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ORGANOBORANES

XIX *. THE PREPARATION AND SOME UNUSUAL CHEMISTRY OF *B*-ALLYL DERIVATIVES OF 9-BORABICYCLO[3.3.1]NONANE

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Summary

Several *B*-allyl derivatives of 9-borabicyclo[3.3.1]nonane (9-BBN) were prepared either by the allylation of *B*-methoxy-9-BBN with allylic aluminum reagents or by the monohydroboration of certain dienes and allenes with 9-BBN. The ^{1}H NMR spectra of these derivatives were examined at various temperatures, revealing the presence of either permanent allylic rearrangements or *cis*—*trans* isomerizations about the allylic double bond. The protonolyses of both *B*-allyl- and *B*-crotyl-9-BBN occur readily, giving propene in the former case and 1-butene in the latter, presumably via allylic rearrangement. Bromination of *B*-allyl-9-BBN leads to the formation of allyl bromide and *B*-bromo-9-BBN. Three mechanistic schemes are offered for this reaction. The hydroboration-oxidations of *B*-allyl- and *B*-crotyl-9-BBN were studied. The allyl derivative affords only 1,3-propanediol, while the crotyl isomer gives mostly 1,3-butanediol.

Introduction

The chemistry of unsaturated organoboranes often differs substantially from that of their saturated analogs. Both α,β-unsaturated (vinyl- and alkynylboranes) and β,γ-unsaturated (allylboranes) organoboranes react readily with many substrates to which trialkylboranes are inert [2,3]. Over the past decade, Mikhailov and his coworkers have extensively examined the chemistry of simple triallylboranes [4,5]. In our laboratory, recent studies of saturated organoboranes have shown that *B*-alkyl derivatives of 9-borabicyclo[3.3.1]nonane (9-BBN) offer unique advantages over simple trialkylboranes in many synthetic applications [6,7]. Consequently, we undertook an investigation of the preparation

* Taken in part from the Ph.D. Thesis of G.W. Kramer [1]. For part XVIII see ref. 14.

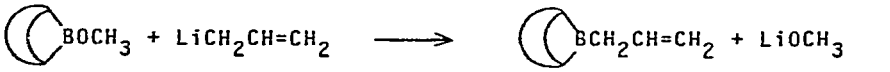
and chemistry of some *B*-allyl derivatives of 9-BBN. The initial results of this study are presented in this paper.

Results and discussion

Allylboranes have been synthesized previously by many routes [4,8,11,13,18, 19]. In this study, we examined only three methods: allylation of dialkylborinate esters with other allylorganometallics, monohydroboration of certain conjugated dienes, and monohydroboration of certain allenes.

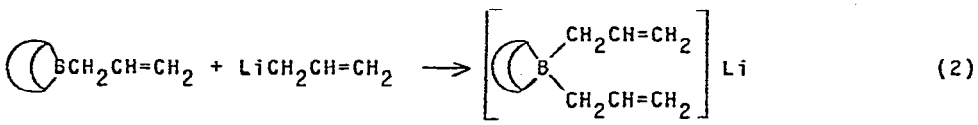
Allylation of dialkylborinate esters with allylorganometallics

We recently reported the synthesis of *B*-allyl-9-BBN from the reaction of allyllithium with *B*-methoxy-9-BBN (eqn. 1) [9]. Although this preparation can be carried out in high yield, there are certain disadvantages. Allyllithium is not readily available, and its preparation in high yield is, at best, indirect [10].



(1)

Problems were encountered in separating the final allylborane from the by-products of the allyllithium preparation. The stoichiometry of this allylation must be carefully controlled to avoid loss of product through formation of the diallyl "ate" complex (I) (eqn. 2). Fortunately, these problems disappear if



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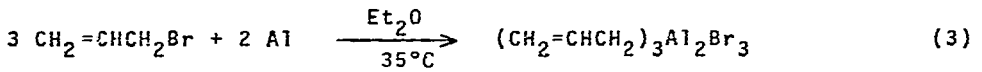
allylaluminum sesquibromide is used in place of allyllithium (eqns. 3, 4) [11]. The allylaluminum reagent is easily prepared in the same way as a simple Grig-



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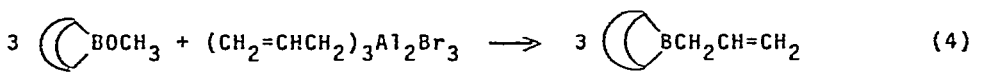

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nard reagent. The aluminum salt by-products of the alkylation are difficult to remove by filtration; however, they are easily handled by centrifugation/decantation. Aluminum bromide is soluble in diethyl ether, but the allylborane can easily be purified by simple vacuum distillation. No product loss was observed through diallyl "ate" complex formation. Consequently, excess allylaluminum reagent may be employed to ensure complete allylation, and the borinate ester may be added concurrently with the allyl bromide. Perhaps the only drawback of this method, other than removal of the by-products, is that higher molecular weight analogs of the aluminum reagent are not easily prepared [12]. We have used this method to prepare the *B*-allyl, *B*-crotyl, and *B*-2-methylallyl derivatives of 9-BBN in high yield (Table 1).

TABLE 1

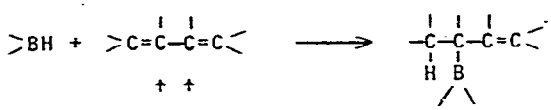
PREPARATION AND PROPERTIES OF *B*-ALLYL DERIVATIVES OF 9-BBN

R	Route [a]	Yield isolated (%)	Purity [b] (%)	B.p. (°C/mmHg)	^{11}B NMR [c] (δ, ppm)
Allyl	M [d]	95 [d]	99+		
Allyl	M	83	98+	41.5—42/0.05	—85.6
Crotyl	M	98	93+	55—56/0.05	—86.0
2-Methylallyl	M	84	98+	55—56/0.04	—86.2
3,3-Dimethylallyl	HBA	87	97	54—56/0.01	—85.3
3,3-Dimethyl-1-isopropylallyl	HBD	87	— [e]	84—86/0.001	—77.9
2-Cyclohexen-1-yl	HBD	71	~90	84—87/0.03	—85.2

[a] M = allylation via aluminum reagent, HBA = hydroboration of allene, HBD = hydroboration of diene. [b] VPC analyses. [c] ^{11}B NMR chemical shift from BF_3/OEt_2 in ppm. [d] Allylation with allyllithium, VPC yield. [e] Product decomposed during VPC analysis.

