Hydration with Mercuric Acetate and the Reduction with 9-BBN−H of 2-(1-Alkenyl)-4,6-dimethyl-*s*-triazines

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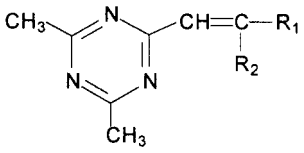
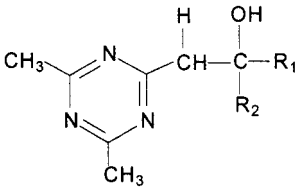
Oxymercuration−demercuration of a double bond in conjugation with the 4,6-dimethyl-*s*-triazin-2-yl substituent as in alkenes **1a,b** gave anti-Markovnikov regioselectivity, which is explained by the electron-withdrawing nature of the triazinyl substituent. However, hydroboration of the conjugated alkenes with 9-BBN−H gave the corresponding alkanes **5a**−**c** under normal workup conditions with or without oxidation. With time and without workup the hydroboration of **1b** gave spectral evidence for the formation of intermediates **9**−**13** resulting from the migration of the 9-BBN moiety from the α-carbon to a ring nitrogen with concurrent formation of an exocyclic double bond to an α-carbon of the ring. Hydrolysis of the intermediates gave **5a**−**c**. A possible mechanism involving successive allylic rearrangements is presented.

Introduction

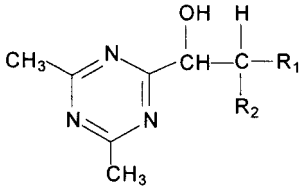
In a previous paper we reported that the 4,6-dimethyl-*s*-triazin-2-yl substituent was electron withdrawing by both the field effect and the resonance or conjugative effect.[1] In view of this influence, the substituent should destabilize any intermediate or transition state which may develop a positive charge on the adjacent α-carbon.[2] Hence, it was of interest to investigate the extent to which this behavior, as well as that of possible steric factors, would influence the regioselectivity of the hydration of a conjugated carbon−carbon double bond by possibly forcing any developing positive charge to form on the less, or equally, substituted *β*-carbon. Thus, the substituent in alkenes **1a,b**, upon oxymercuration−demercuration, would enhance the formation of alcohols **2a,b**, but in hydroboration−oxidation, it would favor alcohols **3a,b**.



1a-c



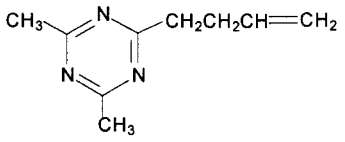
2a-c



3a-c

a: $R_1 = R_2 = H$
b: $R_1 = CH_3$, $R_2 = H$
c: $R_1 = R_2 = CH_3$

The above triazinylalkenes, **1a**−**c,** and **4** were synthesized for the above study, and we now wish to report the results of their reactions with mercuric acetate and 9-BBN−H. The former gave abnormal regioselectivity with **1a,b**, and the latter reacted with **1a**−**c** to give the unexpected corresponding alkanes **5a**−**c** with either oxidative or hydrolytic workup. In addition, further investigations via ^1H, ^{13}C, and ^{11}B NMR of the latter reaction with no workup gave conclusive evidence of the migration of the 9-BBN moiety from the α-carbon to a ring nitrogen with concurrent formation of exocyclic double bonds to the α-carbons of the ring. Similar behavior was shown to occur in the hydroboration of 2-(1-propenyl)pyridine.[3]



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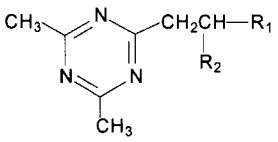

5a-c

Most previously reported general preparations of alkanes from alkenes via hydroboration have required acidic conditions and prolonged heating,[4] and trialkylboranes are also reported to be stable under neutral conditions.[5] Noteworthy exceptions particularly relevant to the present investigation are the hydrolyses under relatively mild conditions (pH 8) of the hydroboration−oxidation of vinyl- and propenylpyridines[3] and of substituted styrenes.[2a]

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Table 1. Results of Oxymercuration−Demercuration of Triazinylalkenes

alkene	mole ratio[a]	% recovered **1**	% **2**[b]
1a	1:1	*c*	57
1b	1:1	55	39[d]
1b	1:2	29	68
1b	1:3	12	78

[a] Alkene:$Hg(OAc)_2$. [b] No detectable alcohol **3** by NMR. [c] Spectral data indicated the possibility of a few percent. [d] A higher temperature (53 °C) did not alter the yield.

Results and Discussion

The results of the oxymercuration−demercuration of **1a,b** are given in Table 1.

The above results would support the conclusion that the triazine ring, as a substituent, is sufficiently electron-withdrawing to destabilize any developing charge on the more or equally substituted α-carbon atom within the intermediate bridged acetoxymercurinium ion.[2c,6] Thus, the normal regioselectivity is not realized. In addition, two other factors need to be considered.

First, in considering the steric influence of the triazine ring, it could direct the attacking mercuric acetate away from the α-carbon and toward the *β*-carbon and hence increase the yield of **3a,b**, or second, it could inhibit the attack by water on the acetoxymercurinium ion at the α-carbon and thus favor the formation of **2a,b**. The absence of any detectable alcohols **3a,b** within the products would indicate that the first influence is negligible, and the second influence would not appear to be substantial in view of the fact that 3,3-dimethyl-2-butanol is formed in 94% yield from the oxymercuration−demercuration of 3,3-dimethyl-1-butene in which water attacks the carbon adjacent to the *tert*-butyl group.[7] Thus, the regioselectivity appears to be primarily due to the electronic influence of the triazinyl substituent. A third factor to be considered is that the mercuric acetate, as a Lewis acid, may initially coordinate with the lone pair of electrons[8] on a nitrogen of the triazine ring and thereby enhance the electron-withdrawing influence of the ring above and beyond that which the neutral ring possesses. The increased yield of alcohol **2b** with an increase in the mole ratio of mercuric acetate to alkene may support this involvement of the mercuric acetate with the ring independent of the mercuration of the double bond.

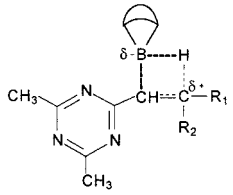
The hydroboration−oxidation with 9-BBN−H was carried out on the conjugated alkenes **1a**−**c** and on the unconjugated alkene **4**. The results are given in Table 2.

In the normal hydroboration−oxidation, alkene **1a** was the only conjugated alkene which gave evidence of the formation of any alcohol (∼10% **2a**). On the basis of the experimental data from the hydroboration−oxidation of **1b** and the large withdrawing resonance effect of the *s*-trianzinyl substituent,[1] one would conclude that, in contrast to the hydroboration−oxidation of 2-vinylpyridine (α:*β* ≈ 1:2),[3] the 9-BBN−H in this case added predominantly to the α-carbon (α:*β* ≈ 6:1) to form a transition state species, **6a**, which places a partial positive charge on the primary *β*-carbon rather than the destabilized secondary α-carbon to ultimately form the adduct **7a**. It is also reasonable that the alkane would arise only from adduct **7a** in which any carbanion character on the α-carbon[3] would be stabilized by the *s*-triazinyl ring.

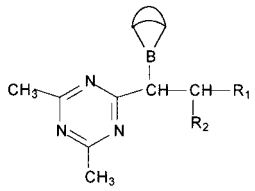
Table 2. Results of Hydroboration of Triazinylalkenes with 9-BBN−H in Hexane

		yields (mol %)[a,b]			
alkene	workup	**5**	**2**	**1**[c]	cyclooctanone[d]
1a	H_2O_2	62[a]	10[a,e]		
1b	H_2O_2	81[a]	0	10[f]	
1b	EtOH, H_2O	72[b]	0	10	25
1b	CD_3OD, D_2O	46[b]	0	8	19
1b	none[g]	23[b,g]	0	10[g]	13[g]
1c	H_2O_2	75	0	21[f]	
1c[h]	H_2O_2	75	0	26[f]	
4	H_2O_2	0	60[e]		

[a] Based upon GLC data. [b] Based upon NMR data. [c] Recovered. [d] Based upon moles of 9-BBN−H. [e] 1° alcohol. [f] Based upon epoxide yield. [g] Products distilled from reaction. [h] With 9-BBN-D in hexane.



6a-c



7a-c

When the hydroboration−oxidation was initially carried out on **1b,c** with an excess of the alkene, and the normal period of time,[9] a minor amount of the corresponding epoxy compound was also isolated.[10] Consequently, subsequent reactions were carried out with 5−10% mole excess of 9-BBN−H. In view of the fact that the triazinylalkane **5b**, and not the alcohol, was the only product isolated from the hydroboration−oxidation of **1b**, it became apparent that only a source of hydrogen, and not an oxidizing agent, was involved in the workup. Thus, the workup of the hydroboration of **1b** with ethanol and water in the absence of hydrogen peroxide gave isolated **5b** (72 mol %). A comparable experiment with methanol-d_4 and deuterium oxide gave **5b** with increased multiplicity in the ^{1}H NMR for the α-methylene proton due to the presence of deuterium which had replaced the 9-BBN moiety on the α-carbon. This mode of addition to give the adduct **7** was also consistent with the results of the reaction of 9-BBN−D with **1c**. There was no spectral evidence in $CDCl_3$ (^{1}H and ^{11}B NMR) for the migration of the 9-BBN moiety along the propyl group,[11] but there was evidence in the ^{11}B NMR spectra for the initial association of the 9-BBN−H dimer or monomer[12] with the nitrogens of the ring (K_b for 3,5,6-trimethyl-1,2,4-triazine: $\sim 7 \times 10^{-12}$)[13] as reported with amines,[14] as well

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Table 3. NMR Chemical Shifts from the Hydroboration of 1b with 9-BBN−H in $CDCl_3$[a]

	α-CHB<			α-CH_2−		β-CH_2−		γ-CH_3		ring CH_3	
compd	^1H	^{13}C	^{11}B	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}H
adduct **7b**	2.98 (b)	30.6 (b)	+84[b]			c	20.85	0.92 (t)	14.79	2.50 (s)	25.70
intermediates[d,e]				2.72 (t)	41.01	1.77 (m)	21.61	0.94 (t)	14.01	2.55 (s)	25.71
alkane **5b**[f]				2.71 (t)	40.64	1.75 (m)	21.26	0.93 (t)	13.69	2.54 (s)	25.33

[a] Under argon in sealed NMR tubes. [b] See ref 20. [c] Initially obscured by 9-BBN signal. [d] Intermediates, **9b**−**13b**, and/or **5b**. [e] With time the ^1H NMR spectra began to show eight small signals (total area ∼ 2−3 H): two triplets (δ 0.86 and δ 4.87), a quintet (δ 2.03), a multipet (δ 2.21), and two pairs of singlets (δ 4.04, 4.06 and δ 4.39, 4.48). The ^{13}C NMR spectra also showed several small signals between δ 60 and 150. Within the ^{11}B NMR spectra the δ +84 signal decreased as the δ +59 signal increased. [f] Authentic sample.

as with the nitrogen of a nitrogen−nitrogen double bond.[15] Boron has also been reported to associate with oxygen in the 1,4-addition of 9-BBN−H in $CDCl_3$ to give reduction of the double bond in 1-phenyl-2-alken-1-ones[16] and in 4-hexen-3-one,[17] as well as in the 1,2-reduction of a number of conjugated aldehydes to the corresponding allylic alcohols.[18]

In view of the above unanticipated results and the uncertainty of the origin of some products, such as cyclooctanone,[19] the progress of the reaction of 9-BBN−H with **1b** under argon in standard reaction apparatuses was abandoned. Thus, all subsequent reactions, except those for ^{11}B NMR spectra, were carried out in degassed solvents under argon in sealed ampules or NMR tubes. Although abstraction of hydrogen from the glass or the deuterium from the solvent was considered, experimental evidence did not support either possibility. The products arising from the reactions were examined during, and/or after, many months (4−20) at room temperature or at elevated temperatures (∼55 °C) for many days (25−60) by NMR, GC-MS, and/or by quenching with deuterated solvents followed by GC-MS. The following spectral changes were observed for the reaction of 9-BBN−H with **1b** in $CDCl_3$ at room temperature. Within a few hours, in addition to the signals from the alkene and the 9-BBN moiety, the ^1H, ^{13}C, and ^{11}B NMR spectra began to show signals consistent with those of adduct **7b** as shown in Table 3. The broad signal at δ 2.98 within the ^1H NMR spectra due to the presence of boron on the α-carbon requires some comment. A three-coordinate, but not a four-coordinate, boron on carbon is reported not to undergo two-bond coupling with hydrogen.[21] Therefore, this situation is either anomalous or the boron is partially four-coordinated with a nitrogen of the ring or is still partially associated as a dimer. The ^{11}B NMR spectra at δ +59[22] would support an early (2 h) and an increasing association of a boron with a nitrogen as the reaction progressed. As the reaction continued, the signals from **7b** increased and those of the alkene decreased. However, after 3−4 days at room temperature, all of the signals attributed to **7b** had maximized and a sharp triplet at δ 2.72 (α-CH_2) in the ^1H NMR spectra became increasingly evident. Thus, the signals from **7b** began to decrease as new signals consistent with those of the alkane **5b** began to appear and continue to increase over a period of months. However, in addition to the signals attributed to **5b**, the final ^1H NMR spectrum showed a total of eight small signals (Table 3) totaling approximately two to three protons. The final ^{13}C NMR spectrum also gave an increasing number (∼10) of small signals between δ 60 and 150 which a DEPT spectrum showed to be sp^2 carbons. Essentially the same sequence of NMR spectra was obtained when the reaction was carried out at 60 °C for 8 days. Since the additional signals could not be assigned to **7b** or **5b**, they were attributed to species resulting from the rearrangement of **7b** to possible species such as **8a**−**c** and **9a**−**c** through **13a**−**c**. Table 4 shows the relative yields of products from the GC-MS analyses of the reaction solutions of **1b** with 9-BBN−H in a variety of solvents before hydrolysis. The transformation of **7b** into **5b** and intermediates **9b**−**13b** appears to proceed more rapidly in more polar solvents. Quenching of the NMR solutions with water after completion of the reaction caused all of the ^1H NMR signals unique to the intermediates **9b**−**13b** to disappear and leave only

Table 4. Relative Yields of Products from Reaction Solutions of 9-BBN−H with Alkene 1[a]

				rel yields (%)		
alkene	solvent	temp[b]	time (months)[c]	alkane (**5**)	alkene (**1**)	adduct (**7**)
1b	hexane[d,e]	rt[f]	4	75[g]	25[g]	
1b	hexane[h,i]	56	9 days	35[j]	22[j]	43[j]
1b	hexane[h,i]	56	1	50[k]	24[k]	26[k]
1b	hexane[h,i]	55	2	35	10	55
1b	hexane[d,l]	75	2 days	81[m]	19[m]	
1b	$CDCl_3$[i,n]	rt	2	71[o]	25[o]	4[o]
1b-d_6	$CDCl_3$[i,n]	rt	20	85		15[p]
1b	$CDCl_3$[i,n]	60	7 days	97[o]	0[o]	3[o]
1b	CD_2Cl_2[i,n]	rt	4	100[o,q]	0[o]	0[o]
1b	C_6D_6[i,n]	rt	20	51		49[r]
1b	THF-d_8[d,i,n]	rt	1	37[o]	40[o]	23[o]
1b	THF[d,l]	75	52 h	61[s]	39[s]	
1c	$CDCl_3$[i,n]	rt	20 days	64[o]	17[o]	19[o]
1c	$CDCl_3$[i,n]	rt	4	85[o]	15[o]	0[o]

[a] Based upon GC-MS data before workup unless otherwise designated. [b] Bath temperature, °C. [c] Unless otherwise designated. [d] Commercial 9-BBN−H solution. [e] Vial with septum. [f] Precipitate formed. [g] Absolute yields relative to nonane: **5b**, 62%; **1b**, 21%. [h] Sealed ampule. [i] Prepared 9-BBN−H solution. [j] Absolute yields relative to nonane: **5b**, 38%; **1b**, 23%; **7**, 46%. [k] Absolute yields relative to nonane: **5b**, 38%; **1b**, 18%; **7**, 20%. [l] Reaction flask (Ar). [m] Absolute yields relative to nonane: **5b**, 61%; **1b**, 15%. [n] Sealed NMR tube. [o] Based upon NMR data (alkane yield also includes intermediates **8**−**13**). [p] *m/z* 399 (**7**-d_6 + 9-BBN−H). [q] Absolute yields relative to 2,4,6-tripropyl-s-triazine: **5b**, 52 mol %. [r] *m/z* 393 (**7** + 9-BBN−H). [s] Absolute yields relative to bibenzyl: **5b**, 33 mol %; **1b**, 25 mol %.

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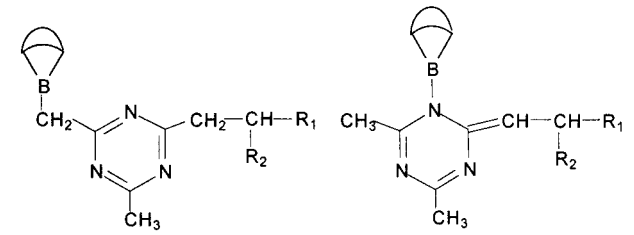
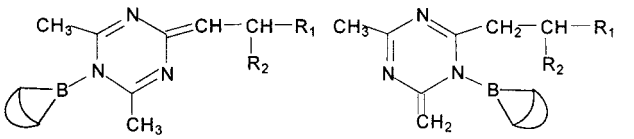
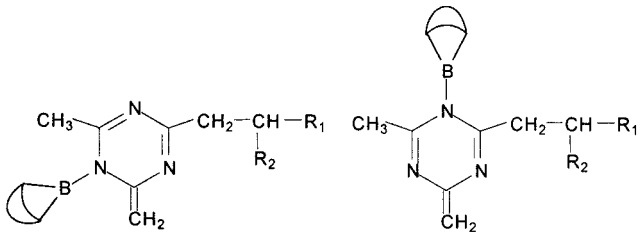
those signals attributable to **5b** and the 9-BBN moiety, whose broad envelope (δ 1.25−2.0) had sharpened. Within the ^{13}C NMR spectra the signals between δ 60 and δ 150 disappeared and the broad signals due to the 9-BBN moiety (δ 23.3 and δ 33.2) narrowed.



8a-c **9a-c**



10a-c **11a-c**



12a-c **13a-c**

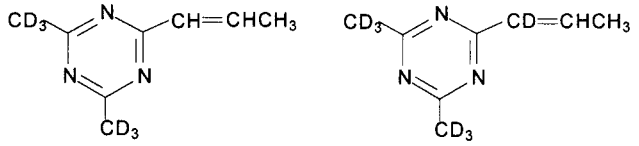
The following experimental evidence supports the formation of alkane **5**, adduct **7**, and intermediates **9**−**13** in the reaction of 9-BBN−H with **1a**−**c**. Although intermediate **8** is a feasible species, no experimental evidence was found to support its existence.

(1) When the reaction of **1b** with 9-BBN−H in $CDCl_3$ was permitted to proceed only until the adduct **7b** was fully formed (70 h, room temperature) and then quenched with methanol-d_4, the ^{1}H NMR gave a multiplet at δ 2.65 (α-CHD) and showed essentially a quantitative conversion of **7b** to **5b** relative to bibenzyl as an internal reference. However, when the reactions were permitted to proceed for longer periods of time past the formation of **7b** before quenching, the yields of alkane **5b** relative to bibenzyl in the NMR or to nonane in GC-MS were within 40−60% depending upon the solvent (Table 4). These lower yields could indicate that unidentified products were formed before quenching as a result of disproportionation between the intermediates. Also, after deuterium quenching, unidentified products (5−6%) containing deuterium were frequently found in the GC-MS of the products. The MS also showed an enrichment of deuterium in the spectrum of **5b** (*m*/*z* 150−155) relative to that of **5b** from nondeuterated quenches (*m*/*z* 150−152). The ^{13}C NMR spectrum of the **5b** from the deuterium quench showed ^{13}C−D coupling[23] both at the carbons of the ring methyl groups (^1J = 19.6 Hz) and the α-carbon (^1J = 19.5 Hz) giving evidence consistent with the formation of **5b** from the quenching of intermediates **9**−**13**. The 9-BBN−O−CH_3 (65−75% yield) from the quenching experiments did not show any incorporation of deuterium. Derivatization of the 9-BBN moiety at the end of the reaction with ethanolamine[24] or oxidation with peroxide gave yields of approximately 90% of the ethanolamine adduct and 95% of the *cis*-1,5-cyclooctanediol.

