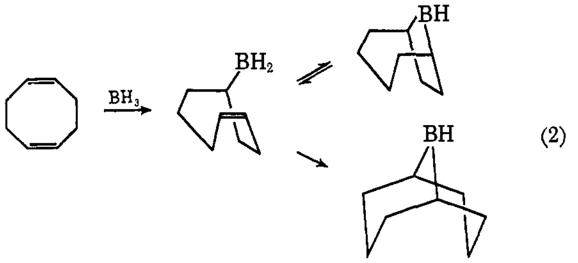
sequence,[8] the following mechanism (2) is indicated.



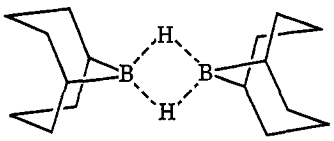
On simple thermodynamic consideration, it is easy to see that the 1,5 isomer, with two fused six-membered rings, should be more stable than the 1,4 isomer, with a seven-membered ring fused to a five-membered ring.

This makes possible an exceedingly simple preparative procedure. A 2-l. flask equipped with a reflux condenser, an addition funnel, a magnetic stirring bar, and a side arm fitted with a silicone rubber serum stopple was flushed with nitrogen and maintained under a static nitrogen atmosphere. In the flask was placed 800 ml of 1.0 M borane in THF and the flask was immersed in an ice bath. In the dropping funnel was placed 86.4 g (800 mmol) of 1,5-cyclooctadiene, made up to 200 ml with THF. The diene solution was added dropwise, with vigorous stirring, over a period of 20–30 min. The solution was then heated under reflux for 1 hr and then cooled to room temperature. A small amount of 9-BBN crystallized on cooling, leaving a saturated solution 0.78 M in the reagent. The crystalline compound was obtained by cooling the solution in an ice bath and filtering under nitrogen, followed by thorough washing with dry pentane. The yield of product in THF was essentially quantitative. The yield of crystalline material was approximately 65%.

9-Borabicyclo[3.3.1]nonane possesses the most remarkable thermal stability. Samples have been distilled at 195° (12 mm) or heated for 24 hr to 200° under nitrogen without loss of hydride activity or any noticeable change. This contrasts sharply with the behavior of other dialkylboranes, such as disiamylborane which isomerizes at 75°[9] or dicyclohexylborane which undergoes pyrolysis at 180–200° to yield cyclohexene and a polymeric borane.[10]

Even more unexpected, the white crystalline 9-BBN proved to be extraordinarily stable to air. A sample left in an open watch glass did not undergo any noticeable change over 24 hr. A bottle containing the product was opened at intervals over a 2-month period without appreciable loss of hydride activity. In spite of this unexpected inertness toward air, it exhibits the usual reactivity of a dialkylborane in hydroboration.[2] There are obviously major advantages in being able to store, weigh, and utilize such a reagent without the precautions required by the usual dialkylborane.

The infrared spectrum of 9-BBN, either as a THF solution or as a mineral oil mull, exhibits strong absorption at 1560 cm^{-1}, indicating the presence of a B–H–B bridge. Hence, 9-BBN must exist as the dimer (3), both in solution and in the crystalline state. The chair–chair conformation is selected in analogy to bicyclo[3.3.1]nonane, which exists in that conformation according to the X-ray analysis of Laszlo.[11] It has been reported that the C-3 and C-7 methylenes of bicyclo[3.3.1]nonanes will interact in the chair–chair conformation, giving rise to a characteristic infrared absorption at 1490 cm^{-1}.[12] Such absorption was observed in the spectrum of 9-BBN.



