Hydroboration. 57. Hydroboration with 9-Borabicyclo[3.3.1]nonane of Alkenes Containing Representative Functional Groups[1]

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The hydroboration of alkenes containing representative functional groups was examined with 9-borabicyclo[3.3.1]nonane (9-BBN) in order to extend the hydroboration reaction for the preparation of functionally substituted organoboranes. Terminal alkenes containing a remote functional group are hydroborated with a remarkable regioselectivity (≥98% terminal), producing the corresponding stable organoboranes. 9-BBN hydroborates the allylic derivatives so as to place boron essentially on the terminal carbon atom (≥97%). The directive effect is further enhanced (≥99%) in the case of β-methylallyl derivatives. The hydroboration of crotyl derivatives attaches boron predominantly at the 2-position, followed by an elimination–rehydroboration sequence. However, crotyl alcohol can be protected against elimination as the *tert*-butyl or tetrahydropyranyl ethers. The hydroboration–oxidation of ethyl crotonate involves a series of elimination, hydroboration, and condensation processes. In the vinyl, crotyl, and isobutenyl systems, the mesomeric effect of the substituent favors the placement of boron at the β-position, while the inductive effect favors the α-position, with the former effect predominating in most cases. Acyclic β-substituted organoboranes undergo rapid elimination. Nonpolar solvents and lower reaction temperatures decrease the rate of elimination. However, those derived from cyclic vinyl derivatives are relatively stable under neutral conditions, undergoing facile elimination in the presence of a base.

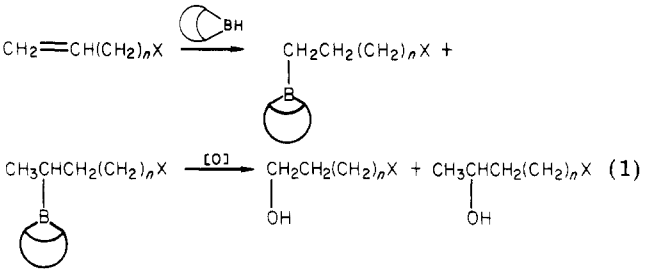
Organoboranes, conveniently prepared by the hydroboration of alkenes, are highly versatile intermediates in organic synthesis.[3,4] The synthetic application of organoboranes would be greatly enhanced if alkenes carrying common functional groups could be conveniently transformed into the corresponding organoboranes. Accordingly, the hydroboration of alkenes containing functional substituents was examined by using diborane as the hydroborating agent.[5-7] However, diborane reduces a number of common functional groups.[8] Moreover, the regiochemistry in the hydroboration of terminal alkenes with diborane is only 94:6 in favor of the terminal position. As a result, the hydroboration of functionally substituted alkenes with diborane often produces considerable amounts of minor products, which can be highly undesirable for the subsequent utilization of the resulting organoborane.

The competitive reduction of functional groups and the formation of the minor hydroboration products were minimized by the use of bis(3-methyl-2-butyl)borane (disiamylborane, Sia_2BH) instead of diborane.[5-7] However, disiamylborane is relatively unstable and must be freshly prepared prior to use, providing a serious handicap in utilizing this reagent. Recently, 9-borabicyclo[3.3.1]nonane (9-BBN) was shown to be an unusual dialkylborane with valuable properties.[9,10] Is is soluble in a variety of organic solvents. Both the crystalline 9-BBN and its solution are indefinitely stable when stored under an inert atmosphere.[9] It hydroborates alkenes with remarkable regio- and stereoselectivity, far superior to those observed with any other hydroborating agent.[3] 9-BBN reduces many of the functional groups at a relatively slow rate.[11] Therefore, it appeared that the use of 9-BBN might circumvent the difficulties encountered in utilizing disiamylborane. Preliminary results obtained with the 3-butenyl derivatives were encouraging.[12] Consequently, we undertook to examine in detail the hydroboration of representative functionally substituted alkenes.

Results and Discussion

Functional Derivatives Containing a Remote Carbon–Carbon Double Bond. A detailed study of the hydroboration of alkenes of the type $CH_2{=}CH(CH_2)_nX$ (where X = OH or OAc for n = 3 or 9 and X = CO_2R for n = 2 or 8) with diborane and disiamylborane was described earlier.[5,13,14] We now report the results of our systematic investigation with the more stable, more selective reagent 9-BBN.

Representative 10-undecenyl and 4-pentenyl derivatives were hydroborated with 9-BBN, and the resulting organoboranes were oxidized by alkaline hydrogen peroxide. Analysis of the product indicates that boron is placed essentially completely on the terminal carbon atom (eq 1).



X = OH, OAc, n = 3, 9; X = CO_2R, n = 2, 8

Similar results were obtained in the case of the 3-butenyl derivatives.[12] The enhanced directive effect exhibited by 9-BBN is evident from the data in Table I. In some cases there were detected small amounts of products from the reduction of functional groups.

Simple Allyl Derivatives. The hydroboration of representative allyl derivatives was examined with the aim

(1) Based on the thesis submitted by J.C.C. to the faculty of Purdue University (1979) in partial fulfillment of the requirements for the degree of Doctor of Philosophy.
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Table I. Stoichiometry and Directive Effects in the Hydroboration of 10-Undecenyl and 4-Pentenyl Derivatives with 9-BBN in THF at 25 °C[a]

compd	time, h	H^- used/alkene, mmol/mmol	oxidation products[b]	yield, %
10-undecenyl alcohol[c]	1.5	2 00	1,11-undecanediol	99
			1,10-undecanediol	trace
ethyl 10-undecenoate	2.0	1.00	ethyl 11-hydroxyundecanoate	78
			ethyl 10-hydroxyundecanoate	trace
			1,11-undecanediol	3
			ethyl 10-undecenoate	11
10-undecenyl acetate	2.0	1.00	11-hydroxyundecyl acetate	80
			10-hydroxyundecyl acetate	trace
			1,11-undecanediol	5
			10-undecenyl acetate	9.6
4-penten-1-ol[c]	2.0	2.00	1,5-pentanediol	98
			1,4-pentanediol	0.5
4-pentenyl methyl ether	2.0	1.00	5-methoxy-1-pentanol	93
			5-methoxy-2-pentanol	0.1
4-pentenyl chloride	2.0	1.00	5-chloro-1-pentanol	97.2
			5-chloro-2-pentanol	0.2
4-pentenyl acetate	2.0	1.00	5-acetoxy-1-pentanol	92
			5-acetoxy-2-pentanol	0.2
			1,5-pentanediol	2
			4-pentenyl acetate	4.5

[a] Compound, 10.0 mmol in all cases; 9-BBN, 10.0 mmol unless mentioned otherwise; see *c*. [b] Oxidation with NaOH/H_2O_2 following the complete uptake of hydride; in the case of esters, oxidized with $NaOAc/H_2O_2$. [c] 20.0 mmol of 9-BBN was added in these experiments.

Chart I[a]

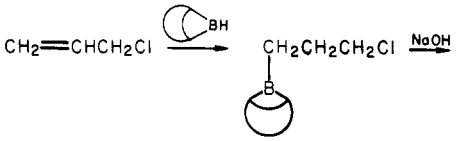
	CH_2=CHCH$_2$Cl		CH_2=CHCH$_2$OAc	
	↑	↑	↑	↑
BH_3[16]	60	40	65	35
Sia_2BH[14]	95	5	98	2
9-BBN	98.9	1.1	97.6	2.4

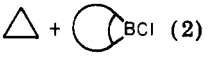
	CH_2=CHCH$_2$OCH$_3$	
	↑	↑
BH_3[16]	81	19
Sia_2BH[14]	98	2
9-BBN	98.4	1.6

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

of preparing the γ-functionalized *B*-R-9-BBN derivatives (R = alkyl).

The hydroboration of allyl derivatives with 9-BBN proceeds smoothly, affording excellent yields of the organoboranes or of the corresponding alcohols following oxidation (Table II). The inductive effect (−*I*) exerted by the allylic substituents results in poor regioselectivity in the hydroboration with diborane.[15] The directive effect of 9-BBN is so powerful that the influence of the allyl substituents in altering its preference for the terminal carbon atom is insignificant. The γ-chloroorganoborane obtained by the hydroboration of allyl chloride with 9-BBN readily cyclizes to cyclopropane upon treatment with aqueous alkali (eq 2).[16] Fortunately, it is possible to use a weaker base, sodium acetate, to achieve the oxidation to the corresponding chlorohydrin.





(2)

The directive effects observed in the hydroboration of allyl chloride, allyl acetate, and allyl methyl ether are summarized in Chart I. Information on the hydroboration of acrolein acetals with diborane or Sia_2BH is not available in the literature. Therefore, we examined the directive effects in the hydroboration of acrolein acetals with these hydroborating agents as well.[17] The results are summarized in Table II.