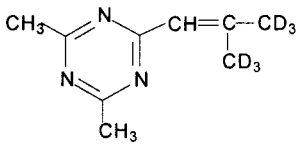
Slow evaporation (14 months) of the $CDCl_3$ of the reaction solution from the hydroboration of **1b** open to the air gave crystals which upon crystallographic analysis showed the presence of a 1:1 complex of boric acid and **1b** together with some **5b** and from which, with time, both of the latter evaporated.[25]

(2) Low-temperature ^{1}H NMR (400 MHz) enabled the signal at δ 2.03 to be resolved into a quintet and the signals between δ 4 and δ 5 to be resolved into a triplet (δ 4.87) and two pairs of singlets (δ 4.04, 4.06 and δ 4.39, 4.48). The quintet and the triplet together with the small upfield triplet (δ 0.86) are supportive of the presence of the propylidene group of intermediates **9b** and **10b**. Likewise, the presence of the two exocyclic methylene groups and the *n*-propyl groups of intermediates **11b**−**13b** is supported respectively by the two pairs of singlets (^2J = 0) and two large triplets (δ 0.94 and δ 2.72) and a sextet (δ 1.77). The latter three multiple signals are also contributed to by the *n*-propyl group of any alkane **5b** present. The possible presence of **5b** before quenching was indicated by a semiquantitative comparison in the ^{1}H NMR in which the calculated areas from the ring methyl groups of **9b**−**13b** (relative to the areas of the sp^2 hydrogens) could account for only 55−60% of the total area from all of the ring methyl groups. Experimentally, the presence of **5b** before quenching was also supported by the GC-MS analyses of the reaction solutions (Table 4). The most probable sources of **5b** before quenching would arise from hydrogen abstraction from between the intermediates (disproportionation) or from the 9-BBN moiety.

(3) To further ascertain whether the methyl groups of the ring or the allylic γ-methyl groups of **1b,c** were sources for the hydrogen that replaced the 9-BBN moiety, the following deuterated compounds were synthesized. Experimentally, within 6 h, the hydroboration of **1b**-d_6



1b-d_6 **1b-d_7**



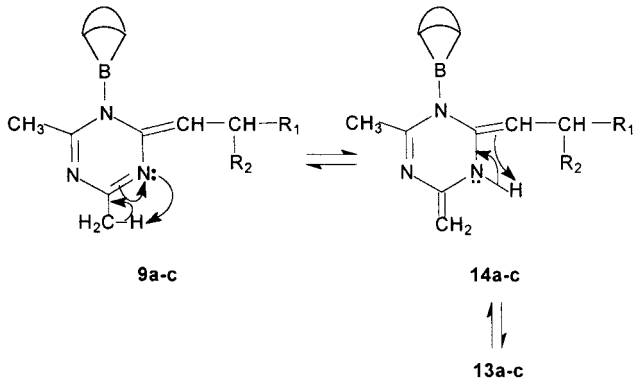
1c-d_6

(23) Friebolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy*, 2nd ed.; VCH Publishers: New York, 1993; pp 49−50 (translated by J. K. Becconsall).

(24) (a) Rondestvedt, C. S., Jr.; Scribner, R. M.; Wulfman, C. E. *J. Org. Chem.* **1955**, *20*, 9−12. (b) Kramer, G. W.; Brown, H. C. *J. Org. Chem.* **1977**, *42*, 2292−2299.

(25) The crystal structure will be reported elsewhere.

Scheme 1



(93 atom % D) in $CDCl_3$ began to show a sharp triplet at δ 2.72 for the α-methylene group. After approximately 5 days, a broad multiplet (^2J = 2 Hz) began to appear superimposed upon the sharp triplet. This multiplicity at δ 2.72 continued to increase until the original broad signal at δ 2.98 (>CHB<) had essentially disappeared (~15 days). No further changes in any of the signals occurred within the following 9 months indicating the absence of scrambling. Simultaneous with the above changes was a significant decrease in the small signal area for the residual protons originally remaining in the methyl groups of the ring (δ 2.54). An approximation of the relative areas of the superimposed sharp and broad signals for the α-methylene group (δ 2.72) was two-thirds ($-CH_2-$) and one-third ($-CHD-$), respectively, which would indicate a 1:1 hydrogen to deuterium migration ratio to the α-carbon. This ratio would be unlikely to originate only from the methyl groups of the ring (93 atom % D) even with a maximum isotope effect, and therefore, this result is supportive of possibly another source for the hydrogen such as the 9-BBN moiety. Also, with time, within the ^{13}C NMR spectra for the above reaction of **1b**-d_6, a small triplet became superimposed on the singlet for the α-methylene group (δ 41.01) giving evidence via coupling of the presence of deuterium on the α-carbon. The ^1H and ^{13}C NMR spectra for the reaction of **1b**-d_7 with 9-BBN−H in C_6D_6 were also supportive of the above conclusions. The hydroboration of **1c**-d_6 with 9-BBN−H in $CDCl_3$ over a period of 10 months gave no evidence of deuterium on the α-carbon thus ruling out the possible involvement of the allylic hydrogens.

It is conceivable that the mechanism by which a hydrogen is transferred intramolecularly from a ring methyl group to the α-carbon proceeds via a series of allylic rearrangements via an enamine tautomer, **14**, formed from **9** as shown in Scheme 1.

The ^{15}N NMR spectrum of the reaction intermediates from **1b** (4 months) did not give evidence of a boron coordinated with a nitrogen[26] but gave only two signals at δ 266.69 and 267.71 which did not differ significantly from the ^{15}N NMR spectrum of 2,4,6-trimethyl-*s*-triazine alone (δ 267.23) or with 9-BBN−H present (δ 267.32). However, the ^{11}B NMR spectra indicated that the 9-BBN moiety became increasingly coordinated to a nitrogen (δ +59) throughout the reaction and was exclusively associated with a nitrogen at the end of the reaction. The failure to observe a ^{15}N NMR signal from a nitrogen coordinated with a 9-BBN moiety may be due to the broadening of the nitrogen signal by the coupling of the boron with the nitrogen.[27]

Although it was difficult to obtain a reproducible rate for the conversion of the adduct **7b** to the intermediates **9b**−**13b** and **5b**, the addition of galvinoxyl[28] to the reaction solution after **7b** had formed appeared to decrease the rate, hence indicating the possibility that the replacement of the 9-BBN moiety by a hydrogen proceeded via a free radical mechanism. However, this result is suspect because a control indicated that 9-BBN−H decolorized galvinoxyl within minutes. Support for a free radical mechanism could also be concluded from the presence within some of the final products of a molecular ion having the mass of a coupled product (*m*/*z* 300). The ESR spectrum of the hydroboration of **1b** in C_6D_6 was taken at appropriate intervals after the adduct **7b** had formed, but no signal was obtained either because of the absence of free radicals or because their concentrations were too low for detection.

To examine whether the behavior observed in the triazinylalkenes **1** would be evident in comparable systems, the hydroboration with 9-BBN−H of 2-vinylpyridine and *trans*-2-(1-propenyl)pyridine as reported by Brown[3] was carried out in sealed NMR tubes over long periods of time. The ^1H NMR spectra of the hydroboration of the 2-vinylpyridine with 9-BBN−H (1:1) at room temperature gave a broad singlet at δ 0.57, two sharp triplets at δ 0.83 and δ 2.9, and an increased multiplicity of the signals associated with the ring hydrogens after 17 days with no additional changes even with heating. With a ratio of 1:2 (alkene:9-BBN−H) the results were similar except for an initial broadening of the signals for the hydrogens of the 2-vinylpyridine. These results were consistent with the reported bonding of the 9-BBN moiety to the β-carbon,[3] but there was no evidence for the formation of the corresponding alkane. Likewise, the hydroboration of 2-(1-propenyl)pyridine gave no evidence of the formation of the alkane, and ^1H NMR spectral evidence indicated that the 9-BBN moiety bonded initially to the α-carbon. In the case of a 1:1 ratio (alkene:9-BBN−H), but not in the case of the 1:2 ratio, a new downfield triplet in the ^1H NMR spectra began to appear after 1 day at δ 1.16 as well as a number of multiplet signals between δ 4.5 and δ 6.3. Simultaneously, the ^{13}C NMR spectra began to show an increased number of signals between δ 110 and δ 170. With the addition of water to the NMR sample, the above signals disappeared from the spectrum to give that of the alkane. The above downfield triplet and the multiplet signals in the ^1H NMR, and the accompanying ^{13}C NMR signals, would be supportive of the migration of the 9-BBN moiety to the nitrogen with the 1:1 ratio giving the formation of an exocyclic double bond to the α-carbon similar to that which formed intermediates **9** and **10** proposed for the hydroboration of the triazinylalkenes. In the case of the 1:2 ratio presumably a second 9-BBN−H was already coordinated with the nitrogen, thus prohibiting the migration of the first 9-BBN moiety to the nitrogen. However, the failure to obtain any alkane in the hydroboration of the alkenylpyridines would tend to preclude the 9-BBN moiety as a source of the hydrogen

(26) Mason, J. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; pp 350−355.

(27) Wrackmeyer, B. *J. Magn. Reson.* **1986**, *66*, 172−175.

(28) (a) Kabalka, G. W.; Brown, H. C.; Suzuki, A.; Honma, S.; Arase, A.; Itoh, M. *J. Am. Chem. Soc.* **1970**, *92*, 710−712. (b) Bartlett, P. D.; Funahashi, T. *J. Am. Chem. Soc.* **1962**, *84*, 2596−2601.

necessary to convert intermediates **7**−**13** into **5**, unless those intermediates had greater affinities for the hydrogens of the 9-BBN moiety than comparable species in the pyridine case.

The following controls were carried out: (a) The ^{1}H NMR spectra of 9-BBN−H in $CDCl_3$ within a sealed NMR tube at room temperature showed no changes over 70 days, and (b) 2,4,6-trimethyl-*s*-triazine with 9-BBN−H in $CDCl_3$ with bibenzyl as a reference in a sealed NMR tube showed no change in the ratio of the signal areas over a period of 8 months at room temperature. Additionally, the hydrolysis of the final solution[29] accounted for 95% of the original 9-BBN−H molarity. Thus, under the conditions in which the hydroborations of **1** was carried out in this study, there were no significant reactions occurring between the 9-BBN−H and the triazine ring or its methyl groups. However, the control studies do not preclude the possibility that the adduct **7** may be capable of abstracting a hydrogen, intra- or intermolecularly, from a methyl group on the triazine ring or the 9-BBN moiety.

