Integrations were performed on a Linear Instruments integrating recorder. Least-squares analysis of the kinetic data was performed on a Hewlett-Packard 3000 computer using a statistics package. Kinetic runs were performed in a circulating water bath (Sargent-Welch heater and circulator). Temperatures were controlled with a Sargent-Welch Model ST temperature controller (±0.01 °C).

Solvents were distilled under nitrogen from potassium benzophenone ketyl. Olefins were distilled from a small quantity of lithium aluminum hydride and stored under nitrogen. Liquid aldehydes were distilled under vacuum just prior to use. Solid aldehydes were used as received after checking their purity by NMR. Solid 9-BBN was prepared by the method of Brown[14] and was dissolved in THF to make a 0.5 M solution.

General Kinetic Procedure. A 500-mL flask equipped with a side arm covered with a rubber stopple, a reflux condenser, and a magnetic stirring bar was flushed with nitrogen. The flask was charged with 200 mL (100 mmol) of a 0.5 M 9-BBN solution followed by 110 mmol of 1-octene. The solution was stirred overnight and then the solvent and excess olefin was removed under vacuum. The product was transferred to a dry, nitrogen-flushed 100-mL volumetric flask equipped with a stopcock. The product was weighed and diluted to 100 mL with THF. The concentration of the stock solution of *B-n*-octyl-9-BBN was verified by oxidizing an aliquot and analyzing for 1-octanol and 1,5-cyclooctanediol.

Prior to each kinetic run a stock solution of the aldehyde was prepared in a nitrogen-flushed volumetric flask. A 10-mL volumetric flask equipped with a stopcock and septum was flushed with nitrogen and flame-dried. The flask was charged with 5.0 mmol of *B-n*-octyl-9-BBN solution and 2.5 mmol of dodecane which was used as an internal standard. Both the aldehyde and organoborane flasks were then equilibrated in the constant temperature bath. After equilibration a 5.0-mmol aliquot of the aldehyde was transferred to the organoborane solution and the volume adjusted to 10.0 mL by the addition of a small amount of THF. The reaction progress was measured at regular time intervals by following the appearance of 1-octene by VPC. A least-squares plot of $1/([\text{1-octene}]_\infty - [\text{1-cotene}]_t]$ vs. time gave a straight line with a slope of the rate constant. Kinetic runs were done in triplicate, and each run used 8-15 data points. Errors quoted are standard deviations. Activation parameters were calculated by least-squares analysis of the Arrhenius plots.

General Competition Studies. A reaction flask was charged with 5.0 mmol of 9-BBN in THF followed by 5.5 mmol of α-pinene. The solution was refluxed for 3 h and then cooled to 25 °. A mixture of 10.0 mmol of two aldehydes (5.0 mmol of each) in THF was then injected into the organoborane. A sample of the reaction was removed and placed in a nitrogen-flushed NMR tube for analysis. The amount of each aldehyde was determined by integration of the two aldehydic protons and comparison of the area to that of the total aromatic protons. The relative rates were determined from the Ingold-Shaw equation:[15]

$$\frac{k_x}{k_y} = \frac{\log x_0 - \log x_t}{\log y_0 - \log y_y}$$

Acknowledgment. We wish to thank the National Institutes of Health for financial support and the University of California, Riverside, for a President's Undergraduate Fellowship to S.A.Z. We thank Professor R. C. Neuman for helpful discussions.

Registry No. *p*-Nitrobenzaldehyde, 555-16-8; *p*-cyanobenzaldehyde, 105-07-7; *p*-chlorobenzaldehyde, 104-88-1; benzaldehyde, 100-52-7; *p*-methylbenzaldehyde, 104-87-0; *p*-methoxybenzaldehyde, 123-11-5; *p*-(dimethylamino)benzaldehyde, 100-10-7; *B-n*-octyl-9-BBN, 30089-00-0; *B*-3-pinanyl-9-BBN, 64106-79-2.