Scheme I

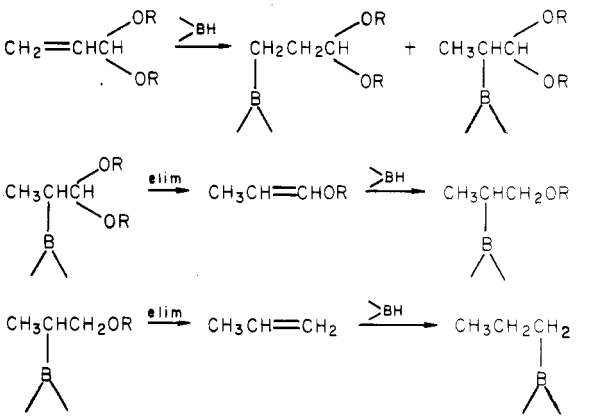
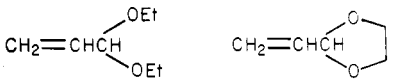


Chart II[a]



	↑	↑	↑	↑
BH_3·SMe_2	67	33	67	33
Sia_2BH	92	8	92	8
9-BBN	98	2	98	2

[a] See footnote *a* of Chart I.

The acetals were hydroborated with an excess of borane–methyl sulfide (BH_3·SMe_2, BMS) or disiamylborane (3 mol of hydride/mol of compound) in THF at 0 °C. If the boron atom attacks the terminal position, only one hydride uptake is expected. On the other hand, if boron attacks the internal carbon of the double bond, up to 3 equiv of hydride can be used: the first equivalent for the

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(17) We actually used a more convenient substitute, BH_3·SMe_2 (BMS), instead of borane–THF.

Table II. Stoichiometry and Directive Effects in the Hydroboration of Allylic Derivatives in THF[a]

compd	reagent	temp, °C	time, h	H^- used[b]	oxidation product	yield, %
allyl alcohol	9-BBN[c]	25	8	1.98	1,3-propanediol	96
					1,2-propanediol	2
					1-propanol	1
allyl chloride	9-BBN	25	2	1.00	3-chloro-1-propanol	93
					1-propanol	1
allyl methyl ether	9-BBN	25	2	1.00	3-methoxy-1-propanol	94
					1-methoxy-2-propanol	trace
					1-propanol	1.5
allyl acetate	9-BBN	25	2	1.00	3-acetoxy-1-propanol	82
					1,3-propanediol	2
					1-propanol	2.1
					allyl acetate	10
acrolein diethyl acetal	9-BBN	25	2	1.00	3,3-diethoxy-1-propanol	94.7
	$BH_3 \cdot SMe_2$	0	4	1.59	3,3-diethoxy-1-propanol	58
	Sia_2BH[d]	0	7	1.17	3,3-diethoxy-1-propanol	90.5
					1-ethoxy-2-propanol	1
acrolein ethylene acetal	9-BBN	25	2	1.00	2-(β-hydroxyethyl)-1,3-dioxolane	96
					acrolein ethylene acetal	1.5
	$BH_3 \cdot SMe_2$	0	6.5	1.65	2-(β-hydroxyethyl)-1,3-dioxolane	67
	Sia_2BH[d]	0	7.0	1.18	2-(β-hydroxyethyl)-1,3-dioxolane	87

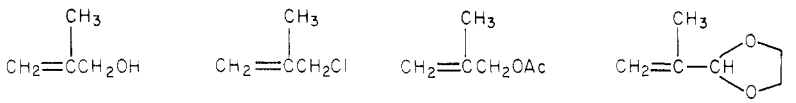
[a] Compound, 10 mmol; reagent, 10 mmol, unless mentioned otherwise. [b] Millimoles of hydride used per millimole of compound. [c] 20 mmol of 9-BBN used. [d] 30 mmol of Sia_2BH used.

Table III. Stoichiometry and Directive Effects in the Hydroboration of β-Methylallyl Derivatives[a]

compd	reagent	temp, °C	time, h	H^- used[b]	oxidation products[c]	yield, %
β-methylallyl alcohol	9-BBN[d]	25	6	2.0	2-methyl-1,3-propanediol	100
					2-methyl-1,2-propanediol	0.5
β-methylallyl chloride	9-BBN	25	1	1.0	2-methyl-3-chloropropanol	96[e]
β-methylallyl acetate	9-BBN	25	1	1.0	2-methyl-3-acetoxypropanol	94.5
					isobutyl alcohol	1.0
methacrolein ethylene acetal	9-BBN	25	2	1.0	2-(β-hydroxyisopropyl)-1,3-dioxolane	98
	$BH_3 \cdot SMe_2$	0	6	1.3	2-(β-hydroxyisopropyl)-1,3-dioxolane	82
	Sia_2BH[f]	0	7	1.04	2-(β-hydroxyisopropyl)-1,3-dioxolane	95

[a] Compound, 10 mmol; reagent, 10 mmol, unless mentioned otherwise. [b] Millimoles of H^- used per millimole of compound. [c] Oxidation with $NaOAc/H_2O_2$. [d] 20 mmol of 9-BBN was used. [e] A low yield (40%) of this alcohol was obtained when oxidized with $NaOH/H_2O_2$. [f] 30 mmol of Sia_2BH was used.

Chart III[a]



	↑	↑	↑	↑	↑	↑	↑	↑
BH_3			88	12[19]			84	16
Sia_2BH			100	0[19]			98	2
9-BBN	99.5	0.5	100	0	99	1	100	0

[a] See footnote a of Chart I.

initial hydroboration, the second equivalent for the rehydroboration following the first elimination, and the third equivalent again for rehydroboration following a second elimination (Scheme I). From the amounts of hydride utilized, one can calculate the relative isomer distribution. A comparison of the directive effect exhibited by these reagents in the hydroboration of two representative acetals is shown in Chart II. It is clear that in the hydroboration of simple allyl derivatives, 9-BBN exhibits a powerful directive effect favoring the terminal position, with only insignificant side reactions such as the reduction of the functional group.

β-Methylallyl Derivatives. In the case of dissymmetric allylic systems containing more β than γ substituents, the directive effect of the β-alkyl group largely overcomes the directive effect of the functional substituent, resulting in predominant γ addition.[18] Excellent yields of the corresponding alcohols were realized after oxidation (Table III). The β-methyl group in these derivatives directs the boron of 9-BBN to the terminal position even more strongly, compared with the simple allylic system, giving a cleaner reaction so that only trace amounts of byproducts are formed (Chart III).

Crotyl (2-Butenyl) Derivatives. The directive effect of the allylic system is partially obscured by different

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degrees of substitution on two ends of the olefinic linkage. Consequently, a more representative series consisting of the crotyl (2-butenyl, γ-methylallyl) derivatives was examined. The crotyl system contains, in most cases, a trans double bond where the steric and electronic effects at both ends of the double bond are similar due to the same degree of alkyl substitution. Only the electronic effect of the functional group, which polarizes the double bond, controls the orientation of the boron becoming attached to the double bond.

The boron atom is placed exclusively at the 2-position in the hydroboration of crotyl acetate, crotyl chloride, and crotyl alcohol, followed by a fast elimination and rehydroboration to give 1-butanol after oxidation. In the case of crotyl methyl ether and crotyl ethyl ether, a mixture is formed with 8% of the boron at the 3-position and 92% at the 2-position, followed by partial elimination–rehydroboration (Table IV). However, the *tert*-butyl group in crotyl *tert*-butyl ether can act as a protecting group, minimizing elimination during the hydroboration reaction. The tetrahydropyranyl (THP) group is even better as a protecting group since it can be easily removed by acid hydrolysis. The directive effects exhibited by 9-BBN in the hydroboration of crotyl derivatives are compared with those realized for diborane and Sia_2BH in Table V.

The hydroboration–oxidation of ethyl crotonate resulted in the formation of ethyl 2-ethyl-3-hexenoate (**1**, 14%) and ethyl 2-ethyl-3-oxohexanoate (**2**, 52%) as major products. The formation of these unusual condensation products can be rationalized on the basis of a series of reactions.

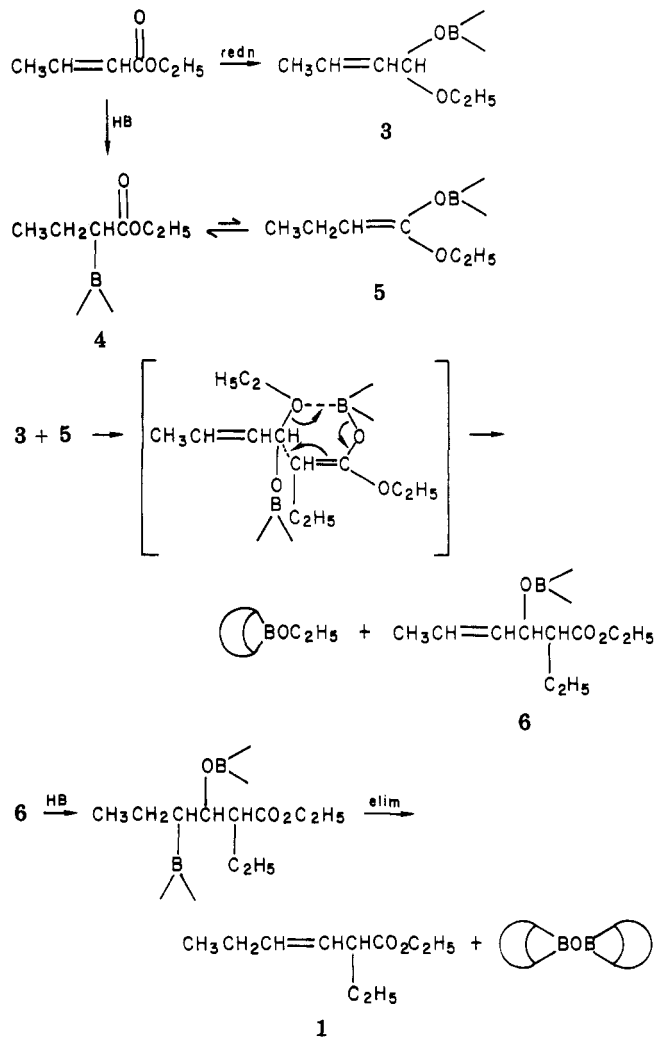
The powerful directive effect of the carbethoxy group in ethyl crotonate favors placement of the boron exclusively at the 2-position, followed by a rapid transfer of boron from carbon to the neighboring oxygen.[14] The resulting (vinyloxy)borane **5** can either hydrolyze to ethyl butyrate or condense with the reduction product of ethyl crotonate, **3**, to form the dimer **6**. The hydroboration of **6**, followed by elimination, can produce **1** (Scheme II).

Alternatively, the condensation of **5** with **4** can afford the dimer **7**, which can form **2** via an elimination–hydrolysis sequence (Scheme III). The ^{11}B NMR examination of the hydroboration mixture prior to oxidation shows the only major absorption at δ 56.17 due to *B*-OR-9-BBN (OR = alkoxy) and the corresponding (vinyloxy)-borane. This supports the mechanism suggested for the formation of **1** and **2**.

The hydroboration of *tert*-butyl crotonate proceeds to form the corresponding *B*-OR- or *B*-(vinyloxy)-9-BBN as the major product (δ 55.75) with only a small amount of *B*-R-9-BBN. Oxidation with alkaline hydrogen peroxide affords 1-*tert*-butoxy-2-butanol (**11**, 16%), *tert*-butyl butyrate (**9**, 10%), and 1-butene (**12**, 4%). The formation of these products is shown in Scheme IV.

Acyclic Vinyl Derivatives. A number of vinylic derivatives such as fluorinated ethylene,[19,20] vinyl chloride,[21] vinyltrimethylsilane,[22] trimethylsilyl enol ethers,[23,24] ethyl vinyl ether,[25] enol acetate,[7,26] and enamines,[27,28] have been

Scheme II



Scheme III

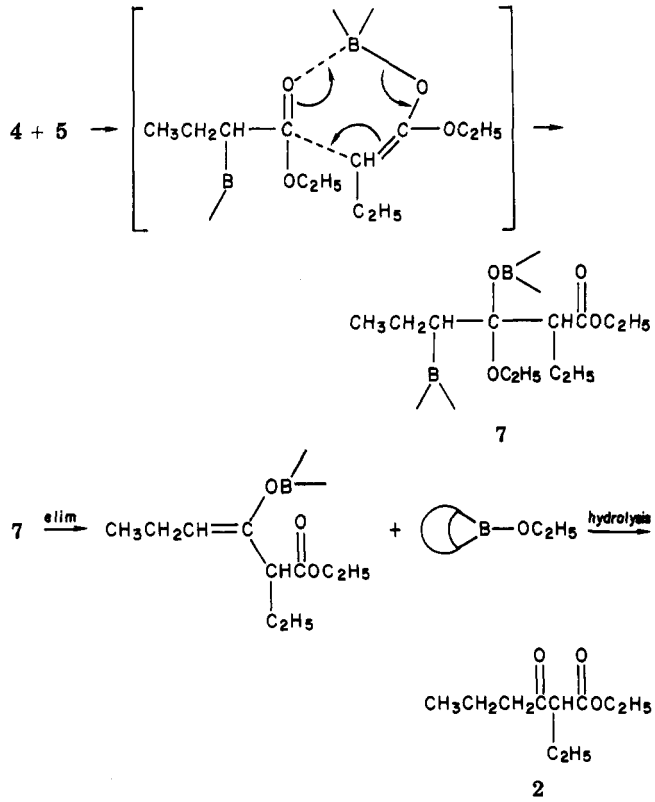


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Table IV. Hydroboration of Various Crotyl Derivatives with 9-BBN at 25 °C Followed by Oxidation

compd[a]	9-BBN, mmol	solvent	time, h	H^- used[b]	oxidation products[c]	yield, %
crotyl alcohol	20	THF	3	1.76	1-butanol	45
			20	2.00→	crotyl alcohol	42
	30	THF	24	2.42	1-butanol	80
			65	2.78→	1,2-butanediol	18
crotyl chloride	20	THF	7	1.33		
			48	1.93→	1-butanol	96.3
	10	CCl_4	4	0.65		
			24	1.00→	1-butanol	46
	20	CCl_4	2	0.71		
			53	1.91→	1-butanol	90
crotyl acetate	20	THF	4	1.34	1-butanol	67
			42	1.99→	crotyl alcohol	4
					crotyl acetate	18
					1,2-butanediol	4.5
crotyl methyl ether	20	THF	6	1.56	1-butanol	89
			51	1.82→	4-methoxy-2-butanol	8
	20	CCl_4	5	1.55	1-butanol	77
			48	1.97→	4-methoxy-2-butanol	6.5
	10	CCl_4	6	0.90	1-butanol	37
			20	1.00→	4-methoxy-2-butanol	3.4
					1-methoxy-2-butanol	20.7
crotyl ethyl ether	10	CCl_4	20	1.00	1-butanol	32
					4-ethoxy-2-butanol	5
					1-ethoxy-2-butanol	23
crotyl *tert*-butyl ether	10	THF	8	0.95	1-butanol	0.5
					4-*tert*-butoxy-2-butanol	15
					1-*tert*-butoxy-2-butanol	74
					crotyl *tert*-butyl ether	11
crotyl tetrahydropyranyl ether	10	THF	6	1.00	1-butanol	4
					4-OTHP-2-BuOH	11.5
					1-OTHP-2-BuOH	55.5
					crotyl tetrahydropyranyl ether	25
	12.5	THF	6	1.25	1-butanol	4
					4-OTHP-2-BuOH	13.8
					1-OTHP-2-BuOH	67.2
					crotyl tetrahydropyranyl ether	8
ethyl crotonate	15	THF	3	0.96	1-butanol	2.5
			55	1.41→	ethyl butyrate	2
					1-butene	2
					ethyl 2-ethyl-3-hexenoate	14
					ethyl 2-ethyl-3-oxohexanoate	52
tert-butyl crotonate	14	THF	3	0.70	*tert*-butyl butyrate	10
			72	1.18→	1-butene	4
					tert-butyl crotonate	2
					1-*tert*-butoxy-2-butanol	16

[a] 10 mmol of the compound was taken. [b] Millimoles of hydride used per millimole of compound. [c] Oxidation products are for experiments with maximum uptake of hydride (H^-).

Table V. Comparison of Directive Effects in the Hydroboration of Crotyl Derivatives

	normalized isomer ratio[a]					
	BH_3[b] at 0 °C		Sia_2BH at 0 °C		9-BBN at 25 °C	
compd	3	2	3	2	3	2
crotyl alcohol	10	90	13	87[b]	0	100
crotyl chloride	0	100	0	100[c]	0	100
crotyl acetate	5	95			0	100
crotyl methyl ether					8	92
crotyl ethyl ether	16	84			8.3	91.7
crotyl *tert*-butyl ether					16.8	83.2
crotyl tetrahydropyranyl ether	8.6	91.4			16.2	83 8
ethyl crotonate					0	100

[a] Determined from the oxidation products: 3 and 2 refer to the position on which boron is placed in hydroboration. [b] Taken from ref 6. [c] Taken from ref 18.