Attempts at aprotic workup of the sealed and unsealed final reaction solutions frequently gave considerable amount of cyclooctanone, presumably due to exposure to air and solvents that had not been degassed. The yields of cylcooctanone exceeded the amount of excess 9-BBN−H and, therefore, would indicate that the 9-BBN moiety associated with intermediates **7**−**13**, as well as unreacted 9-BBN−H, reacted with air to give cyclooctanone.[19] Other minor products evident in the GC-MS analyses and presumably arising from the 9-BBN−H or its moiety, but not necessarily directly involved in the conversion of intermediates **7**−**13** to **5**, were bicyclo[3.3.0]octane, cyclooctane, and cyclooctene. These products were among those reported as products in the reaction of alkaline $AgNO_3$ with 9-BBN−H[30] and in the oxidation of 9-BBN−H with PCC.[19b]

The reductions of **1b** with BH_3·THF and sodium borohydride were also examined. A large excess of BH_3·THF with **1b** at room temperature gave no evidence of any reaction as followed by TLC, and prolonged refluxing (28 h) led to the destruction of the triazine ring. This may not be unexpected in view of boranes reactivity with nitriles[31] and amides.[32] The reaction of **1b** with equal molar amounts of sodium borohydride gave 24% alkane (**5b**) and 76% recovered **1b**.

Conclusion

The oxymercuration−demercuration of **1a,b** gave abnormal regioselectivity due to the electron-withdrawing influence of the triazine ring. Hydroboration−oxidation and hydroboration−hydrolysis of **1a**−**c** gave the corresponding alkane **5**. In the absence of hydrolysis, NMR, GC-MS, and deuterium studies showed that the 9-BBN moiety tautomerized to a ring nitrogen to form intermediates **9**−**13** and that some alkane **5** was formed possibly by disproportionation of the intermediates or hydrogen abstraction from the 9-BBN moiety.

Experimental Section

General Methods. Melting points and boiling points are uncorrected. All reactions were performed in oven-dried glassware under an atmosphere of dried and deoxygenated argon. ^{1}H, ^{13}C, ^{11}B, and ^{15}N NMR spectra were recorded at 200, 50, 160.5, and 50.7 MHz, respectively. Variable-temperature NMR spectra were recorded at 400 MHz. Proton chemical shifts were referenced to residual solvent protons, carbon chemical shifts were referenced to solvent, boron chemical shifts were referenced to external BF_3·OEt_2, and nitrogen chemical shifts were referenced to external trimethyl-*s*-triazine. GLC analyses were performed with a 4 ft × $^1/_4$ in. column packed with DC 200 on Chrom-P and a TC detector. Mass spectra were obtained with a mass spectrometer coupled with a gas chromatograph. Elemental analyses were performed by Desert Analytics Laboratory, Tucson, AZ. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Ether was distilled from sodium benzophenone ketyl under argon, and final distillations of glyme and THF were from LAH. Solvents used for the preparation of 9-BBN−H solutions were degassed. 9-BBN−H was either recrystallized from purified glyme[12] or sublimed (120 °C/0.04 Torr) after a forerun was taken: melting points were within the 150−154 °C range (evacuated, sealed capillaries, lit.[9,33] mp 152−155 °C). Solid 9-BBN−H was transferred within an argon-filled glovebag, and the transfer of solvents, 9-BBN−H solutions, and hydroboration reaction solutions were carried out with oven-dried, argon-flushed syringes. Vinylpyridine was purified by distillation at reduced pressure from calcium hydride.

2,4-Dimethyl-6-vinyl-*s*-triazine (1a). To a solution of **2a**[34] (1.97 g, 12.9 mmol) in 150 mL of dry benzene was added 3 g (0.02 mol) of phosphorus pentoxide with vigorous stirring. The mixture was heated (50 °C) for 4 days, during which time two portions (2 g, 1 g) (0.02 mol) of phosphorus pentoxide were added. The mixture was filtered through Celite, and the solution was extracted with saturated NaCl solution (3 × 1 mL). The aqueous phases were extracted with CH_2Cl_2 (2 × 10 mL), and the organic phases were combined, dried ($MgSO_4$), filtered, and evaporated to yield a liquid residue which was distilled to afford 0.58 g (34%) of the alkene: bp 51−56 °C (4.5 Torr) (lit.[35] bp 73−75 °C (19 Torr)); IR (neat) 3025, 1630, 1530, 955 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.52 (s, 6H), 5.78 (dd, 1H), 6.60 (dd, 1H), 6.77 (dd, 1H).

2,4-Dimethyl-6-(1-propenyl)-*s*-triazine (1b). A solution of **2b**[36] (3.16 g, 19 mmol) in 5.5 mL (58 mmol) of acetic anhydride containing a few crystals of toluenesulfonic acid was refluxed for 2 h and then distilled. After distillation of the acetic acid and excess acetic anhydride, the crude alkene was distilled to afford 2.29 g of product: bp 66−68 °C (4 Torr). The crude alkene was dissolved in ether (15 mL) and stirred at room temperature with saturated $NaHCO_3$ solution (4.5 mL) for 3 days. The phases were separated, the aqueous phase was extracted with ether (2 × 10 mL), and the combined ether phases were dried ($MgSO_4$). The ether phase was evaporated to yield a clear liquid (1.80 g), which was distilled to afford 1.60 g (56%) of **1b**: bp 70−72 °C (4.0 Torr); IR (neat) 3020, 1650, 1530, 955 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.94 (dd, J = 8.5, 2.5 Hz, 3H), 2.53 (s, 6H), 6.35 (dq, J = 17, 2.5 Hz, 1H), 7.38 (dq, J = 17, 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 18.4, 25.5, 129.6, 142.0, 170.6, 175.8. Anal. Calcd for $C_8H_{11}N_3$ (M_r = 149.21): C, 64.40; H, 7.43; N, 28.17. Found: C, 64.25; H, 7.66; N, 28.13.

2,4-Dimethyl-d_6-6-(1-propenyl)-*s*-triazine (1b-d_6). A solution of **1b** (483 mg, 3.2 mmol) in D_2O (5 mL) containing 6 N

(29) Brown, H. C. *Organic Syntheses via Boranes*; Wiley & Sons: New York, 1975; pp 241−245.
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(31) (a) Brown, H. C.; Subba Rao, B. C. *J. Am. Chem. Soc.* **1960**, *82*, 681−686. (b) Emeléus, H. J.; Wade, K. *J. Chem. Soc.* **1960**, 2614−2617.
(32) Brown, H. C.; Heim, P. *J. Am. Chem. Soc.* **1964**, *86*, 3566−3567.
(33) Brown, H. C.; Liotta, R.; Kramer, G. W. *J. Am. Chem. Soc.* **1979**, *101*, 2966−2970.
(34) Schaefer, F. C. U.S. Patent 3,203,550, 1965; *Chem. Abstr.* **1965**, *63*, 14886g.
(35) American Cyanamid Co. Brit. Patent 935,787, 1963; *Chem. Abstr.* **1964**, *60*, 2987d.
(36) Nyquist, H. L.; Davenport, D. A.; Han, P. Y.; Shih, J. G.; Speechly, T. G. *J. Org. Chem.* **1992**, *57*, 1449−1456.

NaOD (2 drops) at pH 10 was permitted to stand at room temperature under argon for 3 days during which the deuterium exchange was followed by ^{1}H NMR. The solvent was distilled under reduced pressure (3.5 Torr), and the residue was dissolved in D_2O (5.0 mL) with 1 drop of 6 N NaOD. After 3 days the solution was neutralized with acetic acid-d_4 and distilled to afford a residue which was saturated with NaCl and extracted with ether (5 × 10 mL) and dichloromethane (2 × 10 mL). The aqueous distillate was also extracted with dichloromethane, and the combined extracts were dried ($MgSO_4$) and evaporated to afford 534 mg (110%) of liquid residue. The residue was eluted on neutral alumina (12 g) with 5% ether/pentane, and selected fractions were combined and distilled to afford 90 mg (18%) of **1b**-d_6: bp 66−68 °C (3 Torr); IR (neat) 2230, 1650, 1525, 965 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.94 (dd, 3H), 2.50 (m, 0.4H), 6.35 (dq, 1H), 7.38 (dq, 1H); ^{13}C NMR ($CDCl_3$) δ 18.6, 25.7 (m), 129.8, 142.1, 170.8, 176.2.

2,4-Dimethyl-d_6-6-(1-propenyl-1-d)-*s*-triazine (1b-d_7). A solution of **2b** (3.02 g, 18.1 mmol) in D_2O (7.0 mL) containing 6 N NaOD (2 drops) was permitted to stand at room temperature for 5 days during which the deuterium exchange was followed by ^{1}H NMR. The solvent was distilled under reduced pressure (3 Torr) to afford a residue and a distillate which was extracted with ether (3 × 10 mL), and the latter was dried ($MgSO_4$) and evaporated to give additional residue. The combined residues were dissolved in D_2O (6 mL), 6 N NaOD (1 drop) was added, and the above procedure was followed. The latter treatment with D_2O was repeated twice. The final reaction solution was worked up as described for **1b**-d_6 to afford 2.15 g (68%) of solid alcohol **2b**-d_9: bp 99−102 °C (3.4 Torr); ^{1}H NMR ($CDCl_3$) δ 1.21 (d, 3H), 2.50 (m, 0.36H), 2.81 (m, 0.39H), 4.22 (m, 1H), 4.4 (br s, 0.3H). Alcohol **2b**-d_9 (863 mg, 4.9 mmol) was treated with acetic anhydride (3 mL) according to the procedure for the preparation of alkene **1b** to afford 488 mg (64%) of alkene **1b**-d_7, whose deuterium content of the methyl groups of the ring had decreased to 71 mol %. Therefore, the alkene was treated with D_2O (5 mL) and 6 N NaOD (4 drops) at room temperature for 1 day and then worked up as previously described for **1b**-d_6 to afford 206 mg of crude **1b**-d_7. The crude **1b**-d_7 (156 mg) was eluted on neutral alumina (10 g) with 5% ether/pentane, and selected fractions were combined and distilled to afford 56 mg of **1b**-d_7: bp 70 °C (4 Torr); IR (neat) 2960, 2270, 1650, 1525, 895 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.92 (d, 3H), 2.52 (m, 0.6H), 6.35 (dq, 0.3H), 7.36 (m, 1H); ^{13}C NMR (C_6D_6) δ 18.1, 141.0, 171.0, 176.3.

