(m, 1 H); ^{13}C NMR ($CDCl_3/Me_4Si$) δ 18.43, 21.49, 23.81, 25.95, 41.87, 74.64, 112.98, 124.45, 135.98, 145.25.

Preparation of *B*-(Allyllimonyl)borane (18). To the cooled solution (−78 °C) of *B*-(chlorolimonyl)borane[17] (5.53 g, 30 mmol) in ethyl ether (35 mL) was added allylmagnesium bromide in ethyl ether (25.4 mL, 1.18 M, 30 mmol) dropwise with stirring. The contents after stirring at −78 °C for 15 min were allowed to warm to 25 °C (~1 h). The formation of *B*-(allyllimonyl)borane was evident by ^{11}B NMR (δ +85). This reagent was then treated with acetaldehyde at −78 °C to furnish 4-penten-2-ol.

Preparation of *B*-Allyldi-10-pinanylborane (19). β-Pinene [16.8 mL, 105 mmol, $[\alpha]^{23}_D$ −21.4° (neat)] was added dropwise to the stirred solution of $H_2BCl{\cdot}OEt_2$[9] (50 mL, 1 M, 50 mmol) at 0 °C. The contents were stirred at 0 °C for 2 h to furnish *B*-chlorodi-10-pinanylborane; ^{11}B NMR (δ +77). It was then cooled to −78 °C and allylmagnesium bromide in ethyl ether (42.3 mL, 1.18 M, 50 mmol) was added dropwise. Stirring was continued for 15 min at −78 °C and the reaction mixture was allowed to warm to room temperature (~1 h). Formation of **19** was indicated by ^{11}B NMR (δ +86). **19** was then used for condensation reaction at −78 °C with acetaldehyde to furnish 4-penten-2-ol.

***B*-Allyldilongifolylborane (20).** The stirred suspension of dilongifolylborane[18] (21.1 g, 50 mmol, prepared from longifolene; $[\alpha]^{23}_D$ +42.2° (*c* 4.6, $CHCl_3$) in THF (50 mL) was treated with methanol (4 mL, 100 mmol). The residue after removal of solvents (14 mmHg/1 h; 1 mmHg/1 h) was dissolved in anhydrous ethyl ether (40 mL) and the resulting solution was cooled to −78 °C. To this was added allylmagnesium bromide in ethyl ether (42.3 mL, 1.18 M, 50 mmol) dropwise with stirring. After complete addition of allylmagnesium bromide, the reaction mixture was allowed to warm to room temperature (~1 h). The formation of **20** was then used for the condensation reaction with acetaldehyde at −78 °C to furnish 4-penten-2-ol.

***B*-Allylbis(10-methylisopinocampheyl)borane (21).** 10-Methyl-α-pinene [9.2 mL, 52.5 mmol, $[\alpha]^{23}_D$ −42.2° (neat)] was added to the stirred solution of $H_2BCl{\cdot}OEt_2$[9] (25 mL, 1 M, 25 mmol) at 0 °C. After complete addition of 10-methyl-α-pinene, the reaction mixture was stirred for 1 h at 0 °C to furnish *B*-chlorobis(10-methylisopinocampheyl)borane. It was then cooled to −78 °C and allylmagnesium bromide in ethyl ether (21.2 mL, 1.18, 25 mmol) was added dropwise. Stirring was continued for 15 min at −78 °C and then it was allowed to warm to room temperature (~1 h). The formation of *B*-allylbis(10-methylisopinocampheyl)borane was indicated by ^{11}B NMR (δ +85). **21** was then used for the condensation reaction at −78 °C with acetaldehyde to furnish 4-penten-2-ol.

***B*-Allyldiisocaranylborane (22).** To the stiirred solution of $BH_3{\cdot}SMe_2$ (5 mL, 50 mmol) in THF (20 mL) at 0 °C was added dropwise 3-carene [18.25 mL, 115 mmol, $[\alpha]^{23}_D$ +18° (neat)]. The mixture was stirred at 0 °C for 1 h and stored at 0 °C for 15 h. The resulting dialkylborane was treated with methanol (4 mL, 100 mmol) at 0 °C (15 min, 25 °C/1 h). The reaction was indicated by ^{11}B NMR (δ +55). The solvents were removed under vacuum (14 mmHg/1 h; 1 mmHg/2 h). The residue was dissolved in anhydrous ethyl ether (40 mL) and the clear solution was cooled to −78 °C. Allylmagnesium bromide in ethyl ether (42.3 mL, 1.18 M, 50 mmol) was then added dropwise with stirring. After 15 min at −78 °C, the reaction mixture was allowed to warm to 25 °C (~1 h). The formation of **22** was indicated by ^{11}B NMR (δ +85.8). **22** was then used for condensation reactions with various aldehydes.

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Hydroboration. 75. Directive Effects in the Hydroboration of Vinyl and Propenyl Heterocycles with Representative Hydroborating Agents

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The hydroboration of representative heterocyclic compounds bearing a vinyl or propenyl substituent with borane–methyl sulfide (BMS), 9-borabicyclo[3.3.1]nonane (9-BBN), dicyclohexylborane (Chx_2BH), and disiamylborane (Sia_2BH) was investigated systematically to establish directive effects in the hydroboration. The directive effects observed for 2-vinylfuran and 2-vinylthiophene are similar to those realized in styrene. The hydroboration of vinylpyridine required an excess of borane hydroborating agent. Alternatively, the nitrogen atom could be protected by complexing with boron trifluoride. When the vinyl group is ortho or para to the pyridine 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 predominantly. Hydroboration of the vinylpyridine–BF_3 complexes results in an increase in the formation of α-organoboranes, as compared to β. The distribution of boron in the hydroboration of 2-propenyl heterocyclic compounds compared to that of *trans*-1-propenylbenzene showed that the effect of the heterocycle is pronounced in directing the boron atom strongly to the α-carbon atom.

The regioselectivity of borane addition to alkenes is dependent upon both steric and electronic effects exerted by the substituents on the hydrocarbon and also on the bulkiness of the hydroborating agent.[2,3] Electronic effects, viz., both inductive and mesomeric effects, play a major role in the hydroboration of functionalized olefins in directing the boron atom.[4-6] Vinyl substituents with strong +M effects direct the boron to the β-position and many

(1) (a) Postdoctoral research associate on Grant GM 10937-23 from the National Institutes of Health. (b) Postdoctoral research associate on Grant GM 10937-17 from the National Institutes of Health.
(2) Brown, H. C.; Zaidlewicz, M.; Negishi, E. "Comprehensive Organometallic Chemistry"; Wilkins, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; Vol. 7.
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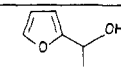
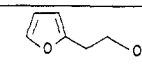
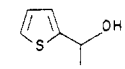
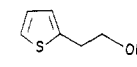
Table I. Hydroboration of 2-Vinylfuran and 2-Vinylthiophene

olefin	hydroborating agent	olefin to hydroborating agent ratio	temp, °C	time, h	total yield,[a] %	product distribution,[a] %		boron distribution, %	
								α	β
	BMS	3:1	25	2	94	13	87	13	87
	9-BBN	1:1	25	2	93	6	94	6	94
		1:1	65	1	97	3	97	3	97
	Chx_2BH	1:1	25	4	99	0	100	0	100
		1:1	25	4	98	0	100	0	100
									
	BMS	3:1	25	2	86	7	93	7	93
	9-BBN	1:1	25	2	100	4	96	4	96
		1:1	65	1	98	2	98	2	98
	Chx_2BH	1:1	25	4	100	0	100	0	100
	Sia_2BH	1:1	25	4	100	0	100	0	100

[a] Determined by GC, using dodecane as internal standard.

allylic substituents also direct the boron predominantly to the β-position.

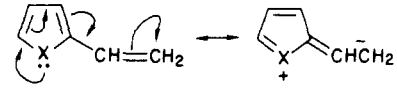
Recently we reported the hydroboration of heterocycles bearing an endocyclic double bond with representative hydroborating agents such as borane–methyl sulfide (BMS), 9-borabicyclo[3.3.1]nonane (9-BBN), dicyclohexylborane (Chx_2BH), and disiamylborane (Sia_2BH), providing a highly convenient and efficient method for the synthesis of heterocyclic alcohols.[7] In all of these cases, the boron atom adds exclusively or predominantly β to the heteroatom. Now we describe a systematic study of the hydroboration of representative heterocycles bearing a vinyl or propenyl substituent with BMS, 9-BBN, Chx_2BH, and Sia_2BH in order to establish the influence of the heterocyclic system on directive effects in the hydroboration.

Results and Discussion

The following vinyl and propenyl heterocycles were selected for study: 2-vinylfuran, 2-vinylthiophene, 2-vinylpyridine, 2-methyl-5-vinylpyridine, 4-vinylpyridine, *trans*-2-(1-propenyl)furan, *trans*-2-(1-propenyl)thiophene, and *trans*-2-(1-propenyl)pyridine. The progress of the reaction was followed either by hydride uptake or by ^{11}B NMR.

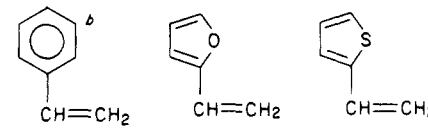
Vinyl Heterocycles. The hydroboration of 2-vinylfuran with BMS (3:1 molar ratio) in THF at 25 °C proceeded smoothly. Oxidation of the product with alkaline hydrogen peroxide yielded α- and β-alcohols in good yields in the ratio of 13:87. Similarly, 2-vinylfuran, upon hydroboration with 9-BBN at 25 °C or 65 °C, proceeded cleanly to afford the corresponding trialkylborane, which, upon oxidation, yielded α- and β-alcohols in the ratio of 6:94 or 3:97, respectively. The hydroboration of this olefin with Chx_2BH and Sia_2BH was also clean. Oxidation of the corresponding trialkylboranes thus obtained gave exclusively the β-alcohol in quantitative yields. The hydroboration of 2-vinylthiophene with BMS, 9-BBN, Chx_2BH, and Sia_2BH behaved similarly. The results are summarized in Table I.