Monohydroboration of conjugated dienes

The monohydroboration of conjugated dienes can potentially lead to the formation of a variety of allylboranes. However, there are three factors which must be considered in this approach. First, the boron must become attached to one of the internal carbons of the diene system (eqn. 5). Secondly, since the diene



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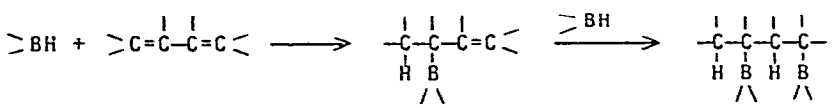
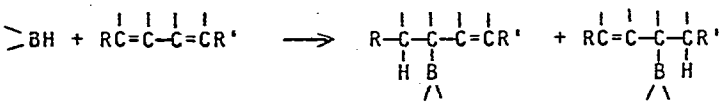
possesses two sites for hydroboration, it is necessary to stop the reaction at the monohydroboration stage (eqn. 6). Thirdly, in the case of unsymmetrical dienes,



(6)

there is the problem of which double bond will be attacked (eqn. 7). This fac-



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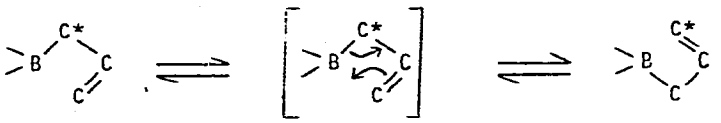
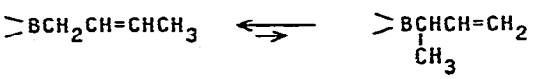
tor may be further complicated by the tendency for the initially formed allylborane to undergo allylic rearrangement leading to a mixture of allylboranes (eqn. 8) [4]. Where there is a clear steric difference between the sites available



(8)

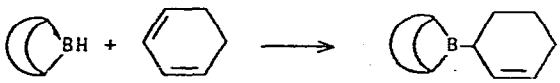
to the boron, the allylborane which places boron at the least sterically hindered site should predominate (eqn. 9) [4,13].



(9)

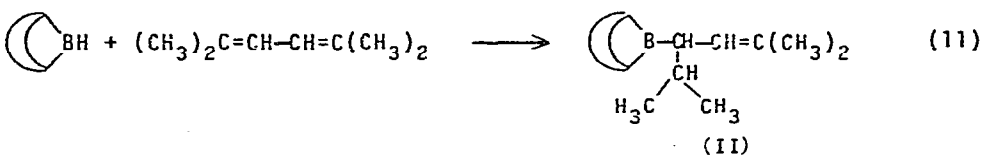
In this study, no attempt was made to carry out a systematic examination of the hydroboration of dienes with 9-BBN *. The dienes examined were those for which simple predictions, based on the directive effects of olefin hydroborations, suggested the possibility of clean allylborane formation [15].

Zweifel and Brown have shown that the monohydroboration of 1,3-cyclohexadiene with disiamylborane leads primarily to the allylborane, as shown by the isolation of an 88% yield of the allylic alcohol after oxidation [16]. Accordingly, we carried out the monohydroboration of 1,3-cyclohexadiene with 9-BBN; *B*-2-cyclohexen-1-yl-9-BBN was realized in high yield (Table 1) (eqn. 10).



(10)

We then examined the monohydroboration of 2,5-dimethyl-2,4-hexadiene with 9-BBN. Hydroboration of the similar olefin, *cis*-4-methyl-2-pentene, with 9-BBN results in the placement of 99.8% of the boron at the 2-position [15]. Consequently, we predicted that the hydroboration of this diene with 9-BBN would place the boron almost exclusively at one of the internal positions. It was hoped that the steric requirements of the remaining double bond would be sufficiently high to avoid dihydroboration. Finally, since the boron should "prefer" to be bound to a secondary rather than to a tertiary center, we expected that only one of the isomeric allylboranes would predominate. The experiment bore out our predictions, affording a high isolated yield of the allylborane (II) (Table 1) (eqn. 11).



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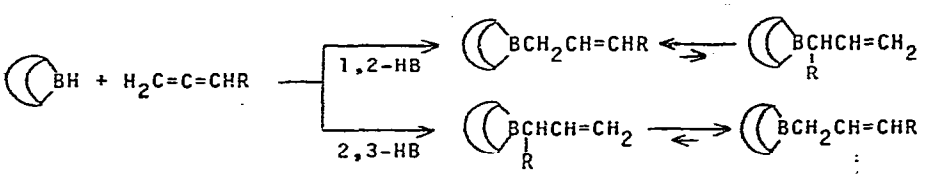
(II)

Monohydroboration of allenes

The monohydroboration of allenes is an attractive method for the preparation of allylboranes. However, this route is open to most of the considerations mentioned earlier for the monohydroboration of conjugated dienes. The boron must become bound to one of the end carbons of the allene system. The initially formed monohydroboration product must be more resistant to hydroboration than the allene, or extensive dihydroboration will occur. However, unlike unsymmetrically substituted dienes, it probably does not matter which double bond is hydroborated. The product isomer distribution should be determined by the relative product stabilities as a result of the allylic rearrangement (eqn. 12). Finally, there is one further complication. Mikhailov has recently reported



(12)

* A systematic study has been carried out with R. Liotta and will be published shortly.

that under certain conditions allylboranes add in a 1,2-manner to allenes [17].

The hydroboration of allenes has been studied in varying detail by several workers [18]. Unfortunately, the earlier reports suggested that allene hydroborations were quite complicated. However, the results of more recent studies have shown that the hydroboration of allenes can be controlled in certain cases to give good yields of allylboranes [19]. Prior to these reports, we had found that the monohydroboration of 3-methyl-1,2-butadiene with 9-BBN gives almost exclusively *B*-3,3-dimethylallyl-9-BBN (Table 1) (eqn. 13).

(13)

The *B*-allyl derivatives of 9-BBN isolated in this study are all colorless oils of moderate viscosity. While the parent compound, *B*-allyl-9-BBN is pyrophoric, the others fume heavily when exposed to air. After exposure to small amounts of air, these materials may polymerize on standing. However, they appear to be stable indefinitely at room temperature if stored under nitrogen. Heating neat samples of each material in sealed NMR tubes to as high as 160°C for several hours, followed by cooling, does not alter their ^{1}H NMR spectra.

^{1}H NMR spectra: evidence for a permanent allylic rearrangement

The ^{1}H NMR spectrum of *B*-allyl-9-BBN at −60°C is much like that observed for many other allyl compounds, such as allyl chloride or tetraallylsilane. Along with the signals due to the bicyclic ring (δ 1.80 and 1.17 ppm), there is an $ABCX_2$ pattern from the allyl group: a multiplet centered at δ 6.0 ppm (1H, internal vinyl hydrogen), multiplets at δ 5.02 and 4.80 ppm (1H each, terminal olefinic protons), and a doublet at δ 2.37 ppm (*J* 7.5 Hz, 2H, allylic methylene protons). As the sample is warmed, its spectrum is slowly transformed from the $ABCX_2$ into an AX_4 pattern. The signals at δ 5.02 and 4.80 ppm first lose their fine structure and then broaden as their intensities diminish. The doublet at δ 2.37 slowly broadens, loses its splitting, and decreases in intensity. A broad signal located equidistant between the methylene and terminal vinyl resonances is apparent when the temperature reaches 10°C. Meanwhile, the splitting pattern of the internal vinyl proton has become less complex and is finally transformed into a regular quintet. At 35.5°C the spectrum consists of this quintet centered at δ 5.97 ppm (*J* 11 Hz, 1H), a broad resonance centered at δ 3.6 ppm (~4H), and the signals due to the bicyclic ring. At 40°C the broad hump at δ 3.6 ppm begins to split and at 80°C is a well-defined doublet (δ 3.63 ppm, *J* 10.4 Hz, ~4H). Further heating only sharpens the spectrum. Cooling the sample to low temperature returns the original spectrum. Dilution of the sample with cyclopentane does not alter the spectra other than to improve resolution at low temperatures by reducing the viscosity-induced line broadening,

This spectral behavior is very similar to that described by Mikhailov for triallylborane and *B*-allylborolane [20,21]. It may be interpreted in terms of a permanent allylic rearrangement in which the boron exchanges between the 1- and 3-positions of the unsaturated chain. This exchange is intramolecular as shown by the lack of a dilution effect. The coalescence temperature is 10°C. Using the chemical shift parameters from the frozen out spectrum and assuming the process to be a simple two-site exchange, equally populated at both sites, with both

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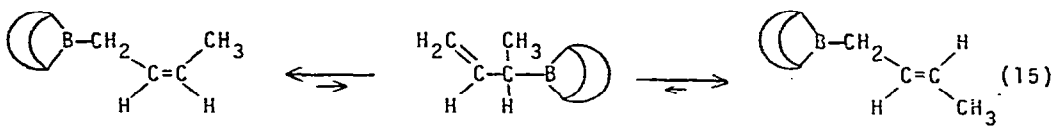
ment. No evidence of the 1-methylallyl isomer was found. Instead, these spectra show that B-crotyl-9-BBN consists of both *cis* and *trans* isomers which can interconvert. At 0°C, the signal due to the terminal olefinic methyl group appears to consist of an overlapping pair of doublets. The signal due to the allylic methylene protons also appears to be a pair of doublets. As the temperature of the sample is raised to 40°C, both of these pairs of doublets collapse into simple doublets. Unfortunately, the large methylene envelope of the bicyclic ring partially obscures both of these signals, so we were not able to use multiple resonance techniques, such as those employed by Mikhailov for tricrotylborane [24], to assign the signals or to determine the *cis/trans* ratio in the mixture. The interconversion between the *cis* and *trans* isomers probably involves an equilibrium between the crotyl derivatives and the 1-methylallyl isomer (eqn. 15). The lat-



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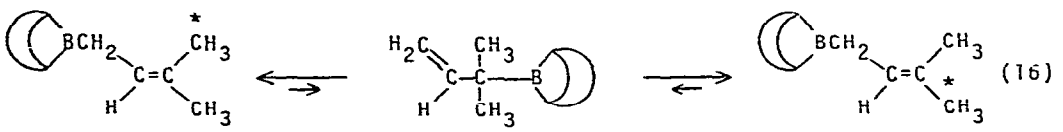
ter is apparently much less stable than either crotyl moiety and is present in concentrations below the detectability of ^{1}H NMR. Once the compound goes to the 1-methylallyl form and then reverts to the crotyl state, it can form either the *cis* or the *trans* isomer.

Like *B*-crotyl-9-BBN, the ^{1}H NMR spectrum of *B*-3,3-dimethylallyl-9-BBN does not show evidence of a permanent allylic rearrangement. No trace of the 1,1-dimethylallyl isomer is detected. At 35.5°C, both of the terminal methyl signals are seen as distinct singlets (δ 1.73 and 1.60 ppm) along with a triplet with some fine structure (δ 5.30 ppm, *J* 8.3 Hz, 1H) and a doublet (δ 2.18 ppm, *J* 8.3 Hz, 2H) indicating that the boron is attached to the primary rather than the tertiary carbon. As the temperature of the sample is raised, the terminal methyl signals broaden, and at 140°C they are fused into a doublet (*J* 1.5 Hz). The vinyl signal appears at this temperature as a triplet of septets (δ 5.80 ppm, J_t 8.3, J_s 1.5 Hz). The identities of the methyl groups are lost at this temperature, and the vinyl hydrogen "sees" equivalent methyl groups resulting in the seven line patterns within the triplet. Like the crotyl case, this *cis—trans* interchange probably proceeds via the 1,1-dimethyl isomer (eqn. 16). That this pro-



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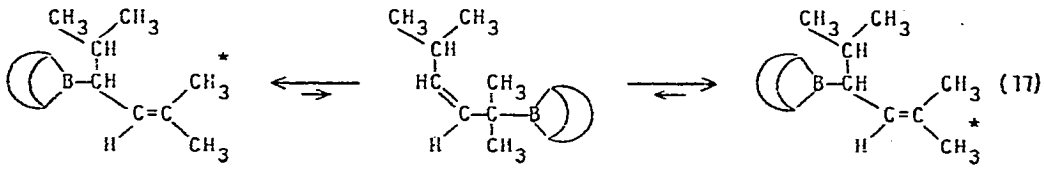
cess occurs at a higher temperature than in the crotyl system probably reflects the greater instability of the α-methallyl intermediate when two methyl groups are involved.

The ^{1}H NMR spectrum of *B*-3,3-dimethyl-1-isopropylallyl-9-BBN at 35.5°C consists of a doublet at δ 4.83 ppm (*J* 10 Hz, 1H), a multiplet centered about δ 2.5 ppm, the methylene envelope of the bicyclic ring (δ 1.8 ppm), a broad singlet at δ 1.70 ppm, a multiplet (bridgehead protons, δ 1.3 ppm), and a doublet centered at δ 0.92 ppm (*J* 6.5 Hz, 6H). At 0°C, the broad singlet is split into two singlets: δ 1.75 and 1.66 ppm. As the temperature is raised, these two

singlets merge into the δ 1.70 ppm singlet, while the vinyl doublet begins to show some fine structure, and the multiplet at δ 2.5 ppm becomes resolved into a double doublet (*J* 10.5 and 9 Hz). Finally at 160°C, the methyl singlet is split into a doublet (*J* 1.5 Hz), and each component of the vinyl doublet is split into a regular septet (*J* 1.5 Hz).

These spectra show that this allylborane does not exhibit permanent allylic rearrangement since no evidence for the 1,1-dimethyl isomer is found. However, like *B*-3,3-dimethylallyl-9-BBN, it is undergoing isomerization around the double bond. The isomerization occurs more readily in this case, since the terminal methyl groups are scrambled at room temperature; whereas this does not occur until around 100°C in the 3,3-dimethylallyl case.