2,4-Dimethyl-6-propyl-*s*-triazine (5b). A 35 wt % dispersion of KH in mineral oil (1.45 g KH, 36.1 mmol) was washed under argon with dry benzene (4 × 8 mL) and then covered with 75 mL of glyme. To the stirred suspension at room temperature was added (22 min) a solution of 2,4,6-trimethyl-*s*-triazine (4.51 g, 36.6 mmol) in glyme (20 mL). After being stirred for 2 days, the rust-colored suspension was added (1 h) to a solution (0 °C) of bromoethane (12.0 g, 110 mmol) in glyme (70 mL). The reaction mixture was stirred overnight, filtered through Celite, and evaporated to afford 5.87 g of a dark red liquid. The liquid was dissolved in ether, extracted with cold, saturated NH_4Cl solution (3 × 2 mL), dried ($MgSO_4$), and evaporated to afford 4.85 g (88%) of a reddish-brown liquid. The liquid was distilled (94−118 °C, 54 Torr) to give 2.90 g of distillate which was chromatographed on neutral alumina (40 g) with 5% ether/pentane. Selected fractions were combined and distilled to give 0.25 g of product: bp 102−106 °C (72 Torr) (lit[37] bp 98.5−99 °C (44 Torr)); IR (neat) 2960, 1530 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.94 (t, 3H), 1.76 (m, 2H), 2.54 (s, 6H), 2.71 (t, 2H); ^{13}C NMR ($CDCl_3$) δ 13.7, 21.3, 25.3, 40.6, 175.7, 178.8.

2-Methyl-1-(4,6-dimethyl-*s*-triazin-2-yl)-2-propanol (2c). To a stirred solution under argon of 2,4,6-trimethyl-*s*-triazine (10.26 g, 83.3 mmol) in 350 mL of anhydrous ether (−78 °C) was added *n*-butyllithium (2.45 M, 85.8 mmol). After the addition was completed (30 min), the bright-yellow reaction mixture was permitted to warm to room temperature for 2 h and then cooled to −78 °C. A solution of dry acetone (6.6 mL, 90 mmol) in ether (100 mL) was then added (25 min), and the mixture was permitted to warm to room temperature overnight. The mixture was cooled (0 °C), and a cold, saturated NH_4Cl solution (15 mL) was added. The ether phase was separated and washed with NH_4Cl solution (6 mL). The aqueous phases were extracted with ether (50 mL), and the ether phases were combined and dried ($MgSO_4$). Evaporation of the solvent gave 17.21 g of liquid which was distilled to afford 7.20 g (48%) of product: bp 107−110 °C (1.9 Torr); IR (neat) 3430, 1525, 1145 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.31 (s, 6H), 2.60 (s, 6H), 3.00 (s, 2H), 5.10 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 25.8, 29.6, 49.9, 70.2, 176.0, 177.0. Anal. Calcd for $C_9H_{15}N_3O$ (M_r = 181.23): C, 59.64; H, 8.34; N, 23.19. Found: C, 59.94; H, 8.55; N, 22.78.

2,4-Dimethyl-6-(2-methyl-1-propenyl)-*s*-triazine (1c). The method for the preparation of **1b** was followed. Alcohol **2c** (3.04 g, 16.8 mmol) afforded 2.19 g of the crude alkene, which after treatment with a saturated $NaHCO_3$ solution and workup afforded 1.98 (72%) of product: bp 128−131 °C (50 Torr); IR (neat) 3010, 1640, 1510, 850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.95 (s, 3H), 2.30 (s, 3H), 2.55 (s, 6H), 6.22 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 20.7, 25.6, 28.4, 123.2, 153.9, 171.7, 175.4; MS *m*/*z* (relative intensity) 163 (24), 162 (27), 148 (60), 121 (16), 81 (34), 42 (100). Anal. Calcd for $C_9H_{13}N_3$ (M_r = 163.21): C, 66.23; H, 8.03; N, 25.75. Found: C, 66.12; H, 8.25; N, 25.68.

2,4-Dimethyl-6-(2-methylpropyl)-*s*-triazine (5c). A 35 wt % dispersion of KH in mineral oil (1.48 g KH, 36.8 mmol) under argon was washed with dry benzene (5 × 5 mL) and then covered with glyme (75 mL). To the stirred suspension at room temperature was added (75 min) a solution of 2,4,6-trimethyl-*s*-triazine (4.64 g, 37.7 mmol) in glyme (20 mL). After being stirred for 3 h, the pumpkin-colored suspension was added (22 min) to a solution of 2-bromopropane (4.72 g, 38.3 mmol) in 75 mL of glyme at −78 °C. The reaction mixture was stirred and warmed to room temperature overnight and then warmed to 70 °C (1 h). The brick-red suspension was cooled to room temperature and worked up as described above for the preparation of **5b** to afford 1.34 g of recovered 2,4,6-trimethyl-*s*-triazine and 1.00 g of impure **5c** (23% yield adjusted for recovered triazine): bp 70−78 °C (2.5 Torr). A portion (653 mg) of the above product was placed on neutral alumina (l cm × 25 cm) and eluted with 4% ether/pentane to afford, after distillation, 450 mg of **5c**: bp 76−78 °C (4.6 Torr); IR (neat) 2960, 1520 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (d, 6H), 2.20 (m, 1H), 2.53 (s, 6H), 2.61 (d, 2H); ^{13}C ($CDCl_3$) δ 22.3, 25.4, 28.0, 47.7, 175.7, 178.3; MS *m*/*z* (relative intensity) 165 (M^+, 2), 150 (11), 123 (49), 68 (16), 42 (100). Anal. Calcd for $C_9H_{15}N_3$ (M_r = 165.23): C, 65.42; H, 9.15; N, 25.43. Found: C, 65.41; H, 9.18; N, 25.42.

2-Methyl-d_3-1-(4,6-dimethyl-*s*-triazin-2-yl)-2-propanol-3,3,3-d_3 (2c-d_6). The method for the preparation of **2c** was followed except that acetone-d_6 was used. Distillation of the product afforded a 54% yield of product. A portion (1.1 g) of the product was eluted from alumina (11 g) with ether, and selected cuts were distilled to afford 36 mg: bp 84−86 °C (2.8 Torr); IR (neat) 3460, 2230, 1530, 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.56 (s, 6H), 2.92 (s, 2H), 5.06 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 25.5, 28.5 (m), 49.7, 69.7, 175.8, 176.7. Anal. Calcd for $C_9H_9D_6N_3O$ (M_r = 187.28): C, 57.72; H + $^1/_2$D, 8.07; N, 22.44. Found: C, 57.66; H, 7.90; N, 22.21.

2,4-Dimethyl-6-(2-methyl-d_3-1-propenyl-3,3,3-d_3)-*s*-triazine (1c-d_6). The method for preparation of **1c** was followed. Alcohol **2c**-d_6 (3.08 g, 16.4 mmol) afforded 2.47 g of the crude alkene, which after treatment with saturated $NaHCO_3$ and workup afforded 1.82 g (65%) of product: bp 88−89 °C (4.8 Torr); IR (neat) 2200, 1640, 1530, 880 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.50 (s, 6H), 6.17 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 25.7, 123.4, 154.0, 171.9, 175.6. Anal. Calcd for $C_9H_7D_6N_3$ (M_r = 169.26): C, 63.86; H + $^1/_2$D, 7.74; N, 24.83. Found: C, 63.50; H, 7.63; N, 25.12.

2-(3-Butenyl)-4,6-dimethyl-*s*-triazine (4). A 35 wt % dispersion of KH in mineral oil (2.14 g KH, 53.2 mmol) under argon was washed with dry benzene (5 × 5 mL) and then

(37) Zaitseva, E. L.; Braz, G. I.; Yakubovich, A. Ya.; Bazov, V. P. *Zh. Obshch. Khim.* **1963**, *33*, 199−202; *Chem. Abstr.* **1963**, *58*, 13957g.

covered with glyme (60 mL). To the stirred suspension at room temperature was added (4 min) a solution of 2,4,6-trimethyl-*s*-triazine (6.41 g, 52.0 mmol) in glyme (20 mL). After being stirred for 1.5 h, the suspension was added to a solution (0 °C) of allyl bromide (6.32 g, 52.2 mmol) in glyme (100 mL). The reaction mixture was stirred overnight and then worked up as described for the preparation of **5b**. Distillation of the liquid residue afforded 2.1 g (25% yield) of crude product: bp 66−102 °C (0.30 Torr). A portion (1.13 g) of the crude product was placed on neutral alumina (1.5 cm × 22 cm), and elution with 10% ether/pentane gave initially the *gem*-diallyl product,[38] as indicated by GLC and NMR results, followed by the monoallyl product **(4)**: bp 78 °C (2.1 Torr); IR (neat) 3085, 1640, 1530, 905 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.50 (m, overlapping s, 2H), 2.54 (s, 6H), 2.83 (t, 2H), 4.92 (dt, J = 11, 2, 0 Hz, 1H), 5.00 (dt, J = 18, 2, 0 Hz, 1H), 5.80 (ddt, J = 18, 11, 9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 25.8, 37.9, 47.9, 116.8, 136.0, 176.0, 180.8. Anal. Calcd for $C_9H_{13}N_3$ (M_r = 163.22): C, 66.23; H, 8.03; N, 25.74. Found: C, 66.17; H, 8.22; N, 25.92.