These results can be explained as follows. As the bulkiness of the dialkylborane increases from 9-BBN to Chx_2BH to Sia_2BH, the boron atom prefers to add to a less hindered primary carbon atom. In addition, there may be a significant electronic factor. The heteroatom in 2-vinylfuran or 2-vinylthiophene may donate electrons more strongly to the β-carbon atom of the vinyl group, resulting in a higher boron distribution on the β-carbon atom.



Upon comparing the boron distribution in the hydroboration of styrene[8-10] with 2-vinylfuran and 2-vinylthiophene, it appears that the heterocyclic ring, viz., furan or thiophene, is as effective as the phenyl ring in influencing the directive effect observed for the hydroboration of the vinyl group (Chart I).

Chart I[a]



	α	β	α	β	α	β
$BH_3 \cdot SMe_2$	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 the hydroboration. [b] References 8 and 9.

2-Vinylpyridine, 2-methyl-5-vinylpyridine, and 4-vinylpyridine, upon treatment with BMS (3:1 molar ratio), initially formed the corresponding pyridine–borane complexes, with subsequent hydroboration being very slow. The reaction mixture was maintained at 25 °C for a prolonged period of time, but oxidation yielded only a small amount of ethylpyridines and about 90% of the unchanged starting materials.

2-Vinylpyridine, upon treatment with 9-BBN (1:1 molar ratio), also gave the 2-vinylpyridine–borane complex. However, the hydroboration then proceeded smoothly at 25 °C or at 65 °C to yield the corresponding organoborane. Oxidation gave 2-ethylpyridine and 2-(β-hydroxyethyl)-pyridine in a 3:7 ratio in good yields, establishing the boron

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(9) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1961**, *83*, 1241.
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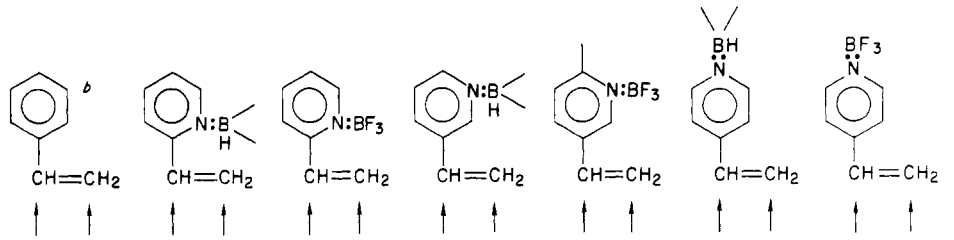
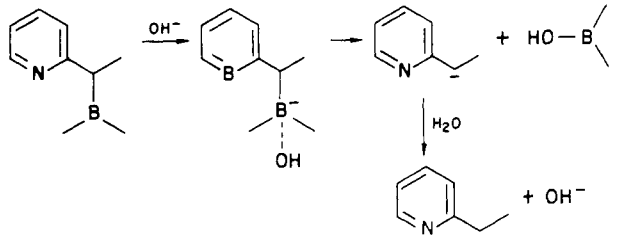
Chart II[a]



$BH_3 \cdot SMe_2$	19	81	67	33	83	17	50	50	40	60	100	0	85	15
9-BBN	2	98	37	63	44	56	8	92	14	86	69	31	74	26
CHx_2BH			83	17	84	16	23	77	29	71	42	58	59	41
Sia_2BH	2	98	85	15	88	12	17	83	13	87	57	43	53	47

[a] The values given indicate relative distribution of boron in the hydroboration. [b] References 8 and 9.

Scheme I



distribution at the α- and β-carbons. It is assumed that the ethylpyridine arises from a facile hydrolysis of the α-boron derivative under the oxidation conditions. It has been observed previously that organoboranes of the benzylic type are susceptible to hydrolysis under the influence of alkali under remarkably mild conditions.[10] Owing to the strong electron-withdrawing properties of the pyridine nitrogen, the C–B bond of the α-boron derivative must be especially susceptible to such hydrolysis. The formation of 2-ethylpyridine can be rationalized as shown in Scheme I.

It appears that in the initial complex the 2-vinylpyridine is only loosely associated with the 9-BBN moiety. Dissociation can occur with concurrent hydroboration. Although the pyridine ring greatly reduces the electron density at the β-carbon atom, as compared to the previous heterocyclic derivatives discussed, addition of boron to the β-carbon is still favored due to the powerful regioselective properties of 9-BBN.