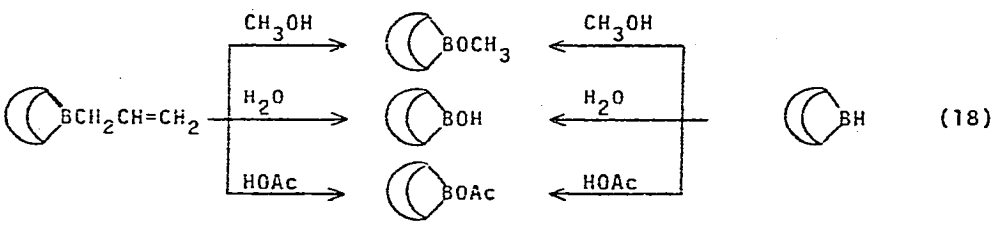
Again this isomerization probably occurs via allylic rearrangement to give the unstable 1,1-dimethyl isomer in low concentration which quickly reverts to the more stable 3,3-dimethyl form; but in this process, the identities of the terminal methyl groups become scrambled (eqn. 17). The isomerization occurs more



easily here than in the previous case because the difference in energy between the 3,3-dimethyl isomer and the 1,1-dimethyl isomer is probably smaller since there is a substituent in the 1-position.

Protonolysis of B-allyl-9-BBN

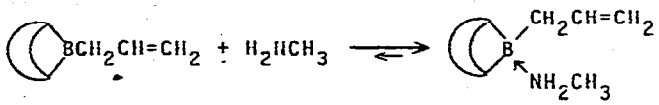
Like triallylborane [4], *B*-allyl-9-BBN is readily protonolyzed by reagents containing labile hydrogens. It reacts nearly instantaneously with water, methanol, and acetic acid (eqn. 18). Treatment of a neat sample of *B*-allyl-9-BBN with



slightly more than one equivalent of methanol results in a vigorous liberation of gas. This gas was trapped and identified as propene by its ^{1}H NMR spectrum. VPC examination of the boron-containing residue (after addition of an internal standard) showed that *B*-methoxy-9-BBN was formed in 99% yield. Treatment of *B*-allyl-9-BBN with water leads to the formation of propene and *B*-hydroxy-9-BBN which was identified by comparison of its ^{1}H NMR spectrum (δ 5.58, 1H; 1.8, ~12H; 1.17 ppm, ~2H) and ^{11}B NMR spectrum (δ −56.6 ppm) with those of authentic samples prepared by treatment of 9-BBN with water. Protonolysis of *B*-allyl-9-BBN with acetic acid leads to the formation of propene and *B*-acetoxy-9-BBN which was identified by comparison of its ^{1}H NMR spectrum (δ 2.30, 3H; 1.73, ~12H; 1.08 ppm, ~2H) and ^{11}B NMR spectrum (δ −16.4

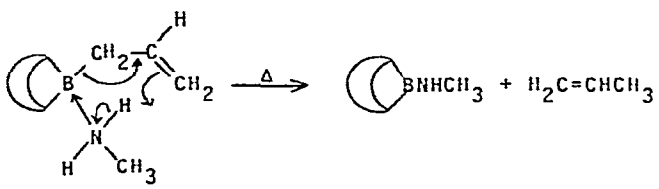
ppm) with those of authentic samples prepared by treatment of 9-BBN with acetic acid.

Treatment of *B*-allyl-9-BBN with one equivalent of methylamine initially gives a borane-amine adduct (^{11}B NMR; δ +5.8 ppm) (eqn. 19). When this ad-



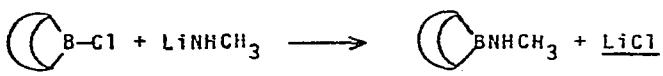
(19)

duct is heated, propene is evolved and *B*(*N*-methylamino)9-BBN is formed (eqn. 20). This aminoborane was identified by comparison of its ^{1}H NMR (δ 2.78,



(20)

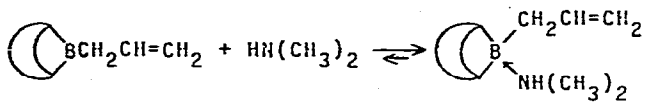
2.68, 3H; 1.78, ~12H; 1.27 ppm, ~2H) and ^{11}B NMR (δ −49.1 ppm) spectra with those of authentic samples prepared by the treatment of *B*-chloro-9-BBN with lithium methylamide (eqn. 21). When two equivalents of *B*-allyl-9-BBN are



(21)

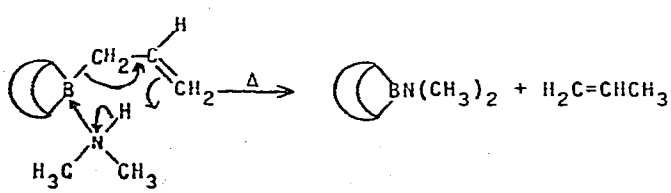
mixed with one equivalent of methylamine, only one equivalent of the allylborane reacts. Even after heating, one equivalent of the allylborane remains unconsumed. ^{1}H NMR shows that there is essentially no complex formed between the aminoborane and the *B*-allyl-9-BBN since the permanent allylic rearrangement of the latter is not affected.

Treatment of *B*-allyl-9-BBN with one equivalent of dimethylamine leads to the formation of a complex (^{11}B NMR; δ +2.7 ppm) (eqn. 22). On heating, this



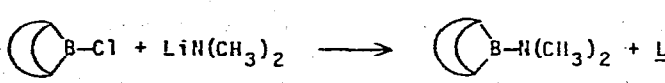
(22)

complex is transformed into *B*(*N*,*N*-dimethylamino)-9-BBN with the liberation of propene (eqn. 23). This aminoborane was identified by comparison of its ^{1}H



(23)

NMR (δ 2.80, 6H; 1.78, ~12H; and 1.28 ppm, ~2H) and ^{11}B NMR (δ −47.7 ppm) spectra with those of authentic samples prepared by treatment of *B*-chloro-9-BBN with lithium dimethylamide (eqn. 24).



(24)

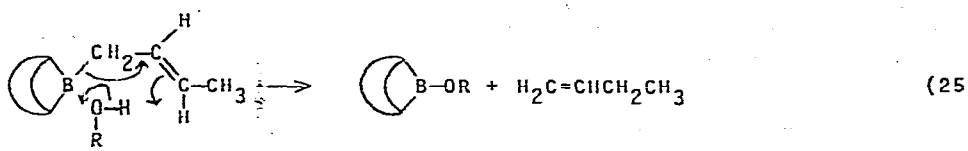
TABLE 2

PROTONOLYSIS OF *B*-CROTYL-9-BBN

Proton source	Butene isomer ratio [a]			Σ Butenes [b]
	1-Butene	*cis*-2-Butene	*trans*-2-Butene	
MeOH	99.2	0.8	0	92
Et_3COH	99.4	0.6	0	98
H_2O	95	5.0	0	110
HOAc	99.4	0.6	0	105
$HOCH_2CH_2NH_2$	97.5	2.5	0	102

[a] Normalized ratios. [b] VPC yields.

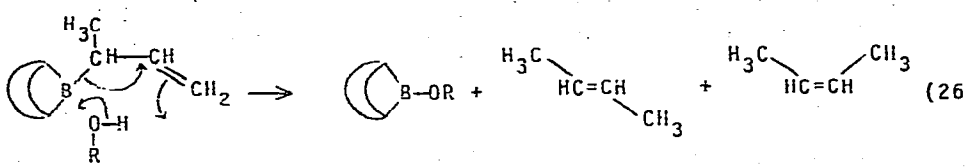
Like *B*-allyl-9-BBN, the *B*-crotyl-9-BBN is readily protonolyzed by compounds having a labile hydrogen. As shown in Table 2 protonolysis with a variety of compounds results predominantly in the formation of 1-butene. This suggests that the protonolysis occurs mostly with allylic rearrangement (eqn. 25).