Oxymercuration−Demercuration of 1a. The general procedure of Brown was followed[39] (*caution: mercuric acetate and mercury are highly toxic; see MSDS's for handling and disposal*). To a stirred solution of mercuric acetate (0.72 g, 2.3 mmol) in water (2.3 mL) at room temperature was added THF (2.5 mL) followed by **1a** (0.31 g, 2.3 mmol). After 3.5 h the yellow color had disappeared. The solution was stirred (18 h), and then 3 M sodium hydroxide (2.3 mL) was added followed by 0.5 M $NaBH_4$ in 3 M NaOH (2.15 mL). After coagulation of the mercury, the aqueous phase was saturated with NaCl, the phases were separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$), the solvent was evaporated, and the liquid residue was flash distilled: bp 80−120 °C (0.1 Torr) (lit.[34] bp 89 °C (1.5 Torr)) to give 0.20 g (57%) of **2a**: IR (neat) 3360, 1530, 1045 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.61 (s, 6H), 3.08 (t, 2H), 3.5 (bs, 1H), 4.07 (t, 2H). Its spectroscopic data was comparable to an authentic sample used to prepare **1a**.

Oxymercuration−Demercuration of 1b. The general procedure of Brown was followed.[39] To a stirred solution of mercuric acetate (0.95 g, 3.0 mmol) in water (2.8 mL) at room temperature was added THF (2.8 mL) followed by **1b** (0.42 g, 2.8 mmol). After 2 h the yellow color had disappeared. The solution was stirred (42 h), and then 3 M NaOH (2.8 mL) was added followed by 0.5 M $NaBH_4$ in 3 M NaOH (2.8 mL). The reaction was worked up as described for the hydration of **1a** to afford 0.43 g of product consisting of a liquid and a low melting solid. After the mixture was homogenized by warming, GLC analysis indicated the product composition to be 55% alkene and 39% alcohol. Upon cooling of the product, the solid alcohol was isolated, and its NMR spectrum was that of **2b**. GLC and NMR results gave no detectable evidence of the isomeric alcohol. Repeating the stoichiometry of the above reaction but with heating (53 °C) for 2 days did not significantly change the alkene/alcohol ratio. Repeating the reaction at room temperature for 2 days with a 2:l mole ratio of mercuric acetate to alkene gave a product composition of 29% **1b** and 68% **2b**, and further increasing the ratio to 3:l gave 12% **1b** and 78% **2b**.

Hydroboration−Oxidation of 1a with 9-BBN−H. The general procedure of Brown was followed.[9] Neat **1a** (164 mg, 1.21 mmol) was added via syringe to a refluxing solution (2.9 mL) of 9-BBN−H (1.4 mmol) in hexane under argon. After 23 h, the standard workup afforded 194 mg of liquid residue: ^1H NMR ($CDCl_3$) δ 1.28 (t, 3H), 2.52 (s, 6H), 2.77 (q, 2H), small signals due to the primary alcohol; GLC **5a** 53% (103 mg, 62 mol %), **2a** 10% (19 mg, 10 mol %), *cis*-1,5-cyclooctanediol and cyclooctanone 37% (71 mg).

Hydroboration−Oxidation of 1b with 9-BBN−H. The general procedure of Brown was followed.[9] Neat **1b** (664 mg, 4.45 mmol) was added via syringe to a refluxing solution (11.0 mL) of 9-BBN−H (5.28 mmol) in hexane under argon. After 18 h, the standard workup afforded 0.65 g of liquid residue: ^1H NMR ($CDCl_3$) δ 0.94 (t, 3H), 1.75 (m, 2H), 2.55 (s, 6H), 2.70 (t, 2H); GLC **5b** 83% (0.54 g, 81 mol %), *cis*-1,5-cyclooctanediol 11%, 1-(4,6-dimethyl-*s*-triazin-2-yl)-1,2-epoxypropane 3%. Further extraction of the ethanol phase gave additional amounts of the diol and the epoxide: ^1H NMR ($CDCl_3$) δ 1.45 (d, J = 5.5, 0.0 Hz, 3H), 2.58 (s, 6H), 3.36 (m, J = 5.5, 1.8 Hz, 1H), 3.62 (d, J = 1.8, 0.0 Hz, 1H); MS m/z (relative intensity) 166 (M + 1, 8), 150 (62), 124 (15), 83 (22), 68 (34), 55 (73), 42 (100), 28 (47), 15 (16). An oxidative workup of a comparable reaction (1.10 mmol of **1b**, 1.09 mmol of 9-BBN−H) using CH_2Cl_2 extractions afforded 149 mg (95%) of crude diol which gave crystals: mp 72−73 °C (lit.[40] mp 73.5−74.3 °C).

A comparable hydroboration−oxidation of **1b** with 9-BBN−H in refluxing THF (17 h) gave a lower yield (50%, distilled) of **5b** but no evidence of **2b** or **3b**.

Hydroboration−Hydrolysis of 1b with 9-BBN−H. The above general procedure[9] for the hydroboration−oxidation was followed in which **1b** (658 mg, 4.41 mmol) was reacted (44 h) with 9-BBN−H (10.2 mL, 4.90 mmol) in hexane except that the addition of 30% H_2O_2 was omitted in the workup and only absolute EtOH (1 mL) and water (3 mL) were added. The mixture was stirred at room temperature for 1 h and saturated with NaCl. The reaction mixture was worked up as above, and the hexane extracts afforded 1.58 g of liquid residue. Flash distillation of the latter afforded 694 mg of distillate. NMR analysis: **5b**, 69% (72 mol % yield); **1b**, 9% (10 mol %); cyclooctanone, 22% (25 mol %).

In a reaction comparable to the above, **1b** (626 mg, 4.20 mmol) was reacted (21 h) with 9-BBN−H (9.6 mL, 4.6 mmol), except that CD_3OD (1 mL) and D_2O (3 mL) were used in the workup. Distillation of the product afforded 457 mg of distillate. NMR analysis: **5b**, 64% (46 mol %); **1b**, 11% (8 mol %); cyclooctanone, 24% (19 mol %); **5b** ^1H NMR ($CDCl_3$) δ 0.94 (t, 3H), 1.76 (m), 2.55 (s, 6.1H), 2.71 (broad m, 1.3H, triazinyl-CHD−).

Hydroborations of 1b with 9-BBN−H in Hexane without Oxidation or Hydrolysis. The above general procedure for the hydroboration−oxidation was followed in which **1b** (462 mg, 3.09 mmol) was reacted (7 days) with 9-BBN−H (6.6 mL, 3.3 mmol) in hexane at room temperature. The volatiles and products were distilled (100 °C (bath), 0.3 Torr) to leave a viscous golden residue. The distillate was treated with $MgSO_4$, filtered, and concentrated to afford a liquid residue (209 mg). NMR analysis: **5b**, 52% (23 mol %), **1b**, 23% (10 mol %), cyclooctanone, 26% (13 mol %). The golden residue (917 mg) remaining after the distillation was analyzed by GC-MS: **5b**, 45% (88 mol %); cyclooctanone, 16%; cyclooctanol, 12%; unidentified products, 28%; a minor amount of **7b** (m/z 271).

The reaction of **1b** (74 mg, 0.50 mmol) in a prepared solution of 9-BBN−H (66 mg, 0.54 mmol) in $CDCl_3$ (0.7 mL) was carried out in a sealed tube at room temperature for 59 days, and then bibenzyl (30.2 mg, 0.17 mmol) was added as a quantitative NMR reference to indicate a 56% yield of **5b** (71%, corrected for unreacted **1b**).

Hydroboration of 1b with 9-BBN−H in $CDCl_3$ without Oxidation or Hydrolysis. A solution of **1b** (100 mg, 0.67 mmol) and 9-BBN−H dimer (92 mg, 0.38 mmol) in $CDCl_3$ (1.1 mL) was prepared under argon in a sealed NMR tube. After 41 days (^1H NMR analysis: **5b**, 93%; **1b**, 7%; cyclooctanone, 0%) the NMR tube was opened and the solvent was removed under house vacuum to afford 293 mg (152%) of a viscous reddish-brown liquid which was triturated with pentane (1 × 1 mL, 2 × 0.5 mL) to afford a pentane solution and a light orange-yellow powder (93 mg) which gave a faint green color and a black residue upon ignition. NMR (DMSO-d_6) analysis: **5b**, 56%; cyclooctanone, 44%. The pentane extract was analyzed via GLC to give 79% **5b** and 21% cyclooctanone. The pentane extract was permitted to evaporate slowly over a period of 2 months to afford crystals and a mother liquor. GC-MS: **5b**, 44%; cyclooctanone, 31%; the latter gave a 2,4-DNP,

(38) Osborne, D. R.; Levine, R. *J. Heterocycl. Chem.* **1964**, *1*, 128−129.

(39) Brown, H. C.; Lynch, G. J. *J. Org. Chem.* **1981**, *46*, 531−538.

(40) Knights, E. F.; Brown, H. C. *J. Am. Chem. Soc.* **1968**, *90*, 5280−5281.

mp 172−173 °C (lit.[41] mp 171−172 °C). The former crystals gave a broad melting point: 70→300 °C, with gas evolution between 125 and 140 °C. Similar crystals for X-ray diffraction studies[25] were obtained by slow evaporation (∼14 months) in air of a solution of the above reaction contained within a cracked NMR tube. A portion (24 mg) of the above powder was oxidized with H_2O_2 by the standard procedure to afford 15 mg of products. GLC analysis: **5b**, 29%; cyclooctanone, 47%; *cis*-1,5-cyclooctanediol, 24%.

Representative Hydroboration Reactions of Alkenes with 9-BBN−H for Extended Periods of Time. The following examples are representative methods for the preparation of hydroboration reactions carried out for extended periods of time (Tables 3 and 4). At the conclusion of the reaction the NMR tube or ampule was opened and equipped with a septum if quenching, or further analyses or reactions were performed.

(1) A solution of **1b** (92 mg, 0.62 mmol) and 9-BBN−H dimer (83 mg, 0.34 mmol) in $CDCl_3$ (1.2 mL) was prepared under argon in a sealed NMR tube and kept at room temperature. The ^1H and ^{13}C NMR spectra were taken at appropriate intervals over a period of approximately 50 days after which there were essentially no changes. The results are given in Table 3. A DEPT spectrum showed the small signals from δ 60 to 150 to be sp^2 carbons. With the addition of water the eight small signals in the ^1H NMR spectra (Table 3, footnote *e*) disappeared, the 9-BBN signal contracted, and the integration areas for the methyl groups of the ring and the α-methylene group increased (∼0.6−0.7H, and ∼0.2H, respectively). Within the ^{13}C NMR all of the peaks between δ 60 and 150 disappeared.

Repeat of the above reaction at 60 °C gave identical results within 5 days.