2-Methyl-5-vinylpyridine, upon treatment with 9-BBN (1:1 molar ratio), also formed the corresponding 9-BBN complex. In this case, the 2-methyl substituent must favor dissociation. Consequently, the hydroboration proceeds readily, either at 25 °C or 65 °C, placing the boron atom predominantly at the β-carbon. Because the vinyl group is at the 5-position of the pyridine ring, the electron-withdrawing properties of the pyridine nitrogen transmitted to the vinyl group only weakly compared to that in 2-vinylpyridine, accounting for the increased boron placement at the β-carbon.

4-Vinylpyridine is more strongly associated with 9-BBN and no hydroboration was observed. Moreover, the unreacted starting material could not be recovered following the usual oxidation of the reaction mixture with alkaline hydrogen peroxide. It is known that 4-vinylpyridine readily undergoes polymerization.[11]

The hydroboration of 2-vinylpyridine and 4-vinylpyridine with Chx_2BH and Sia_2BH (1:1 molar ratio) proceeded at a slow rate, even though the corresponding pyridine–borane complexes were formed. However, the yields of the hydroborated products are low and the boron added exclusively to the α-carbon atom. In the case of 2-methyl-5-vinylpyridine, the β-boron derivatives were formed predominantly.

In order to overcome the retardation of the hydroboration by complexing borane with the nitrogen atom of the pyridine ring, the hydroboration of vinylpyridines with 1 mol excess of hydride or hydroborating agent was studied. Thus, 2-vinylpyridine on hydroboration with BMS (1:1.33 molar ratio) resulted in a boron distribution of 67:33 at the α- and β-carbons, respectively. Similarly, hydroborations with excess Chx_2BH and Sia_2BH gave predominantly boron addition to the α-carbon atom. However, the total yields are low, even though excess hydroborating agent was used.

2-Methyl-5-vinylpyridine was hydroborated with BMS (1:1.33 molar ratio). The organoborane thus obtained upon oxidation with alkaline hydrogen peroxide gave 92% of the products. Since the vinyl group is at the 5-position to the nitrogen atom, the electron-withdrawing effect of the nitrogen atom of the pyridine ring was less than that in 2-vinylpyridine, resulting in a boron distribution at the α- and β-carbons that is nearly the same. The hydroboration with 9-BBN, Chx_2BH, and Sia_2BH yielded the β-organoboranes as the major product.

4-Vinylpyridine, upon hydroboration with BMS (1:1.33 molar ratio) followed by oxidation, gave exclusively 4-ethylpyridine in 52% yield, indicating the addition of the boron atom exclusively at the α-carbon atom. The hydroboration of 4-vinylpyridine with 9-BBN (1:2 molar ratio) proceeded to give a 70:30 distribution of boron at the α- and β-positions. Similarly, 4-vinylpyridine was hydroborated with Chx_2BH and Sia_2BH, resulting in a boron distribution of 42:58 and 57:43 at the α- and β-carbon atoms, respectively. Owing to the electron-withdrawing effect of the pyridine nitrogen, which is associated with 9-BBN, the relative positive charge at the β-carbon is increased, resulting in the formation of α-organoborane. The results are shown in Table II.

The addition of boron to the benzylic carbon is very much increased in the case of 2-vinylpyridine and 4-vinylpyridine, as compared to styrene (Chart II). However, in the case of 2-methyl-5-vinylpyridine, either the boron distribution at both carbon atoms is the same or the β-organoborane is formed predominantly. This showed that the nitrogen heterocyclic ring, pyridine, has a remarkably electron-withdrawing effect when the vinyl group is at the 2- or 4-position to the nitrogen atom compared to the phenyl ring or the oxygen and sulfur heterocyclic compounds.

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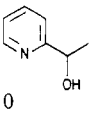
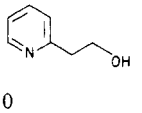
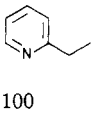
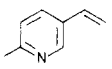
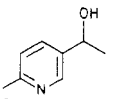
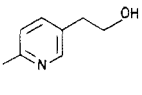
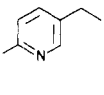
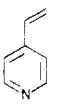
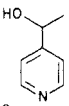
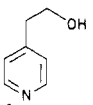
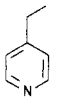
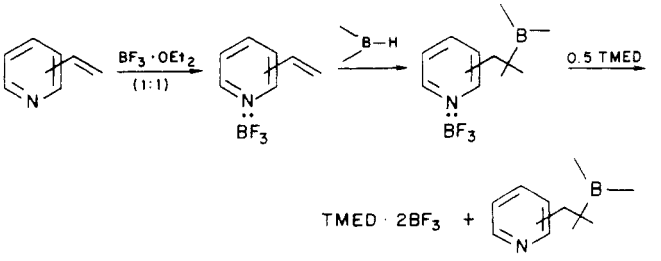
Table II. Hydroboration of Vinylpyridines

olefin	hydroborating agent	olefin to hydroborating agent ratio	temp, °C	time, h	total yield,[a] %	product distribution,[a] %			boron distribution, %	
									α	β
	BMS	3:1	25	96	5	0	0	100	100	0
		3:4	25	1	61	0	33	67	67	33
	9-BBN	1:1	25	24	79	0	68	32	32	68
		1:1	65	24	97	0	71	29	29	71
		1:2	25	18	100	0	63	37	37	63
		1:2	65	10	87	0	64	36	36	64
		1:1.2	65	24	99	0	73	27	27	73
	Chx_2BH	1:1	25	24	28	0	0	100	100	0
		1:2	25	12	10	0	17	83	83	17
	Sia_2BH	1:1	25	24	30	0	0	100	100	0
		1:2	25	12	8	0	15	85	85	15
										
	BMS	3:1	25	44	13	0	0	100	100	0
		3:1	65	16	9	0	0	100	100	0
		3:4	25	24	92	16	50	34	50	50
		3:4	65	9	98	28	47	25	53	47
	9-BBN	1:1	25	44	91	3	90	7	10	90
		1:1	65	17	97	2	92	6	8	92
		1:1.2	65	8	99	3	92	5	8	92
	Chx_2BH	1:1	25	24	49	0	85	15	15	85
		1:2	25	6	100	0	77	23	23	77
	Sia_2BH	1:1	25	24	39	0	88	12	12	88
		1:2	25	6	100	0	83	17	17	83
										
	BMS	3:1	25	19	5	0	0	100	100	0
		3:4	25	19	52	0	0	100	100	0
	9-BBN	1:1	25	8	3	0	0	100	100	0
		1:1	65	7	0					
		1:2	25	22	36	0	31	69	69	31
		1:2	65	22	30	0	37	63	63	37
	Chx_2BH	1:1	25	24	44	0	0	100	100	0
		1:2	25	6	86	0	58	42	42	58
	Sia_2BH	1:1	25	24	46	0	0	100	100	0
		1:2	25	6	65	0	43	57	57	43

[a] Determined by GC, using hexadecane as internal standard.

In all of the above experiments, 2 mmol of hydride per mol of olefin were used. In order to avoid the wastage of 1 mol of hydride, an alternate method was examined. Thus, the vinylpyridines were treated with boron trifluoride etherate. The pyridine–BF_3 complexes thus obtained were hydroborated with the stoichiometric amount of hydride. Following the completion of the reaction, the boron trifluoride was removed by treatment with the addition of *N,N,N′,N′*-tetramethylethylenediamine (TMED). The organoborane obtained was oxidized with alkaline hydrogen peroxide (Scheme II).

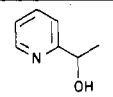
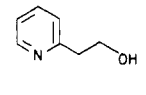
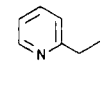
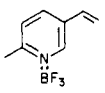
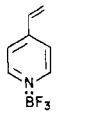
Scheme II



The hydroboration of these vinylpyridine–BF_3 complexes proceeded smoothly, although the rates of the reactions are slower than those of the vinylpyridine–borane complexes. In the case of 2-vinylpyridine and 4-vinylpyridine, α-organoboranes are the major products, whereas 2-methyl-5-vinylpyridine gave the β-organoboranes as the major products. This observation is similar to that observed in the hydroboration of the vinylpyridine–borane derivatives. The results are shown in Table III. However, in the hydroboration of the complexes 2- and 4-vinylpyridine–BF_3, the formation of α-organoboranes is increased (Chart II). Since BF_3 is a stronger Lewis acid compared to boranes such as BH_3 and R_2BH, it forms more strongly associated complexes with vinylpyridines. This results in a relative increase in the electron-withdrawing effect of the pyridine nucleus, causing the electron density at the β-carbon atom to the relatively lower. Thus, 2-vinylpyridine on hydroboration with 9-BBN yielded predominantly the β-organoboranes, whereas with other dialkylboranes such as Chx_2BH and Sia_2BH the α-organoboranes are formed preferentially, even when BF_3 was used as a complexing agent.

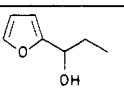
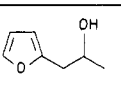
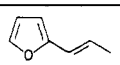
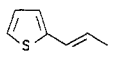
Propenyl Heterocycles. *trans*-2-(1-Propenyl)furan was hydroborated with BMS (3:1 molar ratio). The or-

Table III. Hydroboration of Vinylpyridine-Boron Trifluoride Complexes

olefin	hydroborating agent	olefin to hydroborating agent ratio	temp, °C	time, h	total yield,[a] %	product distribution,[a] %			boron distribution, %	
									α	β
	BMS	3:1	65	10	32	30	17	53	83	17
	9-BBN	1:1	25	42	74	0	56	44	44	56
		1:1	65	12	84	0	64	36	36	64
	Chx_2BH	1:1	25	24	20	0	16	84	84	16
	Sia_2BH	1:1	25	24	38	0	12	88	88	12
	BMS	3:1	65	24	75	20	60	20	40	60
	9-BBN	1:1	25	6	92	2	86	12	14	86
		1:1	65	6	96	3	86	11	14	86
	Chx_2BH	1:1	25	6	91	0	71	29	29	71
	Sia_2BH	1:1	25	6	63	0	87	13	13	87
	BMS	1:1	65	10	26	0	15	85	85	15
	9-BBN	1:1	25	80	68	0	26	74	74	26
		1:1	65	16	73	0	27	73	73	27
	Chx_2BH	1:1	25	6	59	0	41	59	59	41
	Sia_2BH	1:1	25	6	53	0	47	53	53	47

[a] Determined by GC, using hexadecane as internal standard.