(3)

The boiling point of 9-BBN, 195° (12 mm), is unusually high. It should be contrasted with a boiling point of 98° (12 mm) for di-*n*-butylborane.[13] Simple dialkylboranes evidently dissociate and distil as the monomer, whereas 9-BBN must resist dissociation and distil largely as the dimer. Presumably dissociation would be accompanied by a widening of the C–B–C angle at the bridgehead to 120°. Such a widening could be readily accommodated in the acyclic dialkylborane such as di-*n*-butylborane, but would be resisted by the bicyclic structure. The unusual inertness toward oxygen may also be a reflection of the unusual stability of the boron–hydrogen bridge in these derivatives. Finally, we already have evidence that the exposed position of the boron atom at the bridge makes 9-BBN and its derivatives unusually effective in trapping carbanions, carbenes, and similar intermediates of value in applying the organoboranes for organic synthesis.[14]

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(8) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957).

(9) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **88**, 1433 (1966).

(10) Köster[1] reports that the pyrolysis of tricyclohexylborane yields cyclohexene, cyclohexane, hydrogen, and a polymeric borane.

(11) I. Laszlo, *Rec. Trav. Chim.*, **84**, 251 (1965).

(12) W. A. C. Brown, J. Martin, and G. A. Sim, *J. Chem. Soc.*, 1844 (1965); W. A. C. Brown, G. Eglinton, W. Parker, and G. A. Sim, *Proc. Chem. Soc.*, 57 (1964).

(13) R. Köster, G. Bruno, and P. Binger, *Ann.*, **644**, 1 (1961).

(14) Research in progress with M. M. Rogić and M. W. Rathke.

(15) Graduate research assistant on Grant GM 10937 from the National Institutes of Health.

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9-Borabicyclo[3.3.1]nonane as a Convenient Selective Hydroborating Agent

Sir:

Dialkylboranes have many advantages over diborane itself for selective hydroborations.[1,2] The dialkylboranes previously applied, such as disiamylborane and dicyclohexylborane, have been quite sensitive to atmospheric oxygen. Consequently, they were commonly synthesized *in situ* prior to their application.[1,2]

We recently developed a simple procedure for the synthesis of 9-borabicyclo[3.3.1]nonane (9-BBN) *via* the cyclic hydroboration–isomerization of 1,5-cyclooctadiene.[3] The product, a crystalline solid, mp 140–142°, exhibited extraordinary thermal stability, as well as unusual stability (for a dialkylborane) toward atmospheric oxygen. It could readily be weighed and transferred in the open air. These properties indicated a promising future as a reagent provided it possessed the

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(1) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 1241 (1961).

(2) G. Zweifel, N. R. Ayyangar, and H. C. Brown, *ibid.*, **85**, 2066 (1963).

(3) E. F. Knights and H. C. Brown, *ibid.*, **90**, 5280 (1968).

selective hydroborating characteristics of the dialkylboranes previously studied.[1,2]

Indeed, hydroboration of 1-hexene with 9-BBN gave only 1% of the alkyl derivative containing boron at the 2 position, as compared to 6% with diborane itself. Styrene gave only 2% of the α derivative, whereas diborane gives 20% of this isomer. Finally, *cis*-4-methyl-2-pentene gave 97% hydroboration at the less hindered position of the double bond, whereas diborane exhibits almost no selectivity between the two possible positions. Indeed, the results with 9-BBN are quite comparable with those previously realized with the highly selective reagent, disiamylborane (Table I).

Table I. Hydroboration–Oxidation Products in the Reaction of Unsymmetrical Olefins with Diborane,[a] Disiamylborane,[b] and 9-Borabicyclo[3.3.1]nonane (9-BBN)

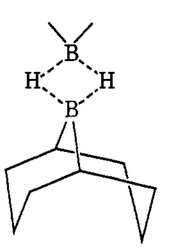
Olefin	Hydro-borating agent	Product distribution, %[c] 1-ol	2-ol	3-ol
1-Hexene	BH_3	94	6	
	Sia_2BH	99	1	
	9-BBN	99	1	
Styrene	BH_3	80	20	
	Sia_2BH	98	2	
	9-BBN	98	2	
cis-4-Methyl-2-pentene	BH_3		57	43
	Sia_2BH		57	3
	9-BBN		97	3

[a] H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 4708 (1960). [b] Reference 1. [c] Total yields of products by glpc were 95 ± 5%. The organoboranes were converted to alcohols by oxidation *in situ* with alkaline hydrogen peroxide.