A comparable run (room temperature) quenched with CH_3OD gave a ^{13}C NMR spectrum showing C−D coupling at δ 25.2 (t, ^1J = 19.6 Hz) and δ 40.5 (t, ^1J = 19.5 Hz) for ring methyl and α-methylene carbons, respectively.

(2) To a prepared solution of 9-BBN−H dimer in degassed, purified hexane (2.5 mL, 0.40 M) at 55 °C in a 5 mL ampule containing a stirrer was added, under argon, a solution of **1b** (147 mg, 0.98 mmol) and nonane (130 mg, 1.02 mmol) in purified hexane (0.5 mL). The ampule was cooled under argon, sealed, and heated at 55 °C for 57 days after which it was opened in an argon-filled glovebag and equipped with a septum. Samples were withdrawn via a syringe for the following.

(a) GC-MS (compound, *m*/*z* (ratio %)): nonane, 128 (100); **5b**, 150−152 (40); cyclooctanone, 126 (3); **1b**, 148−151 (12); **7b**, 271 (63); bis ether, 258 (35); **5b** dimer, 300 (5).

(b) GC-MS (compound, *m*/*z* (ratio %)) of CH_3OD quench: nonane, 128 (100); **5b**, 150−155 (82); cyclooctanone, 126 (3); **1b**, 148−151 (7); 9-BBN−OCH_3, 151−154 (62). Additional time gave no further incorporation of deuterium.

(c) GC-MS (compound, *m*/*z* (ratio %)) of CH_3OH quench: nonane, 128 (100); **5b**, 150−152 (79); **1b**, 148−151 (7); 9-BBN−OCH_3, 151−154 (81).

(d) GC-MS (compound, *m*/*z* (ratio %)) of H_2O quench: nonane, 128 (100); **5b**, 150−152 (67); cyclooctanone, 126 (5); **1b**, 148−151 (10); bis ether, 258 (90).

(e) Titration: 0.05 M in 9-BBN−H.

(f) GC-MS (compound, *m*/*z* (ratio)) of oxidative workup (H_2O_2): nonane, 128 (100); **5b**, 150−152 (66); **1b**, 148−151 (4); *cis*-diol, 116 (M−CO) (46).

(3) To a stirred solution under argon at room temperature of 9-BBN−H in hexane (3.3 mL, 1.6 mmol) in a conical vial equipped with a septum was added **1b** (219 mg, 1.47 mmol) and nonane (160 mg, 1.25 mmol). The vial was kept in an argon atmosphere, and within 1 h an unidentified precipitate began to form. Following the reaction for 4 months with GC-MS showed, with time, a decrease in **1b**, an increase in **5b**, a maximum for **7b** at ∼4 days, and an average sum of 97 for the three compounds relative to nonane as an internal reference (100). GC-MS (compound (ratio %)) of oxidative workup of the reaction gave the following results: nonane (100) (some loss in workup); **5b** (98); **1b** (18); epoxide (14); cyclooctanone (30); cyclooctanol (123); 1,5-cyclooctanediol (170).

(4) The ^{11}B and ^1H NMR ($CDCl_3$) method is as follows. A solution of 9-BBN−H dimer (189 mg, 0.77 mmol) in $CDCl_3$ (3 mL) was prepared under argon in a 10 mm quartz NMR tube, and the latter was equipped with a septum. After performing the ^{11}B and the ^1H NMR spectra of the 9-BBN−H solution, the alkene **1b** (239 mg, 1.6 mmol), dissolved in an equal volume of $CDCl_3$, was added via syringe to the NMR tube, and the latter was shaken. The solution was kept at room temperature, and the ^{11}B and ^1H NMR spectra were taken at appropriate intervals over a period of 9 days and then again after 29 days. The ^{11}B spectrum was also taken of a comparable solution in a sealed standard NMR tube after 10 months to give the same chemical shift (δ +59.6[22]). Results are reported in the text and in Table 3. Control spectra were taken on solutions of 9-BBN−H in $CDCl_3$ with both cyclohexene and 2,4,6-trimethyl-*s*-triazine.

Quenching of Adduct 7b with CD_3OD. A solution of **1b** (97 mg, 0.65 mmol) and 9-BBN−H dimer (79 mg, 0.33 mmol) in $CDCl_3$ (1.0 mL) was prepared under argon in an NMR tube with a septum cap. After the signals from the adduct **6b** were maximized and those from **1b** and **5b** were still small (70 h), 26 μL (0.64 mmol) of methanol-d_4 was added. As a result, within the ^1H NMR spectrum the broad triplet (δ 3.0, −CHB−) became a multiplet (δ 2.65, −CHD−) and the broad multiplet of the 9-BBN moiety (δ 1.03−1.25, 1.45−1.83) shifted downfield (δ 1.10−1.32, 1.51−1.85) with an accompanying change in its profile. A solution of bibenzyl (83 mg) in $CDCl_3$ (0.5 mL) was injected as an internal reference to determine the yield of **5b**-d_1 (104%).

Ethanolamine Ester of the 9-BBN Moiety.[24] A solution of **1b** (98 mg, 0.66 mmol) and 9-BBN−H dimer (95 mg, 0.39 mmol) was prepared in C_6D_6 (1.1 mL) under argon in a sealed NMR tube. The ^1H and ^{13}C NMR spectra were taken at appropriate intervals to give spectral changes comparable to those obtained in other deuterated solvents ($CDCl_3$, CD_2Cl_2, THF-d_8). After 11 months, the tube was opened, 47 μL (0.78 mmol) of ethanolamine was added, and the precipitate was filtered, washed with hexane, and dried (1 Torr) to afford 0.13 g (91%) of the ethanolamine ester of 9-BBN with recrystallization (THF−hexane): mp 203−205 °C dec (lit.[24b] mp 202−203.5 °C).

Hydroboration of 1b with 9-BBN−H in THF. To a stirred refluxing solution (2.1 mL) of 9-BBN−H (1.0 mmol) in THF was added **1b** (154 mg, 1.03 mmol). Reflux was continued for 55 h during which GC-MS samples were taken at appropriate intervals. After approximately 1 day the peak areas of **5b** (34) and **1b** (26) remained constant relative to bibenzyl (186 mg, 1.02 mmol) as an internal reference (100). Comparative quenching with CH_3OD and CH_3OH followed by GC-MS showed evidence of deuterium incorporation into **5b** and the cyclooctanone.

Hydroboration of 1b in the Presence of Galvinoxyl.[28] A solution of **1b** (86 mg, 0.58 mmol) and 9-BBN−H dimer (70 mg, 0.29 mmol) in $CDCl_3$ (0.8 mL) was prepared under argon in a NMR tube with a septum cap. The reaction was followed by ^1H and ^{13}C NMR until the adduct **7b** had maximized, and then solutions of galvinoxyl (recrystalized) in $CDCl_3$ were added as follows: 31 h, 29 mg (12 mol %); 51 h, 13 mg (5 mol %); 70 h, 27 mg (11 mol %). A plot of the logarithm of the ratio of the area of the methyl groups of the ring of **5b** to that of the adduct versus time showed no significant change relative to that of a control with no galvinoxyl until after approximately 90 h when the reaction rate slowed dramatically. A control with galvinoxyl and 9-BBN−H dimer in $CDCl_3$ at room temperature in the dark decolorized within 1 h.

Hydroboration of 1b-d_6 with 9-BBN−H. A solution of **1b**-d_6 (58 mg, 0.37 mmol) and 9-BBN−H dimer (50 mg, 0.20 mmol) in $CDCl_3$ (0.6 mL) was prepared under argon in a sealed NMR tube. The ^1H and ^{13}C NMR spectra were taken at appropriate intervals, and after 63 days the residual hydrogen content of

(41) *Dictionary of Organic Compounds*, 5th ed.; Buckingham, J., Ed.; Chapman & Hall: New York, 1984; Suppl. 2, p 120. Ohtsuka, Y.; Oishi, T. *Chem. Pharm. Bull.* **1983**, *31*, 454−465; *Chem. Abstr.* **1983**, *99*, 121863m.

the methyl groups on the ring (δ 2.55, m, J = 2.2 Hz) had decreased and the signal for the α-hydrogen had increased to a sharp triplet (δ 2.72, J = 7.5 Hz) superimposed upon a broad triplet of triplets (^3J = 7.4, ^2J = 2.3 Hz[42]) with the relative areas ~2:1, respectively. The absolute changes in the areas of the signals were within the integration precision.

Hydroboration of 1b-d_7 with 9-BBN−H. A solution of **1b**-d_7 (32 mg, 0.21 mmol) and 9-BBN−H dimer (46 mg, 0.19 mmol) in C_6D_6 (0.6 mL) was prepared under argon in a sealed NMR tube. The ^{1}H and ^{13}C NMR spectra were taken at appropriate intervals, and after 1 day the ^{1}H NMR continued to show, for a period of 4 months, the gradual decrease in both the weak broad triplet at δ 3.15 (α-CHB−) and the weak multiplet at δ 2.4 (ring methyl groups) and the simultaneous increase of the broad multiplet at δ 2.8 (α-CDH−, ~0.8H, ^3J = 7.5, ^2J = 3.2 Hz[42]). The differences between the absolute changes in the areas of the signals were within the integration precision.

ESR of Reaction of 7b to 5b. A solution of **1b** (89 mg, 0.60 mmol) and 9-BBN−H dimer (77 mg, 0.63 mmol) in C_6D_6 (0.9 mL) was prepared under argon in a sealed NMR tube. After the ^{1}H NMR spectra showed that adduct **7b** had fully formed and the signal for the α-methylene group was apparent (~5 days), the ESR spectrum was taken with no evidence of a signal. The ESR spectra were repeated after 21 days and again after 3 months with no detectable signal.

Hydroboration−Oxidation of 1c with 9-BBN−H. The general procedure of Brown was followed.[9] Neat **1c** (725 mg, 4.44 mmol) was added via syringe to a refluxing solution (9.0 mL) of 9-BBN−H (4.5 mmol) in hexane. After 19 h, the standard workup afforded 712 mg of liquid residue. GLC (NMR) analyses: **5c**, 78% (75 mol %); **1c**-epoxide, 22% (21 mol %); *cis*-1,5-cyclooctanediol (56 mol %). A portion (779 mg) of the liquid residue from a comparable run was placed on 80 g of neutral alumina. Elution with 10% ether/pentane afforded 161 mg of alkane **5c** after distillation: bp 74 °C (4.3 Torr); IR and NMR spectra identical to those of an authentic sample of **5c**. Elution with 100% ether afforded, after distillation, 166 mg of 2-methyl-1-(4,6-dimethyl-*s*-triazin-2-yl)-1,2-epoxypropane: bp 80−86 °C (1.2 Torr); IR (neat) 1525, 1240, 900 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 3H), 1.50 (s, 3H), 2.60 (s, 6H), 3.83 (s, 1H, no exchange with D_2O); ^{13}C NMR ($CDCl_3$) δ 17.7, 24.9, 25.6, 62.2, 63.0, 173.5, 176.2; MS *m*/*z* (relative intensity) 179 (M^+, 2), 162 (6), 138 (20), 97 (23), 69 (13) 42 (100). Anal. Calcd for $C_9H_{13}N_3O$ (M_r = 179.22): C, 60.32; H, 7.31; N, 23.45. Found: C, 60.05; H, 7.33; N, 23.05.

Hydroboration−Oxidation of 1c with 9-BBN-D. The general procedure of Brown was followed.[9] Neat **1c** (545 mg, 3.34 mmol) was added via syringe to a refluxing solution (15 mL) of 9-BBN−D[43] (0.25 M,[29] 3.7 mmol) in hexane under argon. After 21 h, the standard workup afforded 635 mg of liquid residue. GLC: **5c**-d_1, 65% (414 mg, 75 mol %); **1c**-epoxide, 25% (26 mol %). NMR analysis gave 71% and 29%, respectively.

A portion (380 mg) of the above residue was placed on neutral alumina (l cm × 25 cm) and eluted with 2% ether/pentane to afford 139 mg of **5c**-d_1: bp 75−78 °C (4.5 Torr); IR (neat) 2960, 1530 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (s, 6H), 2.55 (s, 6H), 2.61 (s, 2H). Anal. Calcd for $C_9H_{14}DN_3$ (M_r = 166.25): C, 65.02; H + $^1/_2$D, 9.09; N, 25.28. Found: C, 65.22; H, 9.11; N, 25.11. Elution of the column with pure ether afforded approximately 50 mg of epoxide whose spectral data were identical to an authentic sample.

Hydroboration of 1c-d_6 with 9-BBN−H. A solution of **1c**-d_6 (79 mg, 0.47 mmol) and 9-BBN−H dimer (62 mg, 0.25 mmol) in $CDCl_3$ (0.7 mL) was prepared under argon in a sealed NMR tube. The ^{1}H and ^{13}C NMR spectra were taken at appropriate intervals. After 25 days, the sharp doublet (δ 2.61, 2α-H) in the ^{1}H NMR spectrum showed no increased multiplicity, and the triplet at δ 2.16 (1β-H) was broadened. After 10 months, the NMR tube was opened and water (1 drop) was added. The ^{1}H NMR spectrum remained unchanged except that the profile of the 9-BBN moiety had sharpened and the small signals between δ 4.0 and δ 4.8 had disappeared as well as those signals in the ^{13}C NMR spectrum between δ 60 and δ 160.

Hydroboration−Oxidation of 4 with 9-BBN−H. The general procedure of Brown was followed.[9] Neat **4** (904 mg, 5.54 mmol) was added via syringe to a refluxing solution (18.5 mL) of 9-BBN−H (8.88 mmol) in hexane under argon. After 18 h, the standard workup was followed except that further hexane and ether extractions were necessary to afford 1.15 g of liquid residue. GLC: 4-(4,6-dimethyl-*s*-triazin-2-yl)-1-butanol, 52% (60 mol %); recovered alkene **4**, 1%; *cis*-1,5-cyclooctanediol, 40%; unidentified components, 7%. The NMR spectrum gave no evidence for 4-(4,6-dimethyl-*s*-triazin-2-yl)-2-butanol. Lowering the mole ratio of 9-BBN−H to alkene from that cited above (1.6:1.0) to a ratio of 1:1 gave a 43 mol % yield of the primary alcohol, but raising the ratio to 2.2:l.0 did not improve the yield (58 mol %). The product was placed on neutral alumina (1 cm × 24 cm), and after elution with ether, the 4-(4,6-dimethyl-*s*-triazin-2-yl)-1-butanol was eluted with 2% methanol/ether followed closely by the *cis*-1,5-cyclooctanediol. Selected cuts were combined and distilled to afford 200 mg of alcohol: bp 112−124 °C (0.53 Torr); IR (neat) 3370, 1525, 1035 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.61 (quintet, 2H), 1.86 (quintet, 2H), 2.25 (s, 1H), 2.58 (s, 6H), 2.80 (t, 2H), 3.65 (t, 2H); ^{13}C NMR ($CDCl_3$) δ 24.1, 25.6, 32.2, 38.4, 62.0, 176.1, 179.0; MS *m*/*z* (relative intensity) 150 ($M^+ - CH_2OH$, 9), 136 (13), 123 (59), 42 (100), 31 (8). Anal. Calcd for $C_9H_{15}N_3O$ (M_r = 181.24): C, 59.64; H, 8.34; N, 23.18. Found: C, 59.25; H, 8.45; N, 22.91.

Hydroboration of 2-Vinylpyridine. A solution of 2-vinylpyridine (60 mg, 0.57 mmol) and 9-BBN−H dimer (78 mg, 0.32 mmol) (1:1 monomer) in $CDCl_3$ (0.8 mL) was prepared under argon in a sealed NMR tube and permitted to stand at room temperature. The ^{1}H and ^{13}C NMR spectra were taken at appropriate intervals. Within 20 h the ^{1}H NMR showed new signals at δ 0.57 (b), 0.83 (t), 2.92 (t), and increased multiplicity of the signals from the ring protons. The former three signals of equal areas continued to increase for ~6 days, and then the tube was heated for 11 days at ~55 °C until the signals for the alkene protons disappeared, but there was no significant changes in the remaining signals.

A solution of 2-vinylpyridine (48 mg, 0.45 mmol) and 9-BBN−H dimer (118 mg, 0.48 mmol) (1:2 monomer) in $CDCl_3$ (1.2 mL) was prepared and analyzed as above to give an initial spectrum which had broadened signals for the hydrogens of the 2-vinylpyridine but gave final ^{1}H NMR spectra which were the same as the above.

Hydroboration of 2-(1-propenyl)pyridine. A solution of 2-(1-propenyl)pyridine[44] (103 mg, 0.86 mmol) and 9-BBN−H dimer (113 mg, 0.46 mmol) (1:1 monomer) in $CDCl_3$ (1.1 mL) was prepared under argon in a sealed NMR tube and permitted to stand at room temperature. The ^{1}H and ^{13}C NMR spectra were taken at appropriate intervals. Within 6 h a broad singlet (δ 0.24) and a sharp triplet (δ 0.82) appeared. The former remained relatively constant for 62 days, but the sharp triplet decreased with time as a new triplet (δ 1.16) increased. Concurrently with the appearance of the new sharp downfield triplet, small multiplet signals began to appear between δ 4.5 and 6.3, and within the ^{13}C NMR spectra new signals appeared between δ 110 and 170. Heating the reaction (~67 °C) for 7 days caused the remaining alkene to react and the broad singlet and the initial sharp triplet to disappear. No evidence for the formation of the alkane was apparent, but the addition of a drop of water gave rise to the alkane: ^{1}H NMR ($CDCl_3$) δ 0.96 (t, 3H), 1.76 (m, overlaps 9-BBN), 2.78 (t, 2H), 7.10 (m, 1H), 7.15 (d, 1H), 7.59 (dt, 1H), 8.50 (dd, 1H).

A solution of 2-(1-propenyl)pyridine (63 mg, 0.53 mmol) and 9-BBN−H dimer (132 mg, 0.54 mmol) (1:2 monomer) in $CDCl_3$ (1.2 mL) was prepared under argon in a sealed NMR tube. The initial NMR spectrum was identical to that of the above (1:1) except the signals for the ring protons were broadened. Within 5 h the broad singlet (δ 0.25) and the sharp singlet (δ 0.84) appeared and the signals for the ring protons had become

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sharp. The ^{1}H NMR spectra remained as such for 78 days with no evidence of a new triplet at δ 1.15, the small multiplets between δ 4.5 and 6.3, or the additional signals in the ^{13}C NMR spectra.

Controls with 9-BBN−H Dimer and 2,4,6-Trimethyl-*s*-triazine. (a) A solution of 2,4,6-trimethyl-*s*-triazine (78 mg, 0.63 mmol), 9-BBN−H dimer (86 mg, 0.35 mmol), and bibenzyl (146 mg, 0.80 mmol) as a reference in degassed $CDCl_3$ (1.2 mL) was prepared under argon in a sealed NMR tube. The ^{1}H and ^{13}C NMR spectra were taken at appropriate intervals for 51 days with no evidence of any change at room temperature. Hydrolysis of an aliquot of the final solution gave 95% of the original hydride molarity. (b) A solution (3.4 mL) of 9-BBN−H (0.68 mmol) in THF was added (0 °C) with stirring to a mixture of 2,4,6-trimethyl-*s*-triazine (81 mg, 0.66 mmol) and nonane (87 mg, 0.68 mmol) under argon in an ampule, and the latter was sealed. After 21 days at room temperature hydrolysis[29] of an aliquot of the final solution gave 90% of the original hydride molarity, and the GC-MS of a sample quenched with CH_3OD showed no incorporation of deuterium into the 2,4,6-trimethyl-*s*-triazine. A comparable study carried out at 55 °C for 28 days gave 26% of the original hydride molarity, but no deuterium had been incorporated into the 2,4,6-trimethyl-*s*-triazine.

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Supporting Information Available: ^{1}H spectra for compounds **1b**-d_6, **1b**-d_7, **2b**-d_9, and **1c**-d_6; ^{1}H and ^{13}C spectra for compounds **1b**, **5b**, **2c**, **5c**, **1c**, **2c**-d_6, and **4**; ^{1}H, ^{13}C, and ^{11}B spectra for **1b** with 9-BBN-H with time and final ^{15}N spectra; final ^{1}H and ^{13}C spectra for **1b**-d_6 with 9-BBN-H, and ^{1}H and ^{13}C spectra for 2(1-propenyl)pyridine with 9-BBN-H with time. This material is available free of charge via the Internet at http://pubs.acs.org.

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