = n-Bu, $-CH_2C_6H_5$, $-CO_2CH_2C_6H_5$

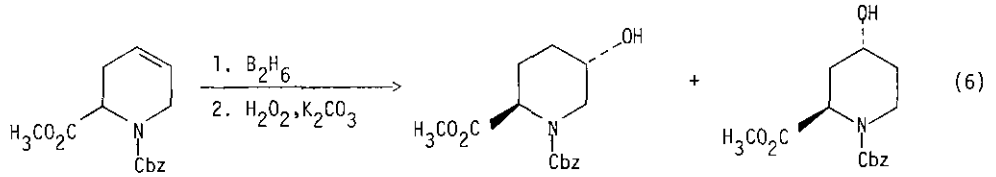
Witkop and coworkers[22] had studied the hydroboration of N-carbebenzyloxy-3,4-dihydro-DL-proline methyl ester with diborane during their synthesis of cis- and trans-3-hydroxyprolines (Scheme 3).

Scheme 3



Cbz = $-CO_2CH_2C_6H_5$

They had also hydroborated the corresponding 6-membered nitrogen heterocycle (eq 6).[23]



(6)

Cbz = $-CO_2CH_2C_6H_5$ (7:3 ratio)

Similarly, enecarbamates undergo hydroboration with diborane. Oxidation furnishes the corresponding alcohols in moderate yields.[24] Various nitrogen heterocycles have been hydroborated with diborane or trimethylamine-diborane complex. Oxidation of the intermediate gives the corresponding alcohols in good yields.[25,26] Directive effects in the hydroboration of tetrahydropyridines and tropidines have also been studied.[27]

The hydroboration-oxidation of chromenes, coumarins and flavenes have also been studied, yielding the corresponding alcohols in good yields.[28-31]

The relative reactivities of these representative heterocyclic olefins with 9-BBN and Sia_2BH have been determined.[32,19] Five-membered oxygen heterocycles, bearing the double-bond adjacent to oxygen, can be selectively hydroborated in preference to the corresponding carbocycle, a property which can be of considerable value in synthetic organic chemistry.

9-BBN, 25°C	0.24	1.00	106
Sia_2BH, 0°C	1.26	1.00	21.8

9-BBN, 25°C	1.00	631
Sia_2BH, 0°C	1.00	45.4

However, related derivatives containing larger rings do not show such rate enhancement relative to the corresponding carbocycle. Similarly, sulfur heterocycles containing the double-bond adjacent to the sulfur atom do not show higher reactivities compared to the analogous carbocycles.

We have recently reported the asymmetric hydroboration of representative five-membered disubstituted heterocycles bearing an endocyclic double bond.[33] Thus, 2,3-dihydrofuran was hydroborated with various chiral dialkylboranes. Of the dialkylboranes studied, diisopinocampheylborane proved to be the best, giving quantitative asymmetric induction (Table I).[17]

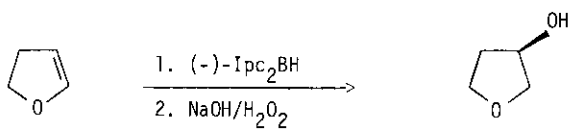
Table I

Hydroboration of 2,3-Dihydrofuran Using Various Chiral Dialkylboranes[a]

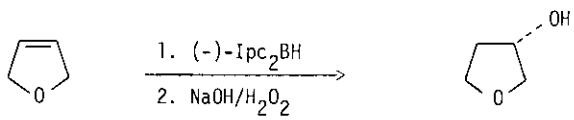
Chiral Dialkylborane	Reaction Temp., °C	$[\alpha]^{23}D$ in Degrees (c 2.43, MeOH)	% ee	Absolute Configuration
Ipc_2BH	-25	-17.243	100	R
Car_2BH	0	- 6.613	39	R
Lgf_2BH	25	- 9.288	54	R

[a]The optical purities of the reagents are of 99% or > 99% and are derived from (+)-enantiomer of the terpene.

One of the interesting features of the asymmetric hydroboration of these five-membered heterocycles is that merely by changing the position of the double bond, hydroboration with Ipc_2BH derived from the same chiral auxiliary leads to product with the opposite enantioselectivity. Thus, 2,3-dihydrofuran and 2,5-dihydrofuran, on hydroboration with (-)-Ipc_2BH, followed by oxidation, yield R- and S-3-hydroxytetrafuran respectively (eqs 7 and 8).



(7)



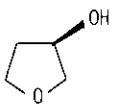
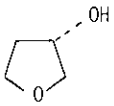
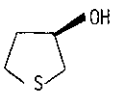
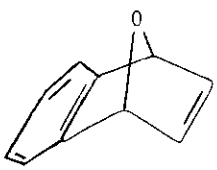
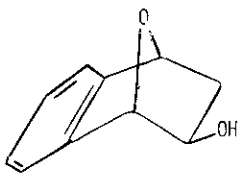
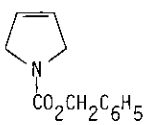
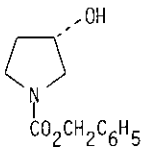
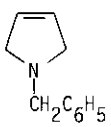
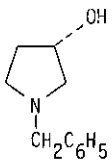
(8)

Similarly, other five-membered heterocyclic olefins on hydroboration with (-)-Ipc_2BH, followed by oxidation, yield the corresponding alcohols in essentially 100% ee. They are listed in Table II.

Table II

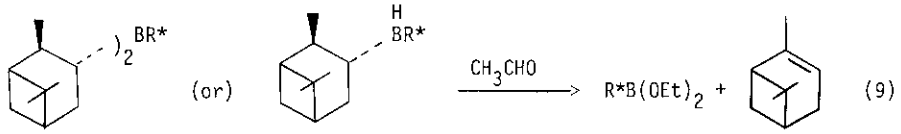
Hydroboration of Five-Membered Heterocycles

With (-)-Ipc_2BH[a,b]

Olefin	Alcohol	$[\alpha]^{23}D$ in Degrees	% ee	Absolute Configuration
		-17.3 (c 2.4, MeOH)	100	R
		+17.3 (c 2.4, MeOH)	100	S
		+14.6 (c 1, MeOH)	100	R
		+29.7 (c 2, MeOH)	100	1R,2S,4R
		+20.5 (c 3.7, MeOH)	89	S
		- 3.145 (c 1.3, $CHCl_3$)	100	S

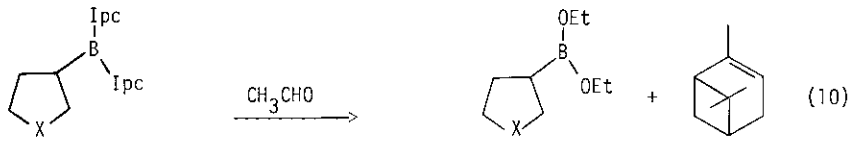
[a](-)-Ipc_2BH of 99% ee prepared from (+)-α-pinene of $[\alpha]^{23}D$ +47.2° (neat), 91.4% ee. [b]The reactions were carried out in THF at -25°C.

Brown, Jadhav and Desai[34] have established the clean elimination of α-pinene from Ipc_2BR^* and IpcBHR* by treatment with acetaldehyde, giving $R^*B(OEt)_2$ without loss of optical activity (eq 9).



(9)

A similar procedure gives five-membered heterocyclic boronates of very high enantiomeric purity (eq 10).[33] The boronates thus formed can be isolated either by column chromatography or by pump-



(10)

100% ee 100% ee

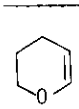
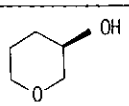
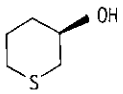
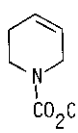
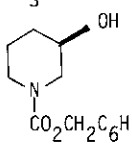
X = O, S, or N–R

ing off the α-pinene liberated in the course of the reaction.

Six-membered heterocyclic olefins were similarly hydroborated with (-)-Ipc_2BH. In these cases the asymmetric yields realized were somewhat lower, in the range of 66% to 83% (Table III).[33]

Table III

Hydroboration of Six-Membered Heterocyclic Olefins With (-)-Ipc_2BH[a,b]

Olefin	Alcohol	$[\alpha]^{23}D$ in Degrees	% ee	Absolute Configuration
		+ 9.8 (neat)	83	R
		+30.1 (c 1, $CHCl_3$)	66	R
		+ 8.0 (C 2.5, MeOH)	70	R

[a](-)-Ipc_2BH of 99% ee prepared from (+)-α-pinene of $[\alpha]^{23}D$ +47.2° (neat), 91.4% ee. [b]The reactions were carried out in THF at 0°C.

3. Hydroboration of Heterocyclic Trisubstituted Olefins

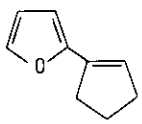
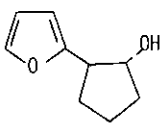
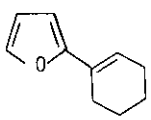
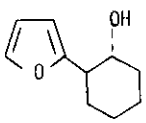
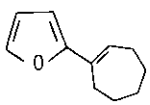
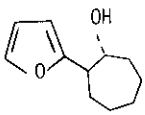
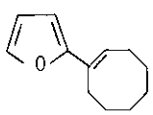
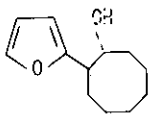
3.1 Heterocycles Containing a Double Bond Outside the Ring

Recently, representative furanyl-, thienyl-, and pyridyl-1-cycloalkenes have been hydroborated with

$IpcBH_2$.[35] In the 2-furanyl-1-cycloalkenes, the asymmetric induction during hydroboration with $IpcBH_2$ increases slightly from the five-membered to the six-membered ring. The asymmetric induction in the 7-membered ring is, as expected, similar to that observed for the 5-membered ring. However, the asymmetric induction dropped dramatically in the case of the 8-membered ring (Table IV).

Table IV

Hydroboration of Heterocyclic Cycloalkenes With $IpcBH_2$[a,b]

Olefin	Alcohol	$[\alpha]^{23}D$ in Degrees	% ee	Absolute Configuration
		+75.6 (c 2.2, MeOH)	86	1S,2S
		+53.04 (c 1.8, MeOH)	90	1S,2S
		+30.04 (c 2.4, MeOH)	86	1S,2S
		+ 8.59 (c 1.56, MeOH)	33	1S,2S

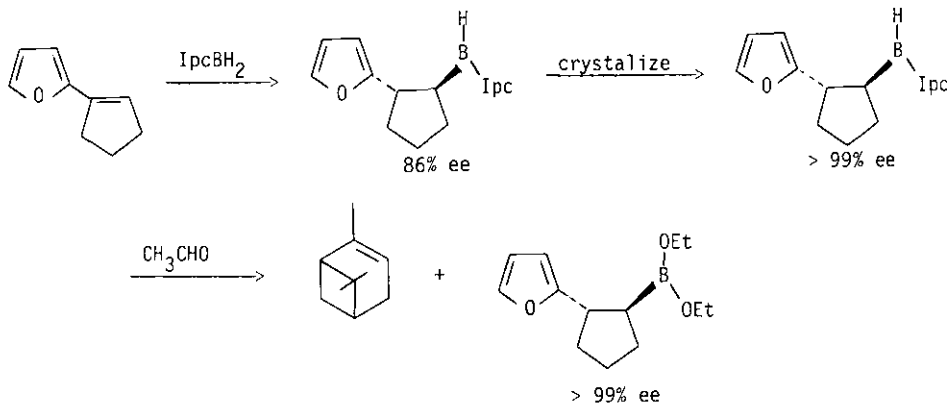
[a]The reagent is of 100% ee, prepared from (+)-α-pinene of $[\alpha]^{23}D$ +47.2° (neat), 91.4% ee. [b]The reactions were carried out in diethyl ether at -25°C.

In the case of the furanyl- and thienyl-1-cyclopentenes, no change was observed for the asymmetric induction achieved by hydroboration with $IpcBH_2$, either by altering the position of the attachment of the cyclopentene moiety to the heterocyclic system, or by introducing substituents into the heterocyclic ring. However, a change in the structure from the cyclopentene derivatives to furanyl- and thienyl-1-cyclohexenes decreases the asymmetric induction modestly to a range of 76% to 90%.

Such dialkylboranes, isopinocampheylheterocyclic borane, derived from $IpcBH_2$ and the heterocyclic olefin are crystalline dimeric compounds. Products of lower optical purities could be upgraded to

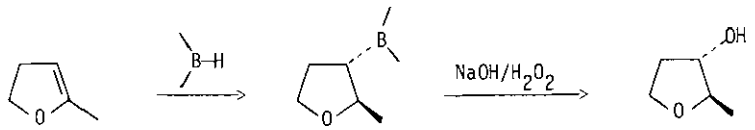
materials approaching 100% ee by simple crystallization of the intermediate. Thus, crystallization of (2-furanyl)cyclopentenylisopinocampheylborane, 86% ee, was upgraded to >99% ee by a single crystallization from ether. The resulting >99% ee material was then converted to the more synthetically useful boronate, >99% ee, by treatment with acetaldehyde (Scheme 4).[35]

Scheme 4



3.2 Substituted Heterocycles Containing the Double Bond Inside the Ring

The hydroboration of a substituted five-membered oxygen heterocycle using BMS, 9-BBN, Chx_2BH and Sia_2BH was examined.[18,19] The reactions proceed readily, giving the corresponding trialkylboranes. Oxidation then furnished trans-2-methyl-3-hydroxytetrahydrofuran in quantitative yields (eq 11).



(11)

Similarly, the hydroboration of substituted six-membered oxygen heterocycles, such as 5-methoxy-2-methyl-3,4-dihydropyran, etc., proceed readily.[28,29,36] The hydroboration of various trisubstituted N-alkyl-1,2,3,6-tetrahydropyridines with diborane and trimethylamine-borane has also been studied, furnishing the corresponding alcohols in good yields.[37,38]

Asymmetric hydroboration of 2-methyl-4,5-dihydrofuran with various dialkylboranes, eg., Ipc_2BH, Lgf_2BH and Car_2BH[39] was also studied.[17] Surprisingly, Ipc_2BH and Car_2BH could undergo simple hydroboration without either disproportionation or elimination of the reagent, furnishing the corresponding trialkylboranes. These, upon oxidation, give optically active alcohols (Table V). This constitutes the first example of the hydroboration of a trisubstituted olefin with Ipc_2BH without disproportionation of the reagent. Possibly it is attributable to the exceptional reactivity of this trisubstituted heterocyclic olefin.[32]

Table V

Hydroboration of 2-Methyl-4,5-dihydrofuran

With Various Chiral Dialkylboranes

Dialkylborane[a]	Reaction Temp. °C	$[\alpha]^{23}D$ in Degrees (c 2.5, MeOH)	% ee	Absolute Configuration
Ipc_2BH	-25	-35.69	83	2S,3R
Car_2BH	0	-29.91	70	2S,3R
Lgf_2BH	25	-19.8	46	2S,3R

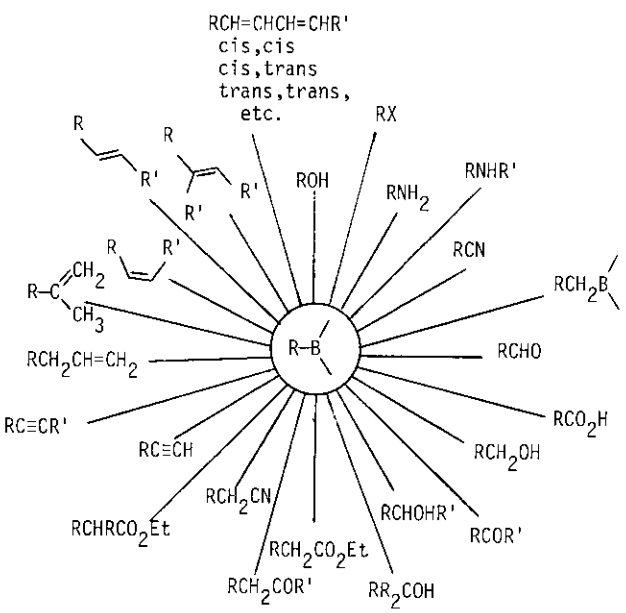
[a]The optical purities of the reagents are of 99% or > 99% ee, and are derived from (+)-enantiomer of the terpene.

The asymmetric hydroboration of various other trisubstituted heterocycles is under current investigation.

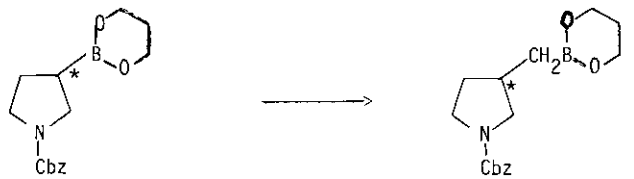
CONCLUSION

A systematic study of the hydroboration of various heterocyclic olefins has uncovered simple procedures for the preparation of various heterocyclic boranes. These boranes undergo the alkaline hydrogen peroxide oxidation normally yielding the corresponding alcohols. Although this has not yet been investigated, it is probable that they undergo other known reactions of organoboranes (Chart V).[40] If so, it will be possible to transform them into essentially any organic derivative desired.

Chart V



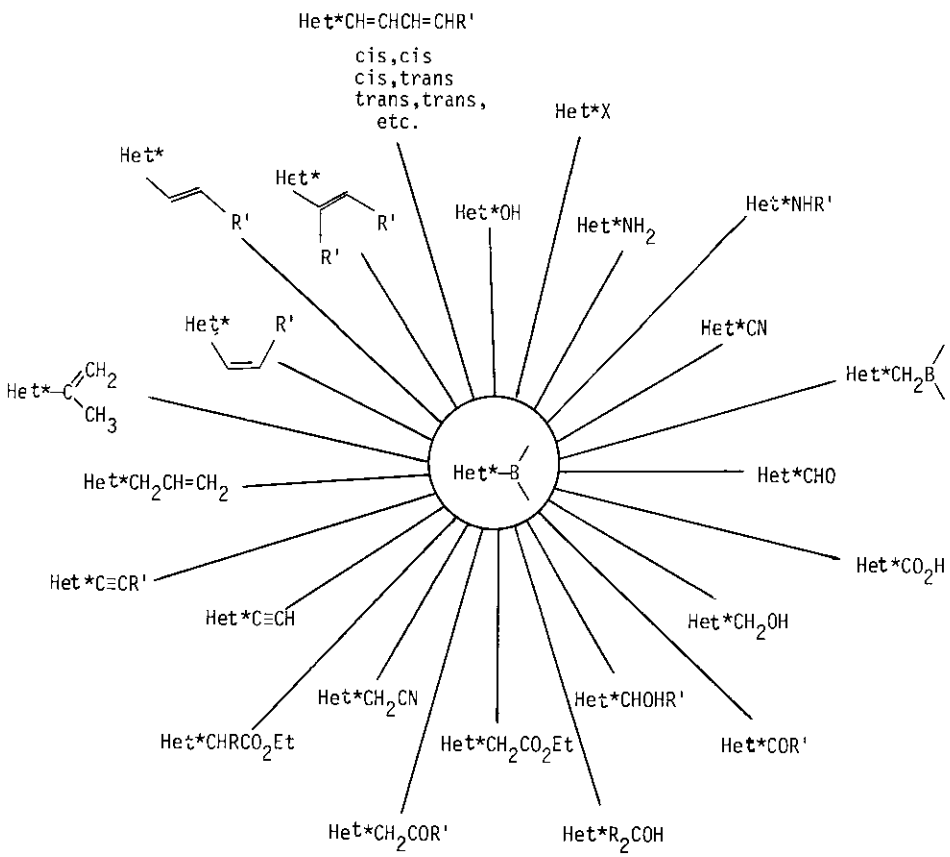
This study has also made it possible to prepare, for the first time, a number of representative heterocyclic boronates of essentially 100% ee. In one case we tested such a derivative to see whether it will undo a typical reaction of the carbocyclic derivatives.[41] Indeed, we observed that homologation[42] proceeds normally (eq 12).



(12)

Consequently, there is good reason to believe that these optically active boronates should also be transformable into enantiomerically pure derivatives, as indicated in Chart VI.

Chart VI



Since both (+)- and (-)-α-pinene are readily available, the process makes it possible to synthesize both enantiomers. In this process, the chiral auxiliary, α-pinene, can also be readily recovered and recycled.

ACKNOWLEDGEMENTS

We wish to express our deep appreciation to the National Institutes of Health for financial support (GM 10937-22). Finally, we wish to acknowledge Sheng-Hsu Zee, P. V. Ramachandran, and A. K. Gupta for their valuable contributions to this project.

REFERENCES

1. H. C. Brown and B. C. Subba Rao, J. Org. Chem., 1957, 22, 1136.
2. H. C. Brown, 'Hydroboration', W. A. Benjamin, Inc., New York, 1962.
3. A. Pelter and K. Smith, 'Comprehensive Organic Chemistry', eds. by D. H. R. Barton and W. D. Ollis, Pergamon Press, Oxford, England, 1979, vol. 3.
4. H. C. Brown, M. Zaidlewicz, and E. Negishi, 'Comprehsneive Organometallic Chemistry', eds. by G. Wilkins, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford, England, 1982, vol. 7.
5. H. C. Brown, 'Boranes in Organic Chemistry', Cornell University Press, Ithaca, New York, 1972.
6. H. C. Brown, G. W. Kramer, A. B. Levy, and M. M. Midland, 'Organic Syntheses via Boranes', Wiley-Interscience, New York, 1975.
7. H. C. Brown, 'Current Trends in Organic Chemistry', ed. by H. Nozaki, IUPAC, Pergamon Press, Oxford and New York, 1984, p. 247.
8. 'Asymmetric Synthesis', ed. by J. D. Morrison, Academic Press, New York, 1983.
9. H. C. Brown, P. K. Jadhav, and A. K. Mandal, Tetrahedron, 1981, 37, 3547.
10. H. C. Brown, M. C. Desai, and P. K. Jadhav, J. Org. Chem., 1982, 47, 5065.
11. H. C. Brown, P. K. Jadhav, and A. K. Mandal, J. Org. Chem., 1982, 47, 5074.
12. P. K. Jadhav and H. C. Brown, J. Org. Chem., 1981, 46, 2988.
13. P. K. Jadhav and S. U. Kulkarni, Heterocycles, 1982, 18, 169.
14. M. Zaidlewicz, A. Uzarewicz, and R. Sarnowski, Synthesis, 1979, 62.
15. R. Chaabouni, A. Laurent, and B. Marquet, Tetrahedron, 1980, 36, 877.
16. H. C. Brown, J. V. N. Vara Prasad, and Sheng-Hsu Zee, J. Org. Chem., 1986, 51, 439.
17. H. C. Brown and J. V. N. Vara Prasad, Unpublished results.
18. H. C. Brown, J. V. N. Vara Prasad, and Sheng-Hsu Zee, J. Org. Chem., 1985, 50, 1582.
19. G. Zweifel and J. Plamondon, J. Org. Chem., 1970, 35, 898.
20. H. C. Brown and J. V. N. Vara Prasad, J. Org. Chem., 1985, 50, 3002.
21. M. M. B. Nemia, J. Lee, and M. Joullié, Synth. Comm., 1983, 13, 117.
22. F. Irreverre, K. Morita, A. V. Robertson, and B. Witkop, J. Am. Chem. Soc., 1963, 85, 2824.
23. Y. Fujita, F. Irreverre, and B. Witkop, J. Am. Chem. Soc., 1964, 86, 1844.
24. T. Shono, Y. Matsumura, K. Tsubata, Y. Sugihara, S. Yamane, T. Kanazawa, and T. Aoki, J. Am. Chem. Soc., 1982, 104, 6697.
25. M. Polivka and M. Ferles, Coll. Czech. Chem. Comm., 1970, 35, 2392.

26. P. Štern, P. Trška, and M. Ferles, Coll. Czech. Chem. Comm., 1974, 39, 2267 and references cited therein.

27. R. E. Lyle, K. R. Carle, C. F. Ellefson, and C. K. Spicer, J. Org. Chem., 1970, 35, 2282.

28. W. Clark Still, Jr. and D. J. Goldsmith, J. Org. Chem., 1970, 35, 2282.

29. J. W. Clark-Lewis and E. J. McGarry, Aust. J. Chem., 1973, 26, 809 and 819.

30. B. S. Kirkiacharian, Bull. Soc. Chim. Fr., 1973, 999.

31. B. S. Kirkiacharian, Chem. Comm., 1975, 162.

32. H. C. Brown, P. V. Ramachandran, and J. V. N. Vara Prasad, J. Org. Chem., 1985, 50, 5583.

33. H. C. Brown and J. V. N. Vara Prasad, J. Am. Chem. Soc., 1986, 108, 0000.

34. H. C. Brown, P. K. Jadhav, and M. C. Desai, J. Am. Chem. Soc., 1982, 104, 4303.

35. H. C. Brown, A. K. Gupta, and J. V. N. Vara Prasad, Unpublished results.

36. R. M. Srivastava and R. K. Brown, Aust. J. Chem., 1970, 48, 2334.

37. M. Ferles, P. Štern, and P. Trška, Coll. Czech. Chem. Comm., 1974, 39, 3317 and references cited therein.

38. M. A. Iorio, G. N. Barrios, E. Menichini, and A. M. Farina, Tetrahedron, 1962, 31, 1959.

39. P. K. Jadhav, J. V. N. Vara Prasad, and H. C. Brown, J. Org. Chem., 1985, 50, 3203.

40. H. C. Brown, P. K. Jadhav, and B. Singaram, International Seminar on Modern Synthetic Methods 1986, Interlaken, Switzerland, April 17 and 18, 1986.

41. H. C. Brown, R. G. Naik, R. K. Bakshi, C. Pyun, and B. Singaram, J. Org. Chem., 1985, 50, 5586.

42. H. C. Brown, J. V. N. Vara Prasad, and M. V. Rangaishenvi, under current investigation.

Received, 12th May, 1986