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Thermal Reactions of *B*-Alkyl-9-borabicyclo[3.3.1]nonane (9-BBN). Evidence for Unusually Facile Dehydroboration with *B*-Pinanyl-9-BBN

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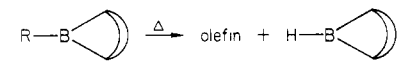
Contribution from the Department of Chemistry, University of California, Riverside, California 92521. *Received June 12, 1981*

Abstract: *B*-Alkyl-9-BBN compounds undergo a slow olefin-alkyl group exchange when refluxed with an olefin in tetrahydrofuran. The half-life of the process for *B-trans*-2-methylcyclopentyl- and *B*-3-methyl-2-butyl-9-BBN is approximately 4 days. However, *B*-3-pinanyl-9-BBN undergoes an exceptionally rapid olefin-alkyl group exchange with a half-life of less than 10 h. Kinetic and competition experiments support a dehydroboration-hydroboration process. The isomerization of the *B*-3-pinanyl-9-BBN to *B*-myrtanyl-9-BBN, which one would expect to accompany such a facile dehydroboration, is not seen until 145 °C. After 24 h at 165 °C, the reaction reaches equilibrium with *B-trans*-myrtanyl-9-BBN as the major product. Treatment of this organoborane with benzaldehyde liberates the rare (+)-β-pinene. The facility with which *B*-3-pinanyl-9-BBN undergoes dehydroboration has important consequences for asymmetric reductions with this reagent.

Certain *B*-alkyl-9-BBN compounds are extremely chemo-[2] and enantioselective[3] reducing agents. For example, *B*-3-pinanyl-9-BBN (prepared from 9-BBN and α-pinene) may be used to reduce alkynyl ketones to propargyl alcohols in enantiomeric excesses which approach 100%.[3c] However, with more hindered ketones or with forcing conditions (refluxing tetrahydrofuran, THF), enantiomeric purities can drop dramatically. For example, acetophenone may be reduced to 1-phenylethanol upon reflux for 24 h (THF) with a 2-fold excess of *B*-3-pinanyl-9-BBN. However, the 1-phenylethanol product exhibits only a 5-7% enantiomeric purity. We suspected that the drop in enantiomeric purity could be attributed to a competitive dehydroboration process which would generate achiral 9-BBN (eq 1). However, in contrast to



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the corresponding trialkylboranes, *B*-alkyl-9-BBN compounds are thought to be remarkably thermally stable.[4] For example, it has been observed that the hydroboration of 1-methylcyclooctene,

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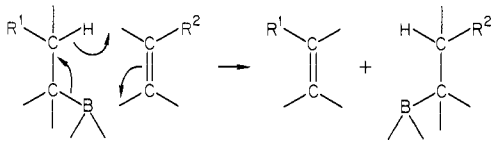
followed by alkaline hydrogen peroxide oxidation, did not yield the pure *trans*-2-methylcyclooctanol. Instead, a complex mixture of methylcyclooctanols was formed. It was concluded that the intermediate organoborane must undergo a rapid isomerization around the cyclooctyl ring to produce isomeric alcohols on oxidation. The use of 9-BBN circumvents this problem. Thus, in order to rule out the possibility that the loss in enantiomeric purity was caused by the dehydroboration process, we have examined in more detail the thermal reactions of *B*-alkyl-9-BBN compounds. Unexpectedly, we have found the *B*-3-pinanyl-9-BBN undergoes a facile dehydroboration process at 65 °C[5] which is not accompanied by isomerization.

Results and Discussion

In order to detect a *B*-alkyl-9-BBN dehydroboration process, we planned to trap the liberated boron hydride by refluxing (THF) the organoborane in the presence of a less hindered olefin. Our initial experiments with *B*-*trans*-2-methylcyclopentyl-9-BBN and 1-octene indicated that the alkyl–olefin exchange did indeed occur, although at a rather slow rate. Furthermore, the *B*-alkyl group participated in preference to the cyclooctyl portion of the borane, as evidenced by the quantitative recovery of 1,5-cyclooctanediol upon oxidation.