Table IV. Hydroboration of 2-Propenylfuran and 2-Propenylthiophene

olefin	hydroborating agent	olefin to hydroborating agent ratio	temp, °C	time, h	total yield,[a] %	product distribution,[a] %		boron distribution, %	
								α	β
	BMS	3:1	25	2	90	96	4	96	4
	9-BBN	1:1	25	3	85	88	12	88	12
		1:1	65	2	90	96	4	96	4
	Chx_2BH	1:1	25	6	99	98	2	98	2
	Sia_2BH	1:1	25	6	98	95	5	95	5
	BMS	3:1	25	2	72	89	11	89	11
	9-BBN	1:1	25	5	85	94	6	94	6
		1:1	65	3	98	91	9	91	9
	Chx_2BH	1:1	25	10	95	95	5	95	5
	Sia_2BH	1:1	25	10	97	96	4	96	4

[a] Determined by GC, using dedecane as internal standard.

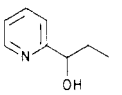
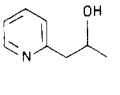
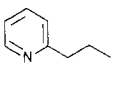
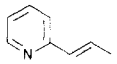
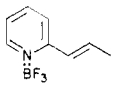
ganoboranes thus obtained upon oxidation with alkaline hydrogen peroxide yielded 1-(2-furanyl)propan-1-ol and 1-(2-furanyl)propan-2-ol in a 96:4 ratio, indicating the boron distribution realized at the α- and β-carbon atoms, respectively. The hydroboration of *trans*-2-(1-propenyl)furan with 9-BBN, Chx_2BH, and Sia_2BH proceeded smoothly, affording α-organoborane as the major product. Similarly, *trans*-2-(1-propenyl)thiophene was hydroborated with BMS, 9-BBN, Chx_2BH, and Sia_2BH and the α-organoborane proved to be the major product. The results are shown in Table IV.

trans-2-(1-Propenyl)pyridine, upon hydroboration with BMS (1:1.33 molar ratio), produced a boron distribution of 96:4 at the α- and β-carbons, respectively. Similarly, *trans*-2-(1-Propenyl)pyridine, upon hydroboration with 9-BBN, Chx_2BH, and Sia_2BH (1:2 molar ratio), gave α-organoboranes in the range of 93–99%. This remarkable increase in the formation of α-organoboranes, compared to that of 2-vinylpyridine, is attributed to the terminal methyl substituent on the olefinic double bond.

trans-2-(1-Propenyl)pyridine, upon treatment with boron trifluoride etherate, formed the corresponding complex. Hydroboration of this complex with BMS, 9-BBN, Chx_2BH and Sia_2BH produced products containing the boron at the α-carbon atom. The results are shown in Table V.

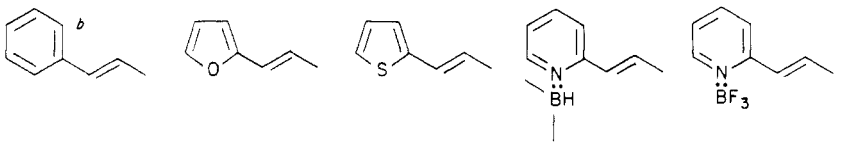
The distribution of boron in the hydroboration of 2-propenyl heterocyclic compounds, compared to that in

Table V. Hydroboration of Propenylpyridine and Propenylpyridine–Boron Trifluoride Etherate Complex

olefine	hydroborating agent	olefin to hydroborating agent ratio	temp, °C	time, h	total yield,[a] %	product distribution,[a] %			boron distribution, %	
									α	β
	BMS	3:4	25	24	63	5	4	91	96	4
		3:4	65	12	99	0	4	96	96	4
	9-BBN	1:2	25	24	54	0	7	93	93	7
		1:2	65	24	88	3	5	92	95	5
	Chx_2BH	1:2	25	24	54	20	5	75	95	5
	Sia_2BH	1:2	25	36	86	3	1	96	99	1
	BMS	3:1	25	12	72	0	1	99	99	1
	9-BBN	1:1	25	24	34	0	8	92	92	8
		1:1	65	18	99	0	1	99	99	1
	Chx_2BH	1:1	25	36	86	3	1	96	99	1
	Sia_2BH	1:1	25	60	78	6	trace	94	100	trace

[a] Determined by GC, using hexadecane as internal standard.

Chart III[a]



	↑	↑		↑	↑		↑	↑		↑	↑	
$BH_3 \cdot SMe_2$	85	15		91	9		89	11		96	4	
9-BBN	97	3		96	4		94	6		93	7	
CHx_2BH				98	2		95	5		95	5	
Sia_2BH				95	5		96	4		99	1	

	↑	↑		↑	↑		↑	↑		↑	↑	
$BH_3 \cdot SMe_2$	99	1										
9-BBN	99	1										
CHx_2BH	99	1										
Sia_2BH	100	0										

[a] The values given indicate relative distribution of boron in the hydroboration. [b] References 8 and 11.

trans-1-propenylbenzene,[12] showed that the effect of the heterocycle is pronounced in directing the boron to the α-carbon atom (Chart III). However, the effect is especially remarkable in the cases of 2- and 4-vinylpyridines.

Experimental Section

The reaction flasks and other glass equipment were stored in an oven at 150 °C overnight and assembled in a stream of dry nitrogen gas. Syringes were assembled and fitted with needles while hot and cooled in a stream of dry nitrogen gas. Special techniques were used in handling air-sensitive materials, as described elsewhere.[13]

Spectra. ^{11}B NMR spectra were recorded on a Varian FT-80A instrument. The chemical shifts are in δ relative to $BF_3 \cdot OEt_2$. ^1H NMR spectra were obtained with a Varian T-60 (60 MHz) instrument.

GC Analyses. All GC analyses were carried out with a Hewlett-Packard 5750 chromatograph using 12 ft × 0.125 in. columns packed with either 10% Carbowax 20M on Chromosorb W (100–120 mesh) or 10% SE-30 on Chromosorb W (100–120 mesh). Analyses were done by the internal standard method with response factors determined from authentic samples.

Materials. Borane–methyl sulfide (BMS) and 9-borabicyclo[3.3.1]nonane (9-BBN) were purchased from the Aldrich Chemical Company. BMS and 9-BBN in THF were estimated according to the standard procedure. Tetrahydrofuran (THF) was distilled over benzophenone ketyl and stored under nitrogen atmosphere in an ampule. 2-Vinylpyridine, 2-methyl-5-vinylpyridine, and 4-vinylpyridine were purified by distillation over calcium hydride under vacuum. 2-Vinylfuran,[14] 2-vinylthiophene,[15] *trans*-2-(1-propenyl)furan,[16] and *trans*-2-(1-propenyl)pyridine[17] were prepared according to the literature procedures. *trans*-2-(1-Propenyl)thiophene was prepared following the procedure used for *trans*-2-(1-propenyl)furan.[16] The internal standards, tridecane and hexadecane (Phillips), were kept over 4-Å molecular sieves under nitrogen atmosphere and used as such.

Some authentic samples for GC analyses were commercially available and others were prepared by literature procedures and purified by preparative GC.

Dicyclohexylborane[18] and disiamylborane[7] were prepared as reported earlier.

Hydroborations with BMS. (i) The following procedure is typical for the hydroboration of vinyl heterocycles. In a 25-mL flask equipped with a septum inlet, magnetic stirring bar, and connecting tube leading to a mercury bubbler was placed 5 mmol of olefin in THF. To it was added 0.5 mmol of internal standard, followed by BMS. The reaction was follwed by analysis for residual hydride or by ^{11}B NMR. Following completion of the reaction, the volatiles were removed under reduced pressure at 25 °C. To it was added 5 mL of THF, and the organoborane was oxidized by using 3 N sodium hydroxide and 30% hydrogen peroxide. The aqueous layer was saturated with anhydrous po-

(12) Brown, H. C.; Nelson, D. J.; Scouten, C. G. *J. Org. Chem.* **1983**, *48*, 641.
(13) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975.
(14) Moureu, M. M. C.; Dufraisse, C.; Johnson, J. R. *Liebigs Ann. Chim.* **1927**, *7*, 22.
(15) Nazzaro, R. T.; Bullock, J. L. *J. Am. Chem. Soc.* **1946**, *68*, 2122.
(16) Paul, R. *Bull. Soc. Chim. Fr.* **1935**, *2*, 2220.
(17) Johnson, A. W. *J. Org. Chem.* **1960**, *25*, 2237.
(18) Brown, H. C.; Mandal, A. K.; Kulkarni, S. U. *J. Org. Chem.* **1977**, *42*, 1396.

tassium carbonate. The organic layer was dried over 4-Å molecular sieves and analyzed by GC.

(ii) The following is the typical procedure for the hydroboration of pyridine-BF_3 complexes. In the usual experimental setup was placed 5 mmol of olefin in THF. The reaction flask was cooled to 0 °C, and to it was added 5 mmol of boron trifluoride etherate. The reaction mixture was stirred at 25 °C for 15 min. To it was added 1.66 mmol of BMS. The reaction was followed by analysis for residual hydride. Following completion of the reaction, the volatiles were removed under reduced pressure at 25 °C. To it was added 5 mL of THF, followed by 2.5 mmol of tetramehtylethylenediamine. The reaction mixture was oxidized with 3 N sodium hydroxide and 30% hydrogen peroxide. The aqueous layer was saturated with anhydrous potassium carbonate and the organic layer was dried over 4-Å molecular sieves and analyzed by GC.

Hydroboration with 9-BBN, Chx_2BH, and Sia_2BH. The reactions were carried out as described above for BMS.

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Hydroboration. 76. Hydroboration of Cyclic Dienes with Representative Hydroborating Agents

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A detailed study was made of the hydroboration of cyclic dienes with representative hydroborating agents: borane-methyl sulfide (BMS), 9-borabicyclo[3.3.1]nonane (9-BBN), disiamylborane (Sia_2BH), dibromoborane-methyl sulfide ($Br_2BH{\cdot}SMe_2$), and dibromoborane (Br_2BH). 1,4-Cyclohexadiene essentially undergoes monohydroboration with a stoichiometric amount of the representative hydroborating agents, whereas 1,5-cyclooctadiene gives the dihydroboration product predominantly. The rapid dimerization of 1,3-cyclopentadiene introduces a complication into its hydroboration. However, monomeric cyclopentadiene undergoes hydroboration primarily to the homoallylic derivative with little of the desired allylic product. Hydroboration of 1,3-cyclohexadiene with a stoichiometric amount of the hydroborating agent furnishes mainly the allylboranes, which upon treatment with acetaldehyde followed by oxidation, furnishes 1-(2-cyclohexenyl)-1-ethanol in good yield. Similarly, hydroboration of 1,3-cycloheptadiene and 1,3-cyclooctadiene furnished dihydroborated products preferentially, with lower yields of the corresponding allylboranes, characterized as 1-(2-cycloheptenyl)-1-ethanol and 1-(2-cyclooctenyl)-1-ethanol, respectively, following reaction with acetaldehyde.

The hydroboration of olefins, followed by oxidation with alkaline hydrogen peroxide of the intermediate organoborane, provides a convenient method for the stereospecific cis- and anti-Markovnikov hydration of double bonds.[2,3] A detailed study of directive effects in the hydroboration of olefins revealed that simple 1-alkenes, $RCH{=}CH_2$, undergo reaction to form predominantly the primary alcohols. 93-94%, accompanied by minor amounts, 6-7%, of the corresponding secondary alcohols.

It was evident that the extension of the hydroboration reaction to dienes probably would involve difficulties. First, the reaction of a polyfunctional olefin such as a diene with the polyfunctional borane molecule could result in the formation of polymers which might not exhibit the customary behavior of organoboranes. Secondly, conjugated dienes are less reactive toward simple addition reactions than related olefins. Consequently, the controlled monohydroboration of such dienes was a questionable possibility. Further, in the past, the hydroboration of symmetrical dienes has been studied in our laboratory.[4] In general, these studies have revealed little hope that this reaction might be synthetically useful. Reports of low conversions, mixtures of products, and substantial amounts of dihydroboration support this conclusion.[5] This is unfortunate, since the hydroboration of symmetrical dienes, if it could be controlled to give monohydroboration products, would provide a general synthesis of valuable allyl or homoallylboranes.[6] Accordingly, we undertook a systematic study of the hydroboration of cyclic dienes with representative hydroborating agents. The results of this study are reported in the present paper.

Results

A major consideration in the successful monohydroboration of cyclic dienes with a hydroborating agent would be a suitable choice of the reagent. Reaction of a difunctional substrate, the cyclic dienes, with a borane reagent (R_2BH) can and apparently frequently does lead to polyhydroboration, depending upon the nature of R. The resulting polymeric organoboranes are difficult to characterize. A second source of difficulty in the earlier work involved a lack of appreciation for the high reactivity of the allylboranes, one of the products which may be

(1) Postdoctoral research associate on Grant GM 10937-22 from the National Institutes of Health.

(2) (a) Brown, H. C.; Subba Rao, B. C. *J. Am. Chem. Soc.* **1956**, *78*, 5694; (b) *J. Org. Chem.* **1957**, *22*, 1135; (c) *J. Am. Chem. Soc.* **1959**, *81*, 6423, 6428.

(3) (a) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1959**, *81*, 247, 4106; (b) *Ibid.* **1960**, *82*, 4708; (c) *Ibid.* **1961**, *83*, 2544.

(4) (a) Zweifel, G.; Nagase, K.; Brown, H. C. *J. Am. Chem. Soc.* **1962**, *84*, 183, 190. (b) Zweifel, G.; Brown, H. C. *Ibid.* **1963**, *85*, 2066. (c) Brown, H. C.; Liotta, R.; Kramer, G. W. *J. Org. Chem.* **1978**, *43*, 1058. (d) Liotta, R.; Brown, H. C. *Ibid.* **1977**, *42*, 2836.

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