(25)

These results are in good agreement with the report of Mikhailov that tricrotylborane affords a 98/2 mixture of 1-butene and 2-butene on treatment with either water or methanol [25].

It is tempting to infer from the data in Table 2 that the small amount of 2-butene formed is derived from protonolysis, with allylic rearrangement, of the α-methylallyl isomer, However, this would imply that the rate of protonolysis is much faster than the allylic rearrangement, thereby trapping out the small amount of α-methylallyl isomer present. While this may be true, it is difficult to understand why in all cases only *cis*-2-butene is formed since protonation via allylic rearrangement should afford equal amounts of both 2-butene isomers (eqn. 26). Furthermore, the amount of 2-butene formed is not the same in every

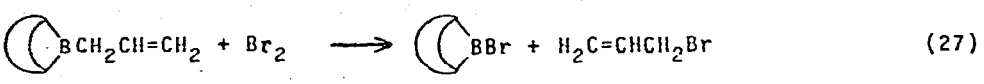


(26)

case as would be predicted if the α-methylallyl moiety were simply being trapped. Direct protonolysis without allylic rearrangement would lead to the formation of 2-butene, but again it is difficult to understand why only the *cis* isomer is formed in most cases. The exclusive formation of *cis* olefin could possibly be accounted for by a small amount of direct displacement leading to an allylic anion which is subsequently protonated, since it has been established by Schriesheim that *cis* isomers are preferentially formed in kinetically controlled processes [26].

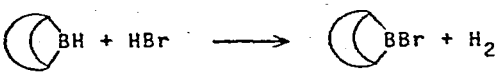
Bromination of B-allyl-9-BBN

Treatment of *B*-allyl-9-BBN with one equivalent of bromine in carbon tetrachloride at −25°C results in the immediate discharge of the bromine color. Examination of the reaction mixture by ^{1}H NMR shows a broad peak at δ 1.93 ppm superimposed on the spectrum of allyl bromide. ^{11}B NMR shows a single resonance at δ −84.1 ppm. When one equivalent of dimethyl sulfide is added, this ^{11}B NMR signals shifts to δ −11.9 ppm. The boron-containing species was shown to be *B*-bromo-9-BBN (eqn. 27) by comparison with samples prepared



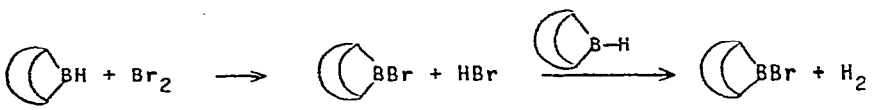
(27)

by two routes: protonolysis of 9-BBN with HBr (eqn. 28) and treatment of 9-



(28)

BBN with half an equivalent of bromine (eqn. 29).



(29)

There are at least three plausible mechanistic schemes which can account for the bromination of *B*-allyl-9-BBN (Fig. 1). One mechanism involves a six-centered

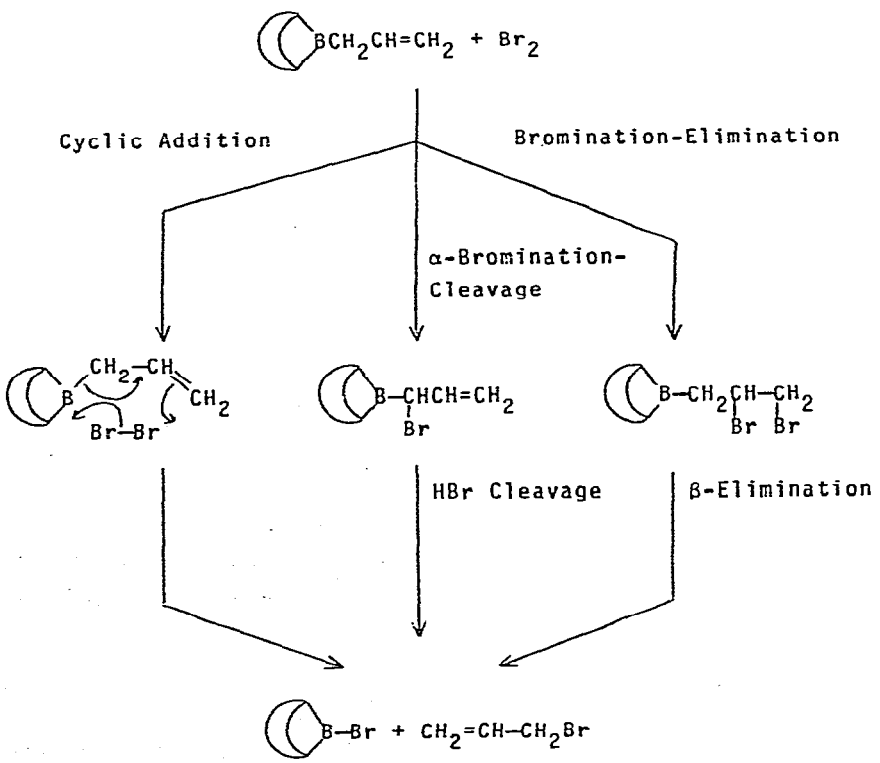
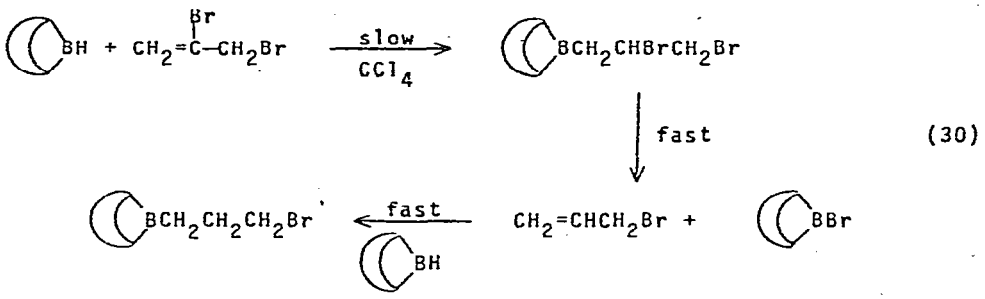


Fig. 1. Mechanistic schemes for the bromination of *B*-allyl-9-BBN.

addition of the allyl moiety to the bromine. This is very similar to the proposed mechanisms for many other reactions of allylboranes [4]. A second proposal invokes a free radical route where a bromine atom abstracts a hydrogen α to the boron. The α-bora radical then attacks a bromine molecule forming an α-bromoborane and a bromine atom which carries the chain. In this process, one equivalent of HBr is formed. Such α-bromoboranes are known to be cleaved by HBr to form alkyl bromides and *B*-bromoorganoboranes [27]. In a third possibility, the bromine adds across the double bond forming *B*-2,3-dibromopropyl-9-BBN. It is known that β-substituted organoboranes of this type readily undergo 1,2-elimination of boron and bromine to form an olefin [28].