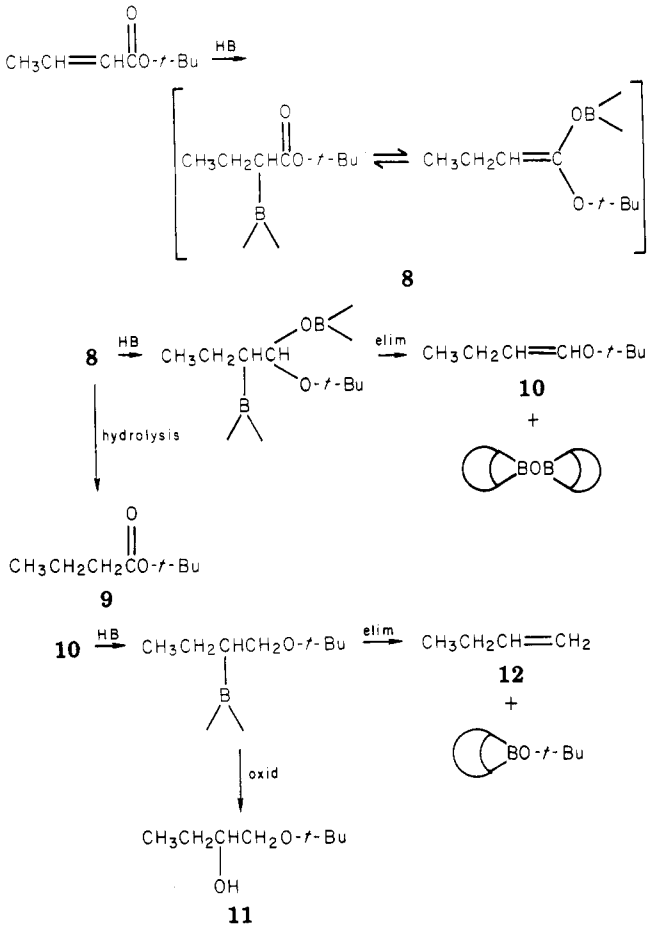
(27) Borowitz, I. J.; Williams, G. J. *J. Org. Chem.* **1967**, *32*, 4157.
(28) Pasto, D. J.; Snyder, R. *J. Org. Chem.* **1966**, *31*, 2777.

hydroborated in the past with diborane and disiamylborane. We carried out a systematic examination of representative vinyl derivatives with respect to hydroboration with 9-BBN (Scheme V).

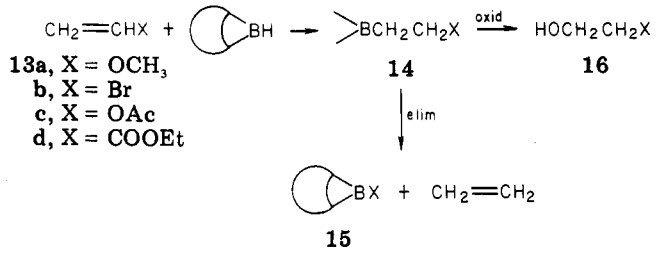
The hydroboration of vinyl methyl ether proceeds rapidly with >94% of boron placed at the β-position, followed by a slow elimination, liberating ethylene. Subsequent oxidation affords trace amounts of 2-methoxyethanol. In order to suppress the elimination reaction, we carried out the hydroboration in a nonpolar solvent, CCl_4, at low temperatures (35, 25, and 10 °C), and the yield of 2-methoxyethanol increased from 6% to 36% and finally to 83% (Table VI). Although a longer reaction time is required for hydroboration at lower temperatures, the elimination is dramatically decreased. Obviously, more polar solvents and higher temperatures favor elimination.

In the hydroboration of vinyl bromide and vinyl acetate, boron is placed essentially at the position β to the substituent, followed by a fast elimination and rehydroboration. A competitive reduction of the acetoxy group is expected in the case of vinyl acetate. Consequently, some of the ethylene generated could not be rehydroborated, as observed by ^1H NMR (Table VI).

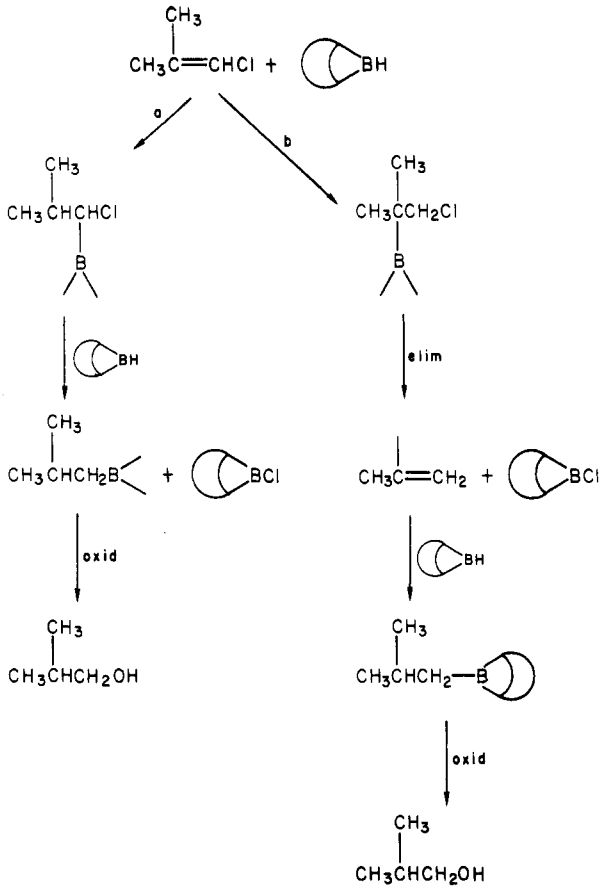
Scheme IV



Scheme V



Scheme VI



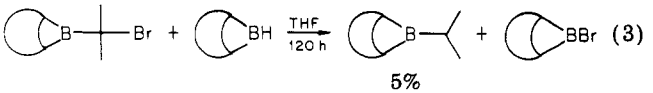
The powerful directive effect of the carbethoxy group orients boron predominantly to the α-position, followed by a rapid transfer of boron from carbon to the adjacent oxygen.[14] This intermediate can hydrolyze to ethyl propionate.[29] The low material balance (35.4%) realized on oxidation might be due to the polymerization of ethyl acrylate.[30] A small amount of boron is placed at the β-position, resulting in 4.2% of ethyl 3-hydroxypropionate after oxidation. However, no 1,3-propanediol was detected.

Isobutenyl Derivatives. In the hydroboration of isobutenyl ethyl ether, boron is placed exclusively at the tertiary position, β to the ethoxy group. The resulting β-ethoxyorganoborane is relatively stable at room temperature, as can be seen from the good yields of β-ethoxy alcohols on oxidation (Table VII).

The ^{11}B NMR examination of the hydroboration product from isobutenyl chloride and 9-BBN in THF (1:1 stoichiometry) revealed the formation of *B*-R-9-BBN (δ 88.1) and *B*-Cl-9-BBN (δ 17.8, THF complex) in 1:1 ratio. Oxidation produced isobutyl alcohol in 45% yield. In CCl_4 solvent, approximately the same ratio of *B*-R-9-BBN (δ 88.1) and *B*-Cl-9-BBN (δ 80.9) was observed. However, the ^1H NMR analysis, with a known amount of benzene as internal standard, indicated the consumption of only 46% of isobutenyl chloride. The possible pathways are shown in Scheme VI.

Pathway "a" involves the placement of boron at a position α to the substituent, followed by the hydride exchange between the α-chloroorganoborane and 9-BBN, leading to the formation of *B*-*i*-Bu-9-BBN. Pathway "b" consists of the placement of boron at the β-position with respect to chlorine, followed by a fast elimination of *B*-Cl-9-BBN and rehydroboration. Both pathways utilize 2 mol of 9-BBN/mol of isobutenyl chloride and produce isobutyl alcohol on oxidation.

The hydride exchange reaction between *B*-(2-Br-2-Pr)-9-BBN[31] and 9-BBN was very slow, proceeding only to 5% completion in 5 days (eq 3). Consequently, pathway "a" is unlikely. When isobutenyl chloride was hydroborated with 2 equiv of 9-BBN, followed by oxidation,



(3)

5%

a 78% yield of isobutyl alcohol was realized. In CCl_4 solvent, 93% of isobutenyl chloride was consumed in 144 h (^1H NMR). It was also observed that the rate of dis-

(29) Similar to the formation of **9** in Scheme IV.

(30) Parallel observation was made in the hydroboration of methyl methacrylate: Stone, F. G. A.; Emeleus, H. J. *J. Chem. Soc.* **1950**, 2775.