It was previously noted by Köster that dialkylboranes do not need to have the large bulky groups of disiamylborane to achieve the selective behavior of the latter reagent.[4] Thus he observed that diethylborane hydroborates terminal olefins almost exclusively at the terminal position.

Although we did not attempt a detailed kinetic study, similar to that made with disiamylborane,[5] we did carry out experiments to establish the time required at 25° to achieve essentially complete hydroboration for olefins of different structural types (1-hexene, cyclopentene, 1-methylcyclopentene, cyclohexene, 2-methyl-1-butene, 2-methyl-2-butene, *cis*-4-methyl-2-pentene, and 2,3-dimethyl-2-butene). The reactions proved to be remarkably rapid, being complete in 5 min or less for all of the olefins, with two exceptions. Cyclohexene, which we have previously noted is relatively sluggish in the hydroboration reaction,[1] required 3 hr, and the highly hindered olefin, 2,3-dimethyl-2-butene, required 24 hr. However, it is noteworthy that both *cis*-4-methyl-2-pentene and 2-methyl-2-butene were completely hydroborated in 5 min, whereas they require 5 and 6 hr with disiamylborane.

The difference in rate can be attributed to a difference in the size of the alkyl groups of the dialkylboranes and a difference in the exposure of the B–H bond.[6] In disiamylborane (**2**) there are six methyl groups crowded around the boron atom. In contrast, the alkyl groups of 9-BBN (**1**) are not as bulky and are tied back in the chair–chair conformation[3] of the bicyclic system, offering maximum exposure of the boron atom.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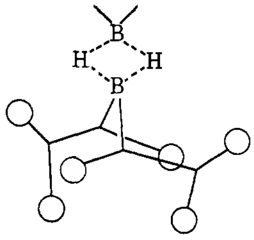
2, ○ = CH_3

As we shall point out in later publications, this openness of the boron atom results in an unexpected dividend in facilitating the capture of carbanions, carbenes, and similar intermediates useful in applying the organoboranes for synthetic purposes.[7]

Table II. Products from the Hydroboration–Oxidation of Representative Olefins with 9-BBN

Olefin	Products,[a,b] %
1-Hexene	1-Hexanol, 99 2-Hexanol, 1
Cyclopentene	Cyclopentanol, 100
Cyclohexene	Cyclohexanol, 100
2-Methyl-1-butene	2-Methyl-1-butanol, 99 2-Methyl-2-butanol, 1
2-Methyl-2-butene	3-Methyl-2-butanol, 99 2-Methyl-2-butanol, 1
2,3-Dimethyl-2-butene	2,3-Dimethyl-2-butanol, 99 2,3-Dimethyl-1-butanol,[c] 1
cis-4-Methyl-2-pentene	4-Methyl-2-pentanol, 97 2-Methyl-3-pentanol, 3
1-Methylcyclopentene	*trans*-2-Methylcyclopentanol, 99 1-Methylcyclopentanol, 1
Styrene	2-Phenylethanol, 98 1-Phenylethanol, 2
Norbornene	*exo*-Norbornanol,[d] 99.5 *endo*-Norbornanol,[d] 0.5

[a] Total yields were 95 ± 5%. [b] Glpc analysis. [c] Evidently formed in a rearrangement. Hydroboration was slow, 24 hr. [d] Analysis by Dr. J. Kawakami.

A number of representative olefins were hydroborated and oxidized and the products characterized. Yields of 95 ± 5% were realized and the products, in general, were those anticipated for a simple hydroboration without rearrangement. Only in the case of the highly

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(4) R. Köster, *Angew. Chem. Intern. Ed. Engl.*, 3, 174 (1964).

(5) H. C. Brown and A. W. Moerikofer, *J. Am. Chem. Soc.*, **83**, 3417 (1961); **85**, 2063 (1963).

(6) The earlier kinetic studies with disiamylborane[5] had indicated that the reaction is second order, first order in olefin and first order in the disiamylborane dimer. Presumably, the same situation holds with 9-BBN (dimer), so that the rate does not involve a prior dissociation of the dimer, which could have been unfavorable in view of the evidence for an unusually strong boron–hydrogen bridge in this derivative.[3]

(7) See, for example H. C. Brown, R. A. Coleman, and M. W. Rathke, *J. Am. Chem. Soc.*, **90**, 499 (1968); H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 818, 1911 (1968).

hindered olefin, 2,3-dimethyl-2-butene, where hydroboration at 25° was slow, requiring approximately 24 hr, was there identified 1% of 2,3-dimethyl-1-butanol, evidently arising from a small amount of isomerization.

The results are summarized in Table II.

Rates of hydroboration were determined by placing 25 ml of 0.78 *M* 9-BBN[8] in THF in the usual hydroborating flask, followed by 5 ml of a 2.00 *M* solution of olefin in THF. The reaction mixture was maintained at 25° and aliquots were removed at appropriate intervals of time and analyzed by hydrolysis for residual hydride. For preparation of alcohols the hydroboration was carried out in a similar manner. Then 5 ml of 6 *M* sodium hydroxide was added, followed by the addition of 4 ml of 30% hydrogen peroxide. The reaction mixture was heated at 60° for 1 hr to ensure completion of the oxidation (the adduct of 9-BBN with 2,3-dimethyl-2-butene was particularly slow to oxidize). To isolate the product, the reaction mixture was cooled to 25°, the aqueous phase saturated with potassium carbonate, and the dry THF phase analyzed by glpc using an internal standard of *p*-dimethoxybenzene.

It is evident that the commercial availability of 9-BBN will make selective hydroboration an exceedingly simple laboratory operation.

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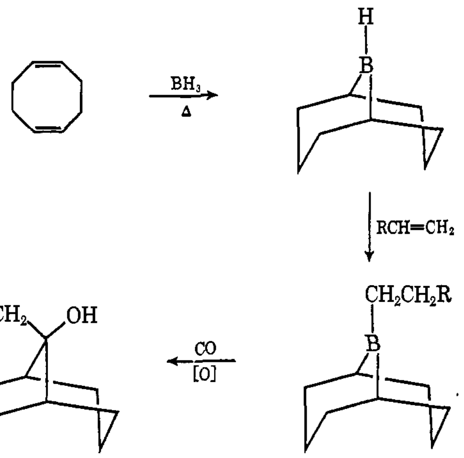
The Reaction of Carbon Monoxide with B-Alkyl-9-borabicyclo[3.3.1]nonanes. A Remarkably Simple Synthesis of 9-Alkylbicyclo[3.3.1]nonan-9-ols

Sir:

The reaction of carbon monoxide with organoboranes[1] produced *via* hydroboration[2] provides convenient synthetic routes to tertiary alcohols,[3a] secondary alcohols,[3b] acyclic[3b,c] and cyclic ketones,[3d] including those with functional groups,[3e,f] methylol derivatives,[3g] aldehydes,[3h] and polycyclic compounds.[3i] We now wish to report that the B-alkyl-9-borabicyclo[3.3.1]nonanes, now readily available *via* the cyclic hydroboration–isomerization of 1,5-cyclooctadiene[4] and the reaction of the 9-BBN intermediate with olefins,[5] undergo carbonylation cleanly and in high yield to produce the corresponding 9-alkylbicyclo[3.3.1]nonan-9-ols (1). This procedure provides a remarkably simple entry into this new interesting series of carbinols in which both the 9-alkyl and 9-hydroxy groups are bonded axially to a six-membered ring.