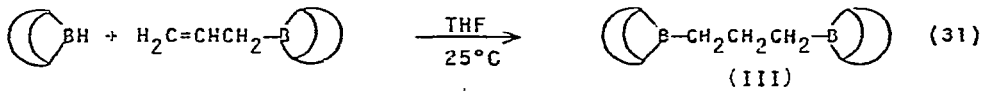
The feasibility of this third route was explored by producing the proposed intermediate, *B*-2,3-dibromopropyl-9-BBN via the hydroboration of 2,3-dibromopropene with 9-BBN in carbon tetrachloride. This hydroboration proved to be sluggish; however, after one week at room temperature, analyses of the reaction mixture revealed the presence of 50% of the starting olefin, 50% *B*-bromo-9-BBN, and 50% of *B*-3-bromopropyl-9-BBN. Obviously, elimination occurs from the original hydroboration product giving the *B*-bromoborane and allyl bromide (eqn. 30).



(30)

Hydroboration of B-allyl-9-BBN

Hydroboration of *B*-allyl-9-BBN with 9-BBN evidently produces the expected 1,3-bis-boron derivative (III) (eqn. 31). Oxidation of III affords a 91% yield of

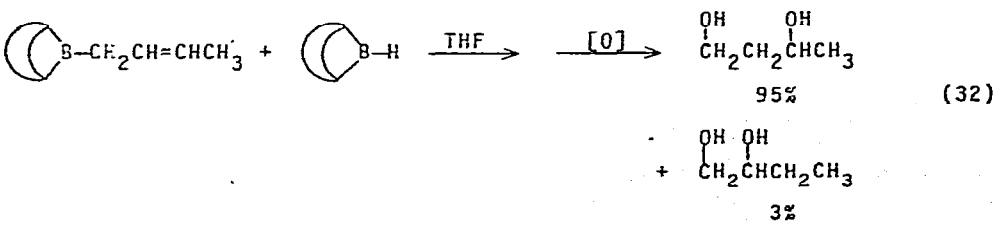


(31)

(III)

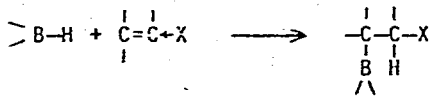
1,3-propanediol. No 1,2-propanediol was detected. The hydroboration step is very rapid, being complete in less than 30 min. These results substantiate the report of Soulié and Cadiot that the direct hydroboration of allene with 9-BBN results exclusively in the formation of dibora products [19].

The hydroboration of *B*-crotyl-9-BBN with 9-BBN is also complete in less than 30 min at room temperature. The reaction mixture was oxidized giving 1,3-butanediol in 95% yield and 1,2-butanediol in 3% (eqn. 32). Only trace amounts

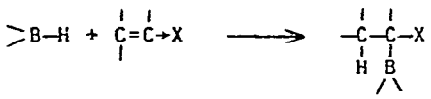


(32)

of 2,3- and 1,4-butanediols were detected. These results indicate a predominant directive effect away from boron, probably due to combined electronic and steric interactions. Attack at the 3-position is favored sterically because the incoming boron can be located next to the smaller methyl group (9-BBN is especially sensitive to steric effects [15]). Hydroboration also exhibits pronounced electronic effects. Boron is directed away from electron-donating groups and toward electronegative substituents (eqns. 33, 34) [6,7]. In this case, since



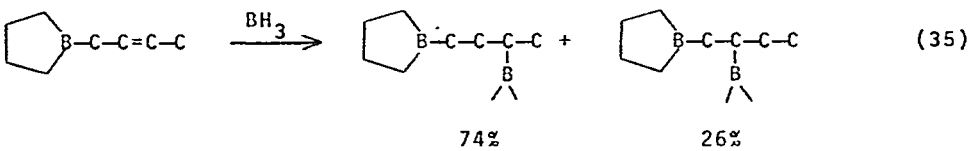
(33)



(34)

boron is electropositive with respect to carbon, the electronic directive effect should also be toward the 3-position. It is also possible that some of the 1,3-product arises through hydroboration of the α-methylallyl isomer. Based on the rates of hydroboration of olefins with 9-BBN, the α-methylallyl derivative should be about 100 times as reactive as the crotyl compound. Furthermore, hydroboration with 9-BBN should give exclusively the 1,3-dibora material. However, since the α-methylallyl isomer is not seen by ^{1}H NMR even in the "frozen out" spectrum, it must be present in very low concentration (<1%). Thus, it seems unlikely that the nearly exclusive formation of 1,3-product can be attributed solely to the hydroboration of the α-methylallyl moiety.

Mikhailov has studied the hydroboration of *B*-crotylborolane with borane (eqn. 35) [29]. His results also show a preference for attack at the 3-position al-



(35)

though, as expected, the selectivity is not as great with borane as with 9-BBN.

Experimental

General comments

The techniques described in Chapter 9 of ref. 7 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. The reaction flasks were fitted with sidearms capped with rubber septa and were flamed out under a nitrogen purge immediately before use. All reactions were carried out under a static pressure of nitrogen. The transfers of liquids and solutions of organometallics were done with oven-dried, nitrogen-purged hypodermic syringes fitted with stainless steel needles or by the double-ended needle technique. Gases were delivered using gas-tight syringes [30]. All reactions were stirred magnetically using over-dried, Teflon-coated stirring bars.

Materials

THF and diethyl ether were distilled from lithium aluminum hydride prior to use, degassed with nitrogen, and stored in large ampoules with Teflon stopcocks. Technical grade pentane (and hexane) was stirred for one day over concentrated sulfuric acid, treated with anhydrous potassium carbonate, distilled from lithium aluminum hydride, degassed with nitrogen, and stored in crown-capped bottles. Benzene (Mallinckrodt SpectAR) and cyclopentane (Chem. Samples 99%) were degassed with nitrogen and stored over 4 Å molecular sieves. Methanol (Mallinckrodt SpectAR) was stored over 3 Å molecular sieves. Methylamine, dimethylamine, trimethylamine, and hydrogen bromide (all Matheson) were used as obtained and transferred directly from the cylinders using gas-tight syringes [30]. Pyridine (Mallinckrodt SpectAR), deuterated NMR solvents (Aldrich), and carbon tetrachloride (Mallinckrodt SpectAR) were used as obtained. ^{1}H NMR samples were doped with tetramethylsilane by adding it, as a gas, through the septum capping the NMR tube from a gas-tight syringe.

The *B*-methoxy-9-BBN, *B*-chloro-9-BBN, and 9-BBN (m.p. 149—151°C) were prepared as described earlier [7,9,15]. The aluminum turnings (Special Grade) were purchased from BDH Chemicals, Ltd. Allyl bromide (99%), crotyl bromide (pract.), olefins, dienes, and allenes were obtained from Chemical Samples Co. and used as received. The *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA + 1% TMCS) was obtained from Pierce Chemical Co.

Analyses

^{11}B NMR spectra were recorded on a Varian XL-100-15 spectrometer (32.1 MHz) using a Nicolet 1080 data acquisition system. The spectra were recorded using either a ^{1}H or ^{2}H internal or ^{19}F external lock, and all chemical shifts are relative to BF_3/OEt_2 (δ 0 ppm). ^{1}H NMR spectra were recorded on Varian T-60 (60 MHz), Perkin—Elmer R-32 (90 MHz), or Varian A-60 (60 MHz) spectrometers. All ^{1}H chemical shifts are relative to tetramethylsilane (δ 0 ppm). Variable temperature ^{1}H NMR spectra were recorded on a Varian A-60 spectrometer fitted with a variable temperature accessory. The probe temperatures were determined using the known variance in the chemical shift parameters of methanol (for temperatures below 35°C) or ethylene glycol (for temperatures above 35°C) [31]. The samples were allowed to equilibrate in the NMR probe for at least 30 min before the spectra were recorded. The probe temperature was determined before and after each spectrum was recorded. Spectra at temperatures above 40°C were recorded on neat samples, while spectra below 0°C were generally recorded on ~30% samples in cyclopentane. Examination of spectra between 0—40°C, both neat and in cyclopentane, showed essentially no change due to the addition of the cyclopentane. Chemical shifts were measured relative to TMS (δ 0 ppm), cyclopentane (δ 1.52 ppm), or the methylene envelope of 9-BBN (δ 1.80 ppm), but are reported relative to TMS (δ 0 ppm).

VPC analyses were carried out on a Hewlett Packard 5752B chromatograph fitted with a Disc Integrator using 6 ft × 1/4 in stainless steel columns filled with 10% loaded liquid phases on AW DMCS 60/80 Chromosorb W. Apiezon L and SE-30 were used for analysis of organoboranes. The isomeric butenes resulting from protonolysis reactions were analyzed on the Hewlett Packard 5752B instrument using a 36 ft × 0.125 in OD column packed with 10% UC

W-98 on 80/100 AW-DMCS Chromosorb W. Diols from the hydroboration-oxidation reactions were analyzed as their bis-TMS derivatives on a Perkin—Elmer 226 Chromatograph fitted with a 150 ft × 0.01 in Golay column coated with OS-138 (5-ring polyphenylether).

Preparation of B-allyl-9-BBN (500 mmol)

To an oven-dried, flamed out, nitrogen-flushed, 500-ml flask, fitted with a septum inlet and magnetic stirring bar, surmounted with a reflux condenser topped with an addition funnel connected to a mercury bubbler, was added 13.45 g (500 g-atom) of aluminum turnings cut into small pieces. The aluminum turnings were dried and deoxygenated by washing with about 10 ml of 2 *M* n-butyllithium in hexane and 10 ml of hexane followed by rinsing with about 25 ml of ether. With nitrogen flowing through the apparatus, the septum was momentarily removed to allow 0.1 g of mercuric chloride to be introduced. Stirring was begun, and 150 ml of ether was added. The reaction was initiated by the addition of 4.9 ml of allyl bromide to the pot. After about 10 min, the solution began to boil. The remaining allyl bromide (60 ml, 750 mmol total) was mixed with 76.0 g (500 mmol) of *B*-methoxy-9-BBN in the addition funnel. This mixture was allowed to drip into the reaction flask at such a rate to maintain a gentle reflux. When the addition was complete, the addition funnel was rinsed into the reaction flask with ether (2 × 25 ml). The reaction mixture was heated at reflux for 2 h. The thick, gray slurry which was formed was transferred under nitrogen into 250-ml crown-capped centrifuge bottles using a 15-gauge double-ended needle. After centrifugation, the supernatant liquid was decanted by double-ended needle into a distillation assembly. The precipitate in the centrifuge bottles was extracted with pentane (4 × 100 ml), and the extracts, after centrifugation, were decanted into the distillation pot. The volatiles were removed under aspirator vacuum, and the residual oil was vacuum distilled giving 67.1 g (83%) of a clear liquid, b.p. 41.5—42°C at 0.05 mmHg. A sizable pot residue remained after the distillation. VPC showed the distillate to be greater than 99% pure.

Preparation of B-crotyl-9-BBN (150 mmol)

This preparation was carried out as described above using 4.05 g (150 g-atom) of aluminum, 20.5 ml (225 mmol) of crotyl bromide, and 22.8 g (150 mmol) of *B*-methoxy-9-BBN. The crude product was vacuum distilled to give 25.8 g (98%) of a clear liquid, b.p. 55—56°C at 0.05 mmHg. VPC showed this material to be greater than 98% pure.

Preparation of B-2-methallyl-9-BBN (150 mmol)

This preparation was carried out as described above using 4.05 g (150 g-atom) of aluminum turnings, 22.8 g (150 mmol) of *B*-methoxy-9-BBN, and 22.7 ml (225 mmol) of 3-bromo-2-methylpropene. This allylic bromide was prepared in 61% yield (98% purity) by a halide exchange from 3-chloro-2-methylpropene (Aldrich) and a three-fold excess of lithium bromide in acetone [32]. The crude allylborane was vacuum distilled to give 22.1 g (84%) of a clear liquid, b.p. 55—56°C at 0.04 mmHg. VPC showed this material to be greater than 98% pure.

Preparation of B-3,3-dimethallyl-9-BBN (20 mmol)

To an oven-dried, flamed out, nitrogen-flushed, 50-ml flask fitted with a septum inlet and a magnetic stirring bar, there was added 48 ml of 0.42 *M* 9-BBN in hexane (20 mmol). Approximately half of the solvent was removed by evaporation under a stream of nitrogen leaving a slurry of the reagent. The 3-methyl-1,2-butadiene (2.0 ml, 20 mmol) was added via syringe. The mixture was allowed to stir about 7 h (VPC indicated that the allene was consumed after 4 h), then the solvent was removed under vacuum and the residual oil vacuum distilled. The product, a clear liquid, was collected in a liquid nitrogen-cooled flask. There was collected 3.32 g (87%), b.p. 54—56°C at 0.01 mmHg. The VPC showed this material to be about 97% pure.

Preparation of B-2-cyclohexen-1-yl-9-BBN (40 mmol)

To an oven-dried, nitrogen-flushed, 100-ml flask fitted with a septum inlet and a magnetic stirring bar, was added 78.5 ml of 0.528 *M* 9-BBN (40 mmol) in pentane. Approximately half of the pentane was removed by evaporation under a stream of nitrogen. The 1,3-cyclohexadiene (3.81 ml, 40 mmol) was added via syringe. The mixture was allowed to stir for 2 days. The VPC showed that that amount of residual diene remained about constant after 6 h. The solvent was removed under vacuum and the residual oil vacuum distilled to give 5.7 g (71%) of a clear oil which was collected in a liquid nitrogen-cooled flask, b.p. 84—87°C at 0.03 mmHg. VPC show this product to be greater than 90% pure; however, the purity was difficult to determine accurately since some on-column decomposition was evident.

Preparation of B-3,3-dimethyl-1-isopropylallyl-9-BBN (50 mmol)

To an oven-dried, nitrogen-flushed, 100-ml flask fitted with a septum inlet and a magnetic stirring bar, there was added 94.7 ml of 0.528 *M* 9-BBN in pentane (50 mmol). Approximately half of the pentane was removed by aspirator vacuum leaving a slurry of the reagent. The 2,5-dimethyl-2,4-hexadiene (7.2 ml, 50 mmol) was added with a syringe. VPC showed that the level of residual diene did not change much after 24 h. The solvent was removed under vacuum and the residual oil vacuum distilled to give 10.1 g (87%) of a colorless oil, b.p. 84—86°C, at 0.001 mmHg. The material decomposed on the column during attempted VPC analysis.

Protonolysis of B-allyl-9-BBN

To an oven-dried, nitrogen-flushed, 25-ml flask, fitted with a septum inlet and a magnetic stirring bar, topped with a water-cooled reflux condenser, there was added a weighed amount of *B*-allyl-9-BBN and a measured amount of n-decane (VPC internal standard). In some cases, solvent (pentane or THF) was added. The outlet of the flask was connected to a trap containing $CDCl_3$ maintained at —78°C. The protonolyzing agent was added via syringe, and the gas evolved was collected in the cold trap. When the reaction was complete, most of the gas remaining in the reaction flask was driven into the trap with a slow stream of nitrogen. The material in the cold trap was shown to be propene by ^1H NMR. The residue in the hydrolysis flask was examined by VPC. When methanol was used, a quantitative yield of *B*-methoxy-9-BBN was found. With other proto-

nolyzing agents, quantitation was not attempted by VPC. Instead, the products were identified by retention time correlation using spiked injections with standard samples. In these cases, the product identity was confirmed by ^{1}H and ^{11}B NMR. In the reactions of *B*-allyl-9-BBN with methylamine and dimethylamine, after the spectra of the initially formed complexes had been recorded, the solvent was removed under a stream of nitrogen, and the residual liquid was heated with a heat gun. When the gas evolution ceased, the samples were allowed to cool, CCl_4 was added, and the spectra were recorded again.

Preparation of standard samples of 9-BBN derivatives

(i) B-Acetoxy-9-BBN. To the usual reaction flask, there was added a known amount of 9-BBN in THF. Stirring was begun and 1 equivalent of acetic acid was added. When the gas evolution ceased, the solvent was removed under aspirator vacuum, leaving a white solid. This material was sublimed at 15 mmHg using a heat gun. The sublimed material melted slightly higher than 100°C, but the melting range was wide. ^{1}H NMR in $CDCl_3$ showed the material to be mostly the expected product; however, the methylene envelope of the bicyclic ring was of larger area relative to the methyl area than expected. This probably indicates some formation of the oxy-bis(9-BBN) through elimination of acetic anhydride. This was confirmed by VPC analysis which showed 2 peaks and by ^{11}B NMR which showed 1 large signal at δ −17 ppm and a smaller resonance at δ −55.4 ppm. The ^{11}B NMR of the unsublimed material showed only the resonance at δ −17 ppm.

(ii) B-Hydroxy-9-BBN. In the usual manner, a sample of 9-BBN in THF was treated with excess water. When the gas evolution ceased, the solvent was removed leaving a white solid. ^{1}H NMR of this material showed the usual methylene envelope and a resonance at δ 5.6 ppm which disappeared when the sample was treated with D_2O. The area ratio of the 2 peaks showed the sample to contain about 87% of the borinic acid and 13% of the oxy-bis(9-BBN). The ^{11}B NMR showed only one signal at δ −55.2 ppm.

(iii) B(N-Methylamino)-9-BBN. Lithium methylamide was prepared by treatment of 1 equivalent of n-butyllithium in hexane at −78°C with 1 equivalent of methylamine. To the stirred slurry of the amide, there was added 1 equivalent of *B*-chloro-9-BBN in pentane. An exothermic reaction ensured, and a white solid remained (LiCl). VPC showed a single peak, the ^{11}B NMR showed a resonance at δ −48.7 ppm, and the ^{1}H NMR showed 2 signals at δ 2.68 and 2.78 ppm as well as the ring methylene envelope at δ 1.78 ppm.

(iv) B-(N,N-Dimethylamino)-9-BBN. In a similar manner as the above preparation, lithium dimethylamide was prepared in hexane and treated with *B*-chloro-9-BBN. The VPC showed a single peak, the ^{11}B NMR showed a resonance at δ −47.1 ppm, and the ^{1}H NMR showed a singlet at δ 2.80 ppm and the ring methylene envelope at δ 1.78 ppm.

Protonolyses of B-crotyl-9-BBN

To an oven-dried, flamed-out, nitrogen-flushed, 10-ml serum vial fitted with a septum inlet and a small magnetic stirring bar, were added a weighed amount of *B*-crotyl-9-BBN (1.2—1.7 mmol) and about 5 ml of dry, olefin-free pentane. Stirring was begun, and the vial was cooled in an ice-water bath, and 100% excess

of the protonolyzing agent was added with a microliter syringe. The mixture was allowed to warm to room temperature and stirred for 1—2 h. The mixture was then cooled again to 0°C and 1 equivalent of ethanolamine was added to precipitate the borane derivative. The reaction mixture was allowed to warm to room temperature, stirred for 1 h, and then cooled to 0°C then the internal standard, 3-methyl-1-butene, was added from a gas-tight syringe. After the addition of the internal standard, the mixture was stirred at 0°C, the precipitate was allowed to settle, and the supernatant liquid was analyzed by VPC. The mixtures were kept at 0°C until the VPC analyses were complete.

Hydroboration of B-allyl-9-BBN

To an oven-dried, nitrogen-flushed, 25-ml flask fitted with a septum inlet and a magnetic stirring bar, was added 0.812 g of *B*-allyl-9-BBN and 8.95 ml of 0.56 *M* 9-BBN in THF. Stirring was begun, and the reaction was monitored by VPC. After 15 min, VPC showed no allylborane remaining. After stirring for 6 h, the mixture was oxidized in the usual manner. The oxidation was unusually vigorous. After heating at 50°C for 2 h, 9 g of anhydrous potassium carbonate was added. The organic layer was separated, and the aqueous layer extracted with THF (3 × 10 ml) [33]. The combined organic layers were dried over anhydrous magnesium sulfate, and 0.5 ml of n-tridecane (VPC internal standard) was added. An aliquot was removed and dried further over crushed 3 Å molecular sieves. About 0.25 ml of this aliquot was transferred to an oven-dried 1-ml serum vial where it was treated with 0.3 ml of BSTFA containing 1% TMCS. This mixture was heated for 7 h at 65°C, then analyzed on a 150 ft × 0.01 in OS-138 Golay column. A 91% yield of the bis-TMS derivative of 1,3-propane diol was found. None of the 1,2-propanediol derivative was detected. The hydroboration of *B*-crotyl-9-BBN was carried out in a similar manner.

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