(31) Prepared from *B*-*i*-Pr-9-BBN and bromine: De Lue, N. R. Ph.D. Thesis, Purdue University, 1977.

appearance of 9-BBN is twice the rate of consumption of isobutenyl chloride (Table VII).

Cyclic Vinyl Derivatives. In the hydroboration of 7-chlorodibenzobicyclo[2.2.2]octatriene, boron is placed predominantly at the position β to the chlorine substituent.[32] An attempted oxidation with alkaline hydrogen peroxide afforded the parent alkene. However, oxidation in a nonaqueous medium gave the desired chlorohydrin (Scheme VII).[32] On the other hand, Pasto[33] reported that the hydroboration of 2-chloronorbornene results in 82:18 regiochemistry in favor of the α-position. Yamamoto[34] observed the placement of boron predominantly at the β-position in the hydroboration of 2-bromonorbornene with 9-BBN. In view of these conflicting reports, we undertook to examine representative cyclic vinyl derivatives.

1-Chlorocyclopentene is hydroborated slowly with 9-BBN, accompanied by elimination to form cyclopentene, which is then rapidly hydroborated with 9-BBN. In the hydroboration of 1-acetoxycyclopentene, 97% of the boron is placed at the β-position, followed by elimination to form cyclopentene. Since the formation of cyclopentene is slower than the consumption of 9-BBN through the initial hydroboration, a considerable amount of cyclopentene remains in the solution, as estimated by ^{1}H NMR (56%) and by GC analysis (46%) following oxidation. There is a slow reduction of the acetoxy group forming 7% of 1,2-cyclopentanediol. The directive effects are summarized in Chart IV.

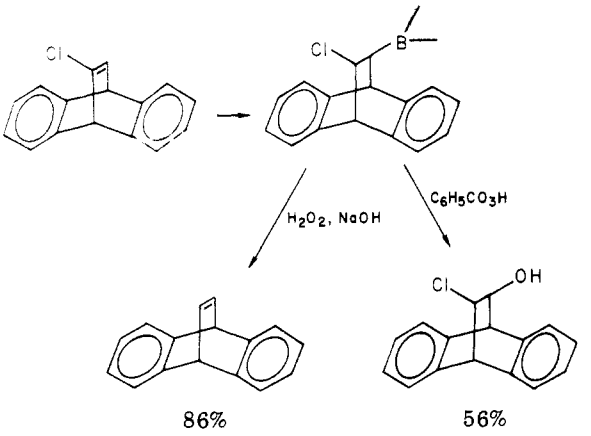
In the hydroboration of 2-chloronorbornene, a low (21%) material balance was realized, and most of it (18%) was the starting material, in addition to small amounts of norbornanol (1%) and norcamphor (2%).[34] Therefore, we investigated the hydroboration of 2-chloronorbornene in detail. The ^{11}B NMR analysis of the reaction mixture after 96 h at 25 °C indicated the presence of *B*-alkyl-9-BBN (δ 87,86%) and *B*-Cl-9-BBN (5.5%) with traces of 9-BBN (δ 27). Oxidation of the reaction mixture with alkaline hydrogen peroxide and GC analysis of the product on a 6-ft CW-20M column showed norbornanol (13%), 2-chloronorbornene (10.2%), the desired chlorohydrin (1.5%), and norcamphor (1%). A low material balance (25.7%) was realized. However, the high yield (95%) of 1,5-cyclooctanediol rules out the possibility of migration of the B–C bond in 9-BBN to the α-position in 2-chloronorbornene. Analysis on a SE-30 column, however, indicated the presence of norbornene (56%).[35]

The oxidation of the reaction mixture from 2-chloronorbornene and 9-BBN by a simultaneous addition of 3 *M* sodium acetate and hydrogen peroxide at 0 °C, followed by stirring at 25 °C for 12 h, afforded the chlorohydrin (42%), norbornene (19.2%), and norbornanol (17%, Table VIII).

The hydroboration of 2-chloronorbornene with 2 equiv of 9-BBN indicated that the consumption of the second hydride is very slow. When the reaction mixture was heated under reflux in THF (65 °C) for 24 h, almost all of the hydride was consumed. *B*-Cl-9-BBN (37%) and *B*-OR-9-BBN (26%) was estimated by ^{11}B NMR. The latter derivatives arise from the cleavage of THF (Scheme VIII).

It is clear that the hydroboration of 2-chloronorbornene with 9-BBN exhibits 99:1 regiochemistry in favor of the β-position. The resulting β-chloroorganoborane (18) readily eliminates *B*-Cl-9-BBN to form norbornene, es-

Scheme VII



Scheme VIII

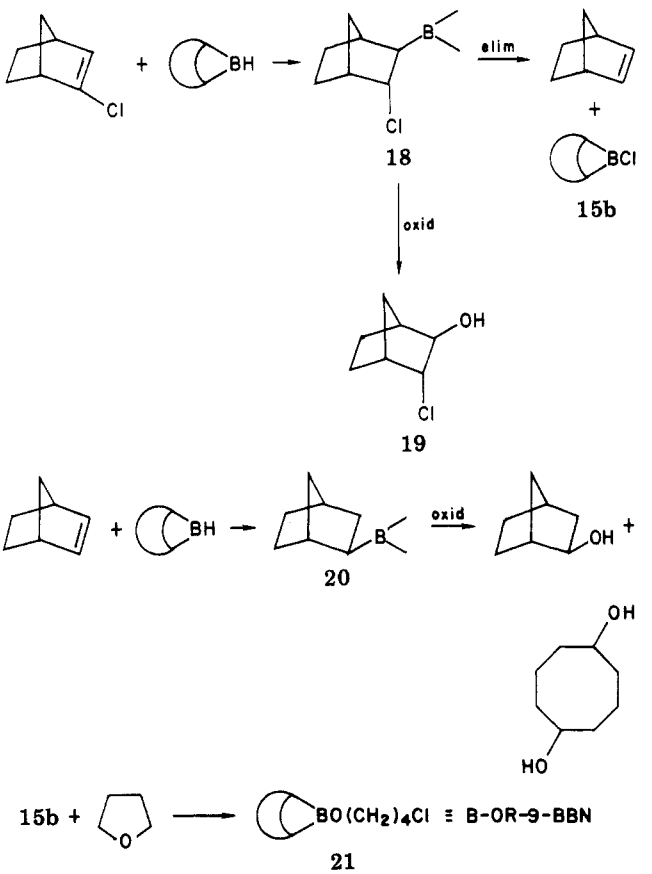
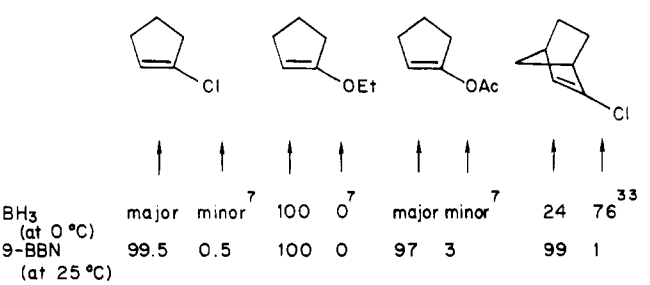


Chart IV[a]



[a] See footnote *a* of Chart I.

(32) Cristol, S. J.; Parungo, F. P.; Plorde, D. E. *J. Am. Chem. Soc.* **1965**, *87*, 2870.
(33) Pasto, D. J.; Hickman, J. *J. Am. Chem. Soc.* **1967**, *89*, 5608.
(34) Yamamoto, Y.; Toi, H.; Moritani, I. *Chem. Lett.* **1974**, 485.
(35) On a 6-ft CW-20M column, THF and norbornene have identical retention times. However, estimation of norbornene was possible on a 6-ft SE-30 column.