(1)

With but two exceptions, the yields were in the range of 85–95%. Indeed, it is remarkable that groups such as isobutyl, 2,3-dimethyl-1-butyl, and cyclohexyl can be introduced into the 9 position without apparent difficulty.

The following procedure is representative. 9-BBN was produced by the dropwise addition of 10.8 g (100 mmol) of 1,5-cyclooctadiene to a flask containing 40 ml of 2.5 *M* borane in THF under nitrogen. The solution was heated under reflux for 1 hr and cooled to 25°, and 7.0 g (100 mmol) of 1-pentene added. After 1 hr (to ensure complete hydroboration) the solution was transferred with a syringe to an autoclave flushed with nitrogen; 10 ml of ethylene glycol was then added. The autoclave was pressured to 70 atm with carbon monoxide and the temperature was raised to 150° and maintained there for 24 hr. The contents were oxidized with 50 ml of 6 *M* sodium hydroxide and 40 ml of 30% hydrogen peroxide at 50–60°. The reaction mixture was maintained at this temperature for 2 hr to complete the oxidation. The flask was cooled, the aqueous phase was saturated with potassium carbonate, and the crude product was isolated by removal of the THF on a rotary evaporator. There was obtained 18.0 g (86%) of 9-*n*-pentylbicyclo[3.3.1]nonan-9-ol, 95% pure by glpc. Redistillation, bp 106° (0.15 mm), gave the pure alcohol, $n^{20}\text{D}$ 1.4967. The results are summarized in Table I.

The assigned structure was confirmed by degradation of the 9-*n*-pentylbicyclo[3.3.1]nonan-9-ol to the known bicyclo[3.3.1]nonan-9-one.[6] Treatment of 9-*n*-pentylbicyclo[3.3.1]nonan-9-ol with phosphorus oxychloride in pyridine[7] afforded a single olefin in 92% yield (bp 88–92° (1.5 mm), $n^{20}\text{D}$ 1.4903). The olefin showed only one vinyl proton (a triplet at 5.15 ppm), consistent with 9-*n*-pentylidinebicyclo[3.3.1]nonane. This olefin was then treated with ozone (−78° in chloroform) and then oxidized in hydrogen peroxide–acetic acid to give 30% bicyclo[3.3.1]nonan-9-one, mp 154–156°, 2,4-dinitro-

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[1] M. E. D. Hillman, *J. Am. Chem. Soc.*, **84**, 4715 (1962); **85**, 892, 1636 (1963).

[2] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

[3] (a) H. C. Brown and M. W. Rathke, *J. Am. Chem. Soc.*, **89**, 2737 (1967); (b) H. C. Brown and M. W. Rathke, *ibid.*, **89**, 2738 (1967); (c) H. C. Brown and M. W. Rathke, *ibid.*, **89**, 4528 (1967); (d) H. C. Brown and E. Negishi, *ibid.*, **89**, 5477 (1967); (e) H. C. Brown, G. W. Kabalka, and M. W. Rathke, *ibid.*, **89**, 4530 (1967); (f) H. C. Brown and E. Negishi, *ibid.*, **89**, 5285 (1967); (g) H. C. Brown and M. W. Rathke, *ibid.*, **89**, 2740 (1967); (h) H. C. Brown, R. A. Coleman, and M. W. Rathke, *ibid.*, **90**, 499 (1968); (i) H. C. Brown and E. Negishi, *ibid.*, **89**, 5478 (1967).

[4] E. F. Knights and H. C. Brown, *ibid.*, **90**, 5280 (1968).

[5] E. F. Knights and H. C. Brown, *ibid.*, **90**, 5281 (1968).

[6] C. S. Foote and R. B. Woodward, *Tetrahedron*, **20**, 687 (1964).

[7] R. R. Sauers, *J. Am. Chem. Soc.*, **81**, 4873 (1959).