Similar alkyl group–olefin exchange reactions also occur when trialkylboranes are heated with olefins at elevated temperatures (130–160 °C).[6] However, two mechanisms have been postulated for the reaction. The first process involves a cyclic or concerted pathway (eq 2).[6a,b] The second postulated mechanism involves



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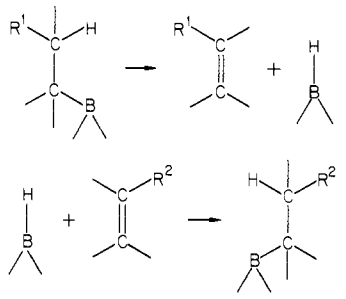
a two-step dehydroboration–hydroboration process (eq 3).[6c-e]



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These two processes are analogous to the proposed mechanisms for the dealkylation of organoboranes by aldehydes. Mikhailov has proposed[7] and we have amply demonstrated[8] that the aldehyde dealkylation reactions occur by the cyclic process. The situation in the case of olefin–alkyl group exchange reaction is less clear. Evidence for a cyclic process for the exchange reaction includes the absence of B–H bonds in the reaction mixture, a greater selectivity for primary alcohol products from styrene and *p*-chlorostyrene during hydroboration than from olefin–alkyl group exchange, and retardation of the rate by a factor of 2 when the reaction is diluted 4-fold.[6a,b] On the other hand, others[6d,e] have found no effect on the rate by increasing the concentration of olefin. A 4-fold decrease in concentration should lead to a much greater decrease in the rate for the bimolecular process. The discrepancy in product distributions could be explained by the fact that the hydroborations were done at room temperature while the exchange reaction was done at 130 °C. Thus we needed to resolve the discrepancies in the data before conclusions could be made about the *B*-alkyl-9-BBN compounds.

Table I. Olefin–Alkyl Group Exchange of *B*-Alkyl-9-BBN Compounds

B-alkyl-9-BBN[a]	olefin	$t_{1/2}$, min[b]
trans-2-methylcyclopentyl	1-octene, 2 M	6030
	1-octene, 0.5 M	6360
	2-methyl-1-pentene	5000
	styrene	3630
	p-methoxystyrene	4000
3-methyl-2-butyl	1-octene	5000
	2-methyl-1-pentene	6000
3-pinanyl	1-octene	500
	2-methyl-1-pentene	540
	cyclohexene	640
	1-methylcyclohexene	1400

[a] All reactions 1.0 M in *B*-alkyl-9-BBN and olefin unless otherwise indicated. [b] Time for 50% completion of the reaction.

Various *B*-alkyl-9-BBN compounds were refluxed in tetrahydrofuran and an olefin. The reactions were followed by monitoring the olefinic region of the NMR spectra or by VPC analysis. The results are presented in Table I. In each case, for a particular organoborane the initial reaction rate is essentially independent of the olefin structure. The independence of the initial rate upon the structure of the added olefin is in agreement with the two-step process. The rate of the bimolecular process should change dramatically with the steric bulk of the added olefin. However, the half-life of the reaction may vary as the reaction approaches equilibrium. For example, the reactions of *B*-3-pinanyl-9-BBN with 1-octene, 2-methyl-1-pentene, cyclohexene, and 1-methylcyclohexene proceed to 90, 90, 75, and 55% completion, respectively. We thus concentrated on the less hindered olefins. The half-life for the styrenes is slightly shorter than normal due to a small loss of styrene during the prolonged reactions.

The reaction of *B*-3-pinanyl-9-BBN with 2-methyl-1-pentene followed first-order rather than second-order kinetics. In further support of the first-order kinetics, the half-life for the reaction of *B*-*trans*-2-methylcyclopentyl-9-BBN with 1-octene did not change appreciably on changing the concentrations from 2.0 M to 0.5 M.

Styrene and *p*-methoxystyrene may be distinguished kinetically by hydroboration with 9-BBN. At room temperature the *p*-methoxystyrene reacts 2.95[9] to 14[10] times faster, while in refluxing tetrahydrofuran it is 2.4 times faster. These two olefins react individually with *B*-*trans*-2-methylcyclopentyl-9-BBN at approximately the same rate. However, when an equimolar mixture of the two olefins is allowed to compete for either the *B*-*trans*-2-methylcyclopentyl- or *B*-3-methyl-2-butyl-9-BBN, the hydroboration product of *p*-methoxystyrene appears approximately 2.5 times faster than the styrene product. These results are consistent with a rate-determining dehydroboration followed by a product-determining hydroboration step.

Finally, the reaction mixture of 2-methyl-1-pentene with *B*-3-pinanyl-9-BBN was oxidized and the 2-methyl-1-pentanol isolated. The alcohol had an optical rotation of $[\alpha]^{25}_{D}$ +0.02° (lit.[11] $[\alpha]^{25}_{D}$ 12.9°). The small observed rotation (<0.2% ee) could be due to a trace of chiral impurity. The *B*-3-pinanyl-9-BBN has previously been shown to be an extremely effective asymmetric reducing agent in a reaction which proceeds through the cyclic mechanism.[3,8] Although the lack of optical purity in the present reaction does not exclude the cyclic process, it certainly is in accord with the dehydroboration–hydroboration mechanism.

We thus conclude that *B*-alkyl-9-BBN compounds can undergo a dehydroboration process under relatively mild conditions. The

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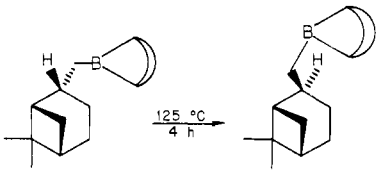
process is normally slow. However, *B*-3-pinanyl-9-BBN stands out for the unusual facility with which it undergoes dehydroboration. This reactivity may be attributed to a relief of steric strain caused by the cis arrangement of the *gem*-dimethyl group and the 10-methyl group in the organoborane.

The facility with which *B*-3-pinanyl-9-BBN undergoes dehydroboration was very interesting since no rearrangement product was seen. Indeed, prolonged reflux in THF followed by oxidation produced only isopinocampheol. This lack of isomerization is potentially due to a combination of the propensity of 9-BBN to eliminate toward a tertiary center, as is observed in aldehyde reductions,[8] and the very high regioselectivity of the hydroboration reaction.[12]

Isomerization finally began to occur upon heating to 145 °C in diglyme solution. After 24 h there was an approximately 4:1 ratio in favor of unrearranged product after oxidation. Only at reflux (165 °C) did isomerization occur at an appreciable rate. After 24 h an equilibrium ratio of 4:1 in favor of the rearranged product was reached. In comparison the corresponding diisopinocampheylborane reaches equilibrium after only 1 h at 160 °C.[6c] Thus, although dehydroboration of the 9-BBN derivative is rather facile, isomerization is a rather sluggish process.

The major product after oxidation of the isomerized product was identified as *trans*-myrtanol. Since hydroboration–oxidation of β-pinene produces essentially pure *cis*-myrtanol, the source of the trans isomer was explored. Heating the hydroboration product of (−)-β-pinene and 9-BBN to 125 °C caused essentially complete isomerization to the trans isomer after only 4 h. (eq 4). The



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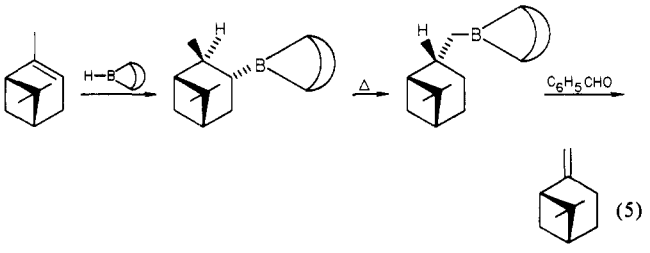
isomerization also occurs at 65 °C, although it requires approximately 2–3 days to reach completion.

Normally the isomerization of organoboranes is catalyzed by a slight excess of boron hydride.[6c] However, the isomerization of the *B*-*cis*-myrtanyl-9-BBN to the trans isomer occurred at approximately the same rate (at 125 °C) even in the presence of 20% excess olefin.

The isomerization of the *B*-3-pinanyl-9-BBN to the myrtanyl derivative suggested that it might be possible to convert (+)-α-pinene to (+)-β-pinene (eq 5). β-Pinene is a useful chiral starting



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material for synthesis. However, only the (−) enantiomer is readily available. The (+) enantiomer of β-pinene has been previously prepared from (+)-10-camphenesulfonyl chloride[13] and in a four-step isomerization of (+)-α-pinene,[14] both in low overall yield. It is also reported that thermal isomerization of diisopinocamphenylborane (from (+)-α-pinene) followed by displacement with a high-boiling olefin gives (+)-β-pinene,[6c] although no rotation is given.

(+)-α-Pinene was hydroborated with 9-BBN and the solution refluxed in diglyme for 30 h to achieve the isomerization. After cooling to room temperature the solution was treated with benzaldehyde to release the β-pinene along with some α-pinene. Although α- and β-pinene may be readily separated by distillation, we found it most convenient to use silver nitrate impregnated silica gel to separate small quantities of the two isomers. The (+)-β-pinene was thus isolated in an overall yield of 51% with an optical purity of 86%. Since the starting (+)-α-pinene was 92% pure, the conversion occurs in 93.5% optical yield.

Conclusion

B-3-Pinanyl-9-BBN undergoes an unusually facile dehydroboration. However, the isomerization of the organoborane does not occur until more drastic conditions are used. Since the *B*-alkyl-9-BBN reagents are useful enantioselective and chemoselective reducing agents via a cyclic process, the rate of dehydroboration places an important lower limit on the reactivity of substrates. As the rate of reaction approaches the dehydroboration rate, competing reduction by 9-BBN may begin to interfere.

Experimental Section

All operations involving air-sensitive reagents were performed under a dry nitrogen atmosphere with syringe techniques.[15] ^{1}H NMR spectra were recorded on a Varian EM-390 (90-MHz) instrument. The VPC analysis of reactions was performed on a Hewlett-Packard 5732TCD chromatograph using 6 ft × $^1/_8$ in. SE-30, DC-710, or XE-60 columns as needed. The *cis*- and *trans*-myrtanol were separated on a 20% TCEP column. Optical rotations were measured on a Perkin-Elmer Model 241 polarimeter.

Solvents were distilled under nitrogen from benzophenone ketyl. Olefins were obtained commercially and were distilled from a small quantity of lithium aluminum hydride and stored under nitrogen. Solid 9-BBN was prepared by the method of Brown[16] and was dissolved in THF to make a 0.5 M solution.

General Procedure. A dry, 50-mL, round-bottom flask equipped with a side arm covered with a rubber stopple, a reflux condenser, and a magnetic stirring bar was flushed with nitrogen. The flask was charged with 10 mmol (20 mL) of 9-BBN and 15 mmol of an olefin. The solution was stirred for the appropriate time,[16] and then the THF and excess olefin were removed under vacuum The second olefin (10 mmol) was then added followed by 10 mL of THF. The solution was then refluxed. Samples were withdrawn periodically and placed in a nitrogen-flushed NMR tube for analysis. The reactions followed first-order kinetics.

Relative Rates of Hydroboration. The relative rate of hydroboration of styrene and *p*-methoxystyrene was determined in refluxing THF by using the procedure of Brown.[10] The 5 mmol of 2-methyl-2-butene was hydroborated with 5 mmol of 9-BBN. To the solution was added a mixture of 5 mmol of styrene and 5 mmol of *p*-methoxystyrene. the solution was refluxed for 1 day, cooled to room temperature, oxidized, and then analyzed for remaining olefin and alcohols by VPC. In separate experiments the reflux was continued for 2 and 3 days. Similar relative rates were obtained in each case.

Attempted Asymmetric Olefin Exchange. A 100-mL reaction flask was charged with 30 mmol of (+)-α-pinene ($[\alpha]^2_{2D}$ +46.6° (neat, l = 1), 92% ee) and 30 mmol of 0.5 M 9-BBN. The solution was refluxed for 4 h, and then 45 mmol of 2-methyl-1-pentene was added. The mixture was refluxed for 3 days and then cooled to room temperature. The organoborane was oxidized with 10 mL of 3 N sodium hydroxide and 10 mL of 30% hydrogen peroxide. The solution was dried over potassium carbonate and the THF removed. The 1,5-cyclooctanediol precipitated upon standing. The solid was washed with hexane to recover the product. The crude product was chromatographed on silica gel. The olefin was eluted with hexane and then the product eluted with 5% isopropyl alcohol in hexane. The product was distilled through a Vigroeux column at 140–143 °C (1 atm) to give 1.60 g (50% yield) of 2-methyl-1-pentanol. The product gave a rotation of $[\alpha]^{25}_D$ +0.02°/(neat).

Isomerization of *B*-*cis*-Myrtanyl-9-BBN to *B*-*trans*-Myrtanyl-9-BBN. To a 100-mL reaction flash was added 12 mmol of (−)-β-pinene and 10 mmol of 0.5 M 9-BBN. The THF was removed with a water aspirator and then replaced under nitrogen with 23 mL of diglyme. The mixture was heated to 125 °C, and 2-mL aliquots were removed periodically for analysis. The aliquots were injected into nitrogen-flushed vials containing 0.3 mL of 3 N sodium hydroxide and then 0.3 mL of 30% hydrogen peroxide. The vials were heated to 50 °C for 15 min and then saturated with potassium carbonate. The solution was analyzed for *cis*- and

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trans-myrtanol by VPC. After 4 h only a trace of the cis isomer remained.

Preparation of (+)-β-Pinene. A 100-mL reaction flask was charged with 27.5 mmol of 9-BBN (0.5 M) and 25 mmol of (+)-α-pinene, $[\alpha]^{25}_D$ +47.23° (92% ee). The solution was refluxed for 3 h and then the THF removed with a water aspirator. Diglyme (40 mL) was added and the solution refluxed for 30 h. After cooling, 25 mmol of freshly distilled benzaldehyde was added and the solution again heated to reflux for a brief time. The solution was cooled and oxidized with the addition of 9.5 mL of 3 N sodium hydroxide and 7 mL of 30% hydrogen peroxide. The mixture was stirred for 2 h at 40–50 °C, cooled to room temperature, and extracted with hexane. The hexane layer was washed several times with water and then with saturated sodium chloride. After drying over potassium hydroxide and concentrating, the crude product (56% VPC yield of β-pinene and 22% of α-pinene) was chromatographed on silica gel–silver nitrate (prepared from 180 g of silica gel and 20 g of silver nitrate in acetonitrile). Elution with 1% ethyl acetate in hexane gave 1.745 g (51.2%) of (+)-β-pinene, bp 45 °C (31 mmHg, Kugelrohr), $[\alpha]^{25}_D$ +19.59° (l = 1, neat) (lit.[13] $[\alpha]_D$ +22.8°).

Acknowledgment. We wish to thank the National Institutes of Health for financial support and the University of California, Riverside, for a President's Undergraduate Fellowship to S.A.Z.

Registry No. *B-trans*-2-Methylcyclopentyl-9-BBN, 63942-79-0; *B*-3-methyl-2-butyl-9-BBN, 63942-78-9; *B*-3-pinanyl-9-BBN, 64106-79-2; 1-octene, 111-66-0; 2-methyl-1-pentene, 763-29-1; styrene, 100-42-5; *p*-methoxystyrene, 637-69-4; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; 2-methyl-1-pentanol, 105-30-6; *B-cis*-myrtanyl-9-BBN, 79919-20-3; *B-trans*-myrtanyl-9-BBN, 79919-21-4; (−)-β-pinene, 18172-67-3; 9-BBN, 280-64-8; (+)-α-pinene, 7785-70-8; (+)-β-pinene, 19902-08-0; *cis*-myrtanol, 51152-12-6; *trans*-myrtanol, 53369-17-8.

Hydroboration Kinetics. 3.[1] Kinetics and Mechanism of the Hydroboration of Alkynes with 9-Borabicyclo[3.3.1]nonane Dimer. Effect of Structure on the Reactivity of Representative Alkynes

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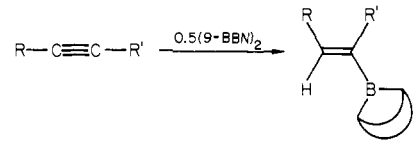
Contribution from the Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907. *Received June 19, 1981*

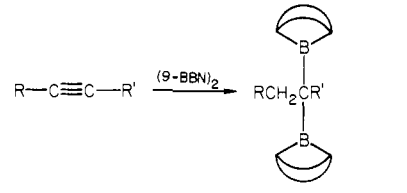
Abstract: The hydroboration of alkynes with 9-borabicyclo[3.3.1]nonane dimer, $(9\text{-BBN})_2$, exhibits kinetics similar to those for the hydroboration of alkenes. For the more reactive alkynes such as 1-hexyne, 3-methyl-1-butyne, 3,3-dimethyl-1-butyne, and cyclohexylethyne, the reaction exhibits first-order kinetics, first order in $(9\text{-BBN})_2$ only. For the less reactive alkynes, such as diphenylethyne, the reaction exhibits three-halves-order kinetics, first order in alkyne and one-half order in $(9\text{-BBN})_2$. Intermediate kinetics between first and three-halves order were observed with phenylethyne. Apparently the reaction proceeds through the same mechanism as the hydroboration of alkenes. There is a prior dissociation of the 9-BBN dimer into the monomer, followed by the reaction of the monomer with the alkyne. The relative reactivities of the alkynes toward 9-BBN, as well as the relative reactivities between the alkynes and their monohydroboration products, were obtained by competitive studies. The experimental results for the relative rates of mono- and dihydroboration of the alkynes are in very good agreement with the calculated numbers obtained by the use of the Runge–Kutta numerical method. This method is also used to predict the percentage of monohydroboration when an excess amount of alkyne is used.

The hydroboration of alkynes with 9-borabicyclo[3.3.1]nonane dimer, $(9\text{-BBN})_2$, has been shown to offer a convenient route to *B*-vinyl-9-BBN derivatives (eq 1), as well as to *gem*-dibora derivatives (eq 2.)[3] Both of these two derivatives are useful intermediates in organic synthesis.[4]

However, the hydroboration of alkynes with $(9\text{-BBN})_2$ has some unusual characteristics. In contrast to the disiamylborane dimer which reacts very rapidly with both terminal and internal alkynes,[5]



(1)



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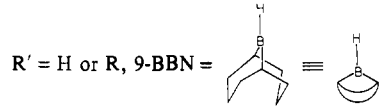

the hydroboration of alkynes with $(9\text{-BBN})_2$ is rather sluggish. One can selectively hydroborate a terminal double bond in the presence of an internal triple bond (eq 3).[6]

(1) For previous studies in this series, see: (a) Brown, H. C.; Scouten, C. G.; Wang, K. K. *J. Org. Chem.* **1979**, *44*, 2589–2591. (b) Brown, H. C.; Wang, K. K.; Scouten, C. G. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 698–702. (c) Wang, K. K.; Brown, H. C. *J. Org. Chem.* **1980**, *45*, 5303–5306.

(2) (a) Graduate research assistant on Grant CHE 76-20846 of the National Science Foundation. (b) Graduate research Assistant on Grant GP-6942X of the National Science Foundation.

(3) Brown, H. C.; Scouten, C. G.; Liotta, R. *J. Am. Chem. Soc.* **1979**, *101*, 96–99.

(4) See ref 3 and references cited therein.

(5) Brown, H. C.; Moerikofer, A. W. *J. Am. Chem. Soc.* **1963**, *85*, 2063–2065.

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