Table VI. Hydroboration of Representative Acyclic Vinyl Derivatives with 9-BBN[a]

compd	solvent	temp, °C	time, h	H^- used[b]	hydroboration products[c] (% yield) ^1H NMR	hydroboration products[c] (% yield) ^{11}B NMR	oxidation products[d] (% yield)
vinyl methyl ether	THF	25	9			**15a**	ethylene (82), 2-methoxyethanol (trace)
vinyl methyl ether[e]	CCl_4	35	1.5		ethylene (28), **15a** (43), **13a** (30), **14a** (20)		ethylene (40), 2-methoxyethanol (6)
vinyl methyl ether	CCl_4	25	3				ethylene (8), 2-methoxyethanol (36)
vinyl methyl ether	CCl_4	10	6				2-methoxyethanol (83)[f]
vinyl acetate	THF	25	24	1.0		**14c** (43.1), **17** (1.7),[g] **15c** (55.2)	
vinyl acetate	CCl_4	25	24	1.0	**13c** (53), ethylene (4)		
vinyl acetate[h]	THF	25	24	2.0		**14c** (44.1), **17** (1.3),[g] **15c** (54.6)	ethanol (92)
vinyl acetate[h]	CCl_4	25	48	2.0	**13a** (15), ethylene (15)		
vinyl bromide	THF	25	24	1.0		**14b** (38.3), **17** (23.9),[g] **15b** (37.8)	
vinyl bromide	CCl_4	25	24	1.0	**13b** (56)	**14b** (40), **15** (60)	
vinyl bromide[h]	THF	25	48	2.0		**17** (23.8),[g] **15b** (31.5)	
vinyl bromide[h]	CCl_4	25	48	1.75	**13b** (10)	**15b** (37.6), **14b** (45.7), 9-BBN (16.4)	
ethyl acrylate	THF	25	3	1.0		**17** (70), **14d** (trace)	ethyl 3-hydroxypropionate (4.2), 1-propanol (1), 1,2-propanediol (7.4), ethyl propionate (17.8), ethyl acrylate (5)
ethyl acrylate	CCl_4	25	20	1.0	**13d** (15)	**17** (70), **14d** (trace)	

[a] 20 mmol of 9-BBN was reacted with 20 mmol of the compound, unless mentioned otherwise. When the vinyl derivative was added via a precooled syringe, the stopcock was closed to avoid any escape of vinyl halide or the ethylene formed. [b] Millimoles of hydride used per millimole of compound. [c] The reaction mixture was examined by NMR: absolute yields in the case of ^1H NMR analysis (benzene as an internal standard for integration) and relative yields in the case of ^{11}B NMR. [d] Oxidation products were analyzed by GC; the volume of ethylene evolved was measured. [e] 24 mmol of 9-BBN was taken. [f] A parallel blank experiment indicated that 89% of 2-methoxyethanol can be transferred into the organic layer by adding K_2CO_3 to the oxidation product containing CCl_4-EtOH-H_2O as solvent. Consequently, the actual yield of 2-methoxyethanol could be ~93%. [g] *B*-OR-9-BBN (**17**) arising from the reductions of OAc or COOEt groups or via the cleavage of THF by **15** (X = Cl, Br). [h] 10 mmol of compound was taken.

Table VII. Hydroboration of Isobutenyl Derivatives with 9-BBN at 25 °C[a]

compd	solvent	time, h	H^- used, mmol	olefin used,[b] mmol	oxidation products[d]	yield, %
isobutenyl chloride	THF	2	3.8		isobutyl alcohol	45
		24	20.0→			
isobutenyl chloride[c]	THF	3.5	5.2		isobutyl alcohol	78
		76.0	19.4→			
isobutenyl chloride	CCl_4	2.0	0.8		isobutyl alcohol	41
		9.5	9.8	3.8		
		60.0	20.0→	9.2		
isobutenyl chloride[c]	CCl_4	2.5	0.5	0.2	isobutyl alcohol	67
		70.0	15.0	7.3		
		144.0	17.5→	9.3		
isobutenyl ethyl ether	THF	3.0	8.6		isobutyl alcohol	8
		48.0	20.0→		1-ethoxy-2-methyl-2-propanol	70
					isobutenyl ethyl ether	9

[a] 20 mmol of 9-BBN and 20 mmol of the compound were used, unless mentioned otherwise. [b] Olefin consumption was determined by ^1H NMR with benzene as an internal standard for integration. [c] 10 mmol of compound was used. [d] Oxidation was carried out after maximum amount of H^- was consumed.

pecially at higher temperatures and in the presence of base. However, oxidation under mild conditions ($NaOAc/H_2O_2$) affords the corresponding chlorohydrin (**19**).

The hydroboration–elimination reaction can be easily

Table VIII. Hydroboration of Representative Cyclic Vinyl Derivatives with 9-BBN[a]

compd	solvent	temp, °C	time, h	H^- used[b]	hydroboration product (% yield)		oxidation product (% yield)
					^1H NMR	^{11}B NMR[c]	
1-chlorocyclopentene	THF	25	23	0.14		*B*-R-9-BBN (18.5), *B*-OR-9-BBN (8.5)	
			144	0.67		9-BBN (33), **15b** (40)	
1-chlorocyclopentene	THF	65	5	1.0		*B*-R-9-BBN (46.4), *B*-OR-9-BBN (5.8), **15b** (47.8)	cyclopentanol (39), cyclopentanone (0.5), 1-chlorocyclopentene (34)
1-chlorocyclopentene[d]	THF	65	24	2.0		*B*-R-9-BBN (42), *B*-OR-9-BBN (4), **15b** (54)	cyclopentanol (83.1), cyclopentanone (0.5), 1-chlorocyclopentene (7)
1-ethoxycyclopentene	THF	25	1.5	1.0		*B*-R-9-BBN (92), *B*-OR-9-BBN (8)	2-ethoxycyclopentanol (82.2) cyclopentanol (2), cyclopentanone (trace), 1-ethoxycyclopentene (5)
1-acetoxycyclopentene	CCl_4	25	22	1.0	cyclopentene (5), 1-acetoxycyclopentene (20)		cyclopentene (46), 1-acetoxycyclopentene (18), cyclopentanol (11.6), cyclopentanone (2.1), 1,2-cyclopentanediol (7)
2-chloronorbornene[j]	THF	25	96			*B*-R-9-BBN (86), *B*-OR-9-BBN (8.5), **15b** (5.5), 9-BBN (trace)	(I)[e] norbornene (56), 2-Cl-norbornene (10.2), norcamphor (1), *exo*-norbornanol (13), 3-chloro-2-norbornanol (1.5), 1,5-cyclooctanediol (95); (II)[f] norbornene (19.2), 2-chloronorbornene (9.7), norcamphor (1), *exo*-norbornanol (17), 3-chloro-2-norbornanol (4.2)
2-chloronorbornene[k]	THF	25	168			*B*-R-9-BBN (37.4), *B*-OR-9-BBN (25.2), **15b** (36.6), 9-BBN (0.8)	*exo*-norbornanol (88.4), norcamphor (1), 3-chloro-2-norbornanol (trace), 1,5-cyclooctanediol (100)
		65	24				
2-chloronorbornene[j]	CCl_4	25	96	0.92[g]	18 (92),[h] 2-chloronorbornene (8)[h]		norbornene (92),[i] 2-chloronorbornene (8)[i]

[a] 10 mmol of compound was treated with 10 mmol of 9-BBN, unless mentioned otherwise. [b] Millimoles of hydride used per millimole of compound. [c] *B*-R-9-BBN ≡ *B*-alkyl-9-BBN; *B*-OR-9-BBN ≡ *B*-alkoxy-9-BBN. In the hydroboration of chlorovinyl derivatives, *B*-OR-9-BBN is the THF-cleaved product, **21**; in other cases, it is either *B*-ethoxy or *B*-acetoxy derivative, obtained via elimination; all of these species possess identical ^{11}B chemical shifts; relative yields. [d] 20 mmol of 9-BBN was added. [e] Oxidized by 3 M NaOH and 30% H_2O_2 added at 0 °C and then 2 h at 50 °C; material balance 81.7%; hydride balance 84.5%. [f] Oxidized by 3 M NaOAc and 30% H_2O_2 added at 0 °C and then 12 h at 25 °C; material balance 88.9%; hydride balance 96.2%. [g] Olefin used, as determined by ^1H NMR (with benzene as standard). [h] While the olefinic proton disappears, the proton α to chlorine appears. [i] β-Chloroorganoborane is readily converted into norbornene when stirred with 3 M NaOH for 5 min. [j] 5 mmol of alkene was treated with 5 mmol of 9-BBN. [k] 5 mmol of alkene was treated with 10 mmol of 9-BBN.

monitored by ^1H NMR when the reaction is carried out in CCl_4 solvent. The disappearance of the olefinic proton in 2-chloronorbornene was estimated by using a known amount of benzene (an internal standard for integration). As the reaction progressed, the proton α to chlorine in **18** (δ 4.2) increases in intensity, with 92% of 2-chloronorbornene consumed in 4 days. On treatment with 3 *M* NaOH, **18**, was quantitatively converted to norbornene (δ 5.8).

In conclusion, this systematic study of the hydroboration of various functionally substituted alkenes with 9-BBN provides an understanding of the influence of such functional groups in hydroboration. In most cases, the hydroboration of carbon–carbon double bonds is much faster than the reduction of a number of functional groups: the halogen and alkoxy groups are generally inert, while hydroxy groups liberate hydrogen, with no further reaction; even slowly reducible groups such as ester and nitrile are tolerated, providing organoboranes containing such substituents. The highly reactive carbonyl groups in aldehydes and ketones can be protected as the acetals or ketals. The elimination in the case of some β-substituted organoboranes leads to unexpected products. However, this can be avoided by using protecting groups or controlled reaction conditions. The results, combined with those obtained from the hydroboration of 3-butenyl derivatives,[12] indicate that there are little or no inductive effects of the substituent on the hydroboration of an alkene when the substituent is separated by three or more methylene groups from the olefinic linkage. Progressively increasing influence, both on the rate of hydroboration and on product distribution, is apparent when the functional group approaches the olefinic linkage. The functionally substituted *B*-R-9-BBN derivatives, now readily available, are highly promising as synthetic intermediates.

Experimental Section

General Comments. The techniques described in chapter 9 of ref 3 were used extensively. All glassware was dried at 140 °C for at least 4 h, assembled hot, and allowed to cool under a purge of prepurified nitrogen. All reactions were carried out under a static pressure of nitrogen in round-bottomed flasks fitted with

side arms capped with rubber septa and were stirred magnetically using oven-dried, Teflon-coated stirring bars. All transfers of liquids and solutions of organometallic reagents were done either with hypodermic syringes fitted with stainless-steel needles or by the double-ended needle technique. Gases were delivered by using gas-tight syringes.

Materials. The *n*-alkanes (Phillips) employed as GC internal standards were used as received. THF was freshly distilled from a small amount of lithium aluminum hydride. 9-BBN was either prepared from borane–tetrahydrofuran and 1,5-cyclooctadiene[10] or purchased from Aldrich and recrystallized once from THF before use. 10-Undecen-1-ol, 4-penten-1-ol, 4-pentenyl acetate, allyl alcohol, allyl chloride, allyl acetate, acrolein diethyl acetal, β-methylallyl alcohol, β-methylallyl chloride, crotyl, alcohol, crotyl chloride, ethyl crotonate, vinyl acetate, vinyl bromide, ethyl acrylate, and isobutenyl chloride were obtained from Aldrich Chemical Co. Allyl methyl ether and 4-pentenyl chloride were obtained from Chemical Samples Co. 10-Undecenyl acetate, β-methylallyl acetate,[36] and crotyl acetate were prepared from the corresponding alcohols by standard acetylation methods. Ethyl 10-undecenoate was prepared from 10-undecenoyl chloride (Aldrich) and ethyl alcohol. Acrolein ethylene acetal and methacrolein ethylene acetal were prepared from the corresponding aldehydes and ethylene glycol by following the procedure described for the preparation of diethyl acetal.[37] *tert*-Butyl crotonate was prepared from crotonic acid (Aldrich) as described elsewhere.[36] Crotyl *tert*-butyl ether, crotyl methyl ether, and crotyl ethyl ether were prepared as described later in this section. Crotyl tetrahydropyranyl ether was prepared from crotyl alcohol and dihydropyran.[38] 2-Norbornanone was first converted to 2,2-dichloronorbornane[39] and then to 2-chloronorbornene.[40] 1-Chlorocyclopentene was also prepared in a similar manner from cyclopentanone. 1-Ethoxycyclopentane and ethyl isobutenyl ether were prepared from cyclopentanone and isobutanol *via* the respective diethyl ketal or acetal.[41] Methyl vinyl ether from Matheson Gas Co. was used as such. 1-Cyclopentenyl acetate was prepared from cyclopentanone according to the procedure described for 2-methylcyclohexanone.[42]

Some authentic samples for the GC analyses were commercially available, some were available from the previous hydroboration studies, and others were prepared and purified by preparative GC. The GC response factors for the isomeric alcohols were assumed to be identical.

The compounds used were examined by GC analysis and judged to be at least 98% pure. The structures were confirmed by IR and ^{1}H NMR spectral examination (also by ^{13}C NMR and mass spectral analyses, when necessary).

Analyses. IR spectra were recorded on Perkin-Elmer 137 and 700 spectrometers from film samples held between salt plates. ^{1}H NMR spectra were recorded either on a Varian T-60 (60 MHz) or a Perkin-Elmer R-32 (90 MHz) instrument. ^{13}C and ^{11}B NMR spectra were obtained on a Varian FT-80A instrument. ^{11}B chemical shifts are with reference to $BF_3{\cdot}OEt_2$ (δ 0), and the resonances upfield from the standard are assigned negative signs. GC analyses were carried out on a Varian 1400 instrument equipped with a flame-ionization detector or a Hewlett-Packard 5750, equipped with a thermal-conductivity detector. Both chromatographs were equipped with stripchart recorders and Disc mechanical integrators for determining peak areas. Analyses were done by the internal standard method with response factors determined from authentic samples.

The hydroboration–oxidation products from 10-undecenyl, 4-pentenyl (Table I), and β-methylallyl derivatives (Table III) were analyzed on a 6 ft × $^1/_4$ in. column packed with 5% CW-20M on Chromosorb W (60/80 mesh). The products from allylic derivatives were analyzed on a 6 ft × $^1/_4$ in. column packed with 10% CW-1540 on Fluoropak or 5% CW-20M. The products from isobutenyl derivatives were analyzed on a 12 ft × $^1/_4$ in. column packed with 19.5% CW-20M and 0.5% Armac 18D deposited on Chromosorb W. The diol products obtained in some cases were analyzed as their bis(trimethylsilyl) derivatives by using a 12 ft × $^1/_4$ in. column packed with 5% SE-30 on Chromosorb W.

A modified Wilkins A-100 chromatograph was used for preparative GC with 6 ft × $^1/_2$ in. column packed with 10% CW-20M coated on acid-washed dimethylchlorosilane-treated 60/80-mesh Chromosorb W.

Preparation of Crotyl *tert*-Butyl Ether. In a 500-mL reaction flask equipped with a reflux condenser and magnetic stirring bar were placed 300 mL of *tert*-butyl alcohol and 23.6 g of potassium *tert*-butoxide (210 mmol). The mixture was stirred vigorously under reflux until all of the KO-*t*-Bu dissolved in *tert*-butyl alcohol. The crotyl chloride (19.5 mL, 18.11 g, 200 mmol) was injected slowly. The reaction mixture became cloudy in 5 min. It was heated gently for an additional 12 h and cooled, and the white precipitate was filtered off, poured into water (150 mL), and extracted with ether (3 × 100 mL). The combined organic layers were dried over anhydrous potassium carbonate. The solvent was removed, and the residue was distilled to provide pure crotyl *tert*-butyl ether: yield 61% (15.6 g); bp 118–121 °C (758 mm).

Crotyl methyl ether, crotyl ethyl ether, and 5-methoxy-1-pentene were prepared by analogous procedures.

Hydroboration of Functional Derivatives. General Procedure. A standard procedure was utilized in this study. A 100-mL reaction flask was connected to a water-cooled condenser topped with a connecting tube leading to a mercury bubbler, and a standard solution of 0.5 *M* 9-BBN in THF or CCl_4 containing an internal standard suitable for GC analyses or a known amount of benzene for NMR integration was added. Stirring was begun, and the alkene was added via syringe. At appropriate intervals of time, aliquots were removed and analyzed carefully for residual hydride by hydrolysis, and the hydride utilized per equivalent of olefin was calculated.[3] The disappearance of the olefinic proton signal was monitored by ^{1}H NMR integration when the solvent was CCl_4. ^{11}B NMR spectra were studied in many cases in order to gain some information on the boron species in the hydroboration mixture. When the reaction was complete, the hydroboration mixture was oxidized with H_2O_2 and NaOH. In the case of ester derivatives, oxidation was carried out by the simultaneous, dropwise addition of 3 *M* solution of NaOAc and H_2O_2 at 0 °C, followed by stirring at room temperature overnight, to avoid possible hydrolysis of these groups under alkaline conditions. GC analyses were used to determine the relative amounts of products formed.[36] For comparison purposes, certain functional derivatives were hydroborated with diborane and disiamylborane at 0 °C.

Hydroboration of Ethyl Crotonate at 25 °C. Ethyl crotonate (6.12 mL, 50 mmol) was reacted with 9-BBN in THF (70 mmol) at 25 °C by the usual procedure. After 72 h, the excess hydride was carefully destroyed by dropwise addition of 5 mL of H_2O. The hydroboration mixture was oxidized by adding 3 *M* of sodium acetate and 30% of hydrogen peroxide at 0 °C, followed by stirring at room temperature overnight. The aqueous layer was saturated with potassium carbonate and the THF layer separated. The aqueous layer was extracted twice with 30 mL of THF. The combined THF layers were dried over magnesium sulfate and distilled under vacuum (6-in. Vigreaux column). There was no sharp boiling point, but the portions distilled at 50–60 (13 mm) and 80–95 °C (13 mm) were collected. These two portions were separately purified by preparative GC. The IR, ^{1}H NMR, ^{13}C NMR, and mass spectral data of the first major product were consistent with the assigned structure, ethyl 2-ethyl-3-hexenoate. The second major product was likewise identified as ethyl 2-ethyl-3-oxohexanoate.

The reaction was repeated on a 20-mmol scale to establish the GC yields of these products in the hydroboration–oxidation experiment.

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Registry No. **13a**, 107-25-5; **13b**, 593-60-2; **13c**, 108-05-4; **13d**,

140-88-5; **14a**, 78782-02-2; **14b**, 78782-03-3; **14c**, 78782-04-4; **15a**, 38050-71-4; **15b**, 22086-45-9; **15c**, 62015-69-4; 18, 78782-05-5; 10-undecenyl alcohol, 112-43-6; ethyl 10-undecanoate, 692-86-4; 10-undecenyl acetate, 112-19-6; 4-penten-1-ol, 821-09-0; 4-pentenyl methyl ether, 1191-31-7; 4-pentenyl chloride, 10524-08-0; 4-pentenyl acetate, 1576-85-8; allyl alcohol, 107-18-6; allyl chloride, 107-05-1; allyl methyl ether, 627-40-7; allyl acetate, 591-87-7; acrolein diethyl acetal, 3054-95-3; acrolein ethylene acetal, 3984-22-3; β-methyl allyl alcohol, 513-42-8; β-methylallyl chloride, 563-47-3; β-methyl allyl acetate, 820-71-3; methacrolein ethylene acetal, 20312-19-0; crotyl alcohol, 6117-91-5; crotyl chloride, 591-97-9; crotyl acetate, 628-08-0; crotyl methyl ether, 18408-99-6; crotyl ethyl ether, 18409-00-2; crotyl *tert*-butyl ether, 56121-50-7; crotyl tetrahydropyranyl ether, 4203-40-1; ethyl crotonate, 10544-63-5; *tert*-butyl crotonate, 3246-27-3; vinyl methyl ether, 107-25-5; vinyl acetate, 108-05-4; vinyl bromide, 593-60-2; ethyl acrylate, 140-88-5; isobutenyl chloride, 513-37-1; isobutenyl ethyl ether, 927-61-7; 1-chlorocyclopentene, 930-29-0; 1-ethoxycyclopentene, 17065-24-6; 1-acetoxycyclopentane, 933-05-1; 2-chloronorbornene, 694-93-9; 1,11-undecanediol, 765-04-8; ethyl 11-hydroxyundecanoate, 6149-49-1; 11-hydroxyundecylacetate, 78782-06-6; 1,5-pentanediol, 111-29-5; 5-methoxy-1-pentanol, 4799-62-6; 5-chloro-1-pentanol, 5259-98-3; 5-acetoxy-1-pentanol, 68750-23-2; 1,3-propanediol, 504-63-2; 3-chloro-1-propanol, 627-30-5; 3-methoxy-1-propanol, 1589-49-7; 3-acetoxy-1-propanol, 36678-05-4; 3,3-diethoxy-1-propanol, 16777-87-0; 2-(β-hydroxyethyl)-1,3-dioxolane, 5465-08-7; 2-methyl-1,3-propanediol, 2163-42-0; 2-methyl-3-chloropropanol, 10317-10-9; 2-methyl-3-acetoxypropanol, 55378-40-0; 2-(β-hydroxyisopropyl)-1,3-dioxolane, 78782-07-7; 1-butanol, 71-36-3; 1,2-butanediol, 584-03-2; 4-methoxy-2-butanol, 41223-27-2; 1-methoxy-2-butanol, 53778-73-7; 4-ethoxy-2-butanol, 53892-34-5; 1-ethoxy-2-butanol, 3448-32-6; 4-*tert*-butoxy-2-butanol, 1927-75-9; 1-*tert*-butoxy-2-butanol, 75567-10-1; crotyl *tert*-butyl ether, 56121-50-7; 4-OTHP-2-butanol, 78791-17-0; 1-OTHP-2-butanol, 78791-18-1; ethyl 2-ethyl-3-hexenoate, 78782-08-8; ethyl 2-ethyl-3-oxohexanoate, 5331-82-8; *tert*-butyl butyrate, 2308-38-5; 1-butene, 106-98-9; ethylene, 74-85-1; 2-methoxyethanol, 109-86-4; ethanol, 64-17-5; ethyl 3-hydroxypropionate, 623-72-3; 1,2-propanediol, 57-55-6; ethyl propionate, 105-37-3; isobutyl alcohol, 78-83-1; 1-ethoxy-2-methyl-2-propanol, 22665-68-5; cyclopentanol, 96-41-3; cyclopentanone, 120-92-3; 2-ethoxycyclopentanol, 78782-09-9; cyclopentene, 142-29-0; 1-acetoxycyclopentene, 933-06-2; 1,2-cyclopentanediol, 4065-92-3; *exo*-norbornanol, 497-37-0; 1,5-cyclooctanediol, 55343-44-7; 3-chloro-2-norbornanol, 4321-46-4; 9-BBN, 280-64-8; B-R-9-BBN (R = 2-chlorocyclopentanyl), 78782-10-2; B-OR-9-BBN (R = 2-chlorocyclopentanyl), 78782-11-3; B-R-9-BBN (R = 2-ethoxycyclopentanyl), 78782-12-4; B-OR-9-BBN (R = 2-ethoxycyclopentanyl), 78782-13-5; B-OR-9-BBN (R = 3-chloronorbornanyl), 78782-14-6.

Pyrolysis of *N,N*-Dihalo Derivatives of Amides and Sulfonamides[1]

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Pyrolysis of *N,N*-dichlorobenzenesulfonamide produced benzene (41%) and chlorobenzene (40%); the dibromo compound gave benzene (19%) and bromobenzene (20%). Toluene (46%), chlorotoluene (27%), and dichlorotoluene (10%) were generated from the *N,N*-dichloro-*p*-tolyl derivative. From each aryl substrate, 1,1,2,2-tetrachloroethane was also produced from reactions involving CH_2Cl_2 solvent. 3-Chloro-*N,N*-dichloroadamantane-1-sulfonamide decomposed to 1,3-dichloroadamantane (52%) and 1,3,5-trichloroadamantane (15%). *N,N*-Dihalobenzamides produced phenyl isocyanate; *N,N*-dichloro and *N*-bromo derivatives gave isocyanate in 16–23% and 21–28% yields, respectively. *N,N*-Dichloroadamantane-1-carboxamide produced 1-adamantyl isocyanate (20–50%) and 1-chloroadamantane (12–46%). The mechanistic features of the various reactions are discussed.

Pyrolyses of organic compounds containing a wide variety of functional groups have been rather extensively investigated.[2a] There are only small numbers of reports dealing with amines[2b,3] and their derivatives, e.g., amides,[4,5] sulfonamides,[6] and *N*-halo compounds.[1,7,8] Similarly, little attention has been devoted to *N*-halo derivatives of amides[4b] and sulfonamides.[9] Among the products from decomposition of chloramine B (*N*-sodio-*N*-chlorobenzenesulfonamide) were diphenyl sulfone, nitrogen, and sulfur dioxide.[10a] On being heated, *N*-chloro-*N*-*tert*-butyl-*n*-butanesulfonamide rearranged to give mainly *N*-*tert*-bu-

Table I. Thermolyses of *N,N*-Dihalo Sulfonamides[a]

substrate	products[b] (% yield)
$C_6H_5SO_2NCl_2$ [c]	C_6H_6 (41), C_6H_5Cl (40)
p-$CH_3C_6H_4SO_2NCl_2$ [d]	$C_6H_5CH_3$ (46), $ClC_6H_4CH_3$ (27),[e] $C_2H_6Cl_2$ (10)[e]
$C_6H_5SO_2NBr_2$ [f]	C_6H_6 (19), C_6H_5Br (20)
3-Cl-1-$AdSO_2NCl_2$ [g,h]	1,3-Cl_2Ad (52), 1,3,5-Cl_3Ad (15), Cl_4Ad (trace)

[a] Metal injector port. [b] 1,1,2,2-Tetrachloroethane was formed from the runs with aromatic substrates. [c] Solution (11% w/w) in CH_2Cl_2 at 425 °C. [d] Solution (17% w/w) in CH_2Cl_2 at 360 °C. [e] Isomer composition unknown. [f] Solution (5% w/w) in CH_2Cl_2 at 400 °C. [g] Solution (11% w/w) in CH_2Cl_2 at 355 °C. [h] Ad = adamantane.

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