Hydroboration. XXXVI. A Direct Route to 9-Borabicyclo[3.3.1]nonane via the Cyclic Hydroboration of 1,5-Cyclooctadiene. 9-Borabicyclo[3.3.1]nonane as a Uniquely Selective Reagent for the Hydroboration of Olefins[1]

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Abstract: The cyclic hydroboration of 1,5-cyclooctadiene, followed by isomerization of the mixture of 1:1 adducts (under reflux for 1 hr), provides a simple, direct synthesis of 9-borabicyclo[3.3.1]nonane (9-BBN). Pure 9-BBN is isolated in 70-80% yield by cooling the reaction mixture and decanting the supernatant liquid. Spectral (ir, mass spectral) and boiling point data indicate that 9-BBN is dimeric in the solid and vapor states and in solution (THF, benzene, hexane). The product can be stored almost indefinitely at room temperature, either as the solid or in THF solution, provided that a nitrogen atmosphere is maintained. It exhibits unusual thermal stability for a dialkylborane and can be maintained at 160-200° for hours without serious change. It also exhibits unusual stability for a dialkylborane toward the atmosphere. Nevertheless, it behaves as an active boron hydride toward hydroxylic compounds and olefins. The reactions of 9-BBN with hydroxylic compounds are rapid and quantitative, yielding hydrogen and the corresponding borinic acid derivative. The hydroborations of olefins of varying structural features with 9-BBN have been studied in three solvents—THF, benzene, and hexane. The reactions of 9-BBN in THF with terminal olefins were complete in 2-4 hr at 25°, while some internal olefins required many hours for complete reaction under these conditions. Hydroborations with 9-BBN in benzene or hexane were slower than those in THF. In general, treatment of an olefin with 9-BBN in refluxing THF for 1 hr, or in refluxing benzene or hexane for 8 hr, effected complete hydroboration. Very sluggish olefins required longer reaction times—8 hr under reflux in THF and 12 hr under reflux in benzene or hexane. Only the exceptionally sluggish olefin, 2,3-dimethyl-2-butene in benzene or hexane solvents, was not completely hydroborated under these conditions. In no case was more than a trace of isomerization of the intermediate organoborane observed. The regioselectivity of 9-BBN in olefin hydroborations is the highest yet achieved. For example, the hydroboration-oxidation of *cis*-4-methyl-2-pentene with 9-BBN gives only 0.2% of the minor product, 2-methyl-3-pentanol, while 3% is obtained with disiamylborane or dicyclohexylborane, and almost no selectivity is observed with either thexylborane or borane. Comparable results were realized with other olefins.

The hydroboration of olefins and acetylenes has made a wide variety of functionally substituted organoboranes readily available for use in organic synthesis.[3] This development has led to the discovery of a number of exciting new reactions of organoboranes.[4] In some cases, notably oxidation to alcohols[3,4] and ketones,[5] protonolysis,[3] displacement,[3] and carbonylation to trialkylcarbinols,[6] it has been possible to achieve utilization of all three groups attached to boron. Unfortunately, utilization of all three groups has not been achieved in other of the potentially useful new reactions. We have, therefore, turned our attention to the development of blocking groups to make possible the efficient utilization of valuable olefins in these reactions.

For example, the thexyl(2,3-dimethyl-2-butyl) group[7] has proved valuable as a blocking group in several reactions involving the union of two groups on boron.[6,8] Chlorine substituents[9] and certain cyclic moieties[10] have been employed as blocking groups in organoborane reactions involving free radicals.[11] The dichloroboryl moiety has also proved useful in reactions of organoboranes with diazo compounds[12] and organic azides.[13] The disubstituted thexylboranes,[7,8,14] alkyl dichloroboranes,[9,15] and *B*-alkylboracyclanes[16] used in these reactions are now readily available via hydroboration.

One of the most useful blocking groups for syntheses via organoboranes is the 1,5-cyclooctyl unit contained in 9-borabicyclo[3.3.1]nonane[1] (9-BBN). The 9-BBN group has proved to be effective in the alkylation of α-halo carbanions[17] derived from α-halo esters, ketones, and nitriles, in the synthesis of secondary alkyl bromides via bromination,[18] and in carbonylation to aldehydes and methylol derivatives.[19] Moreover, the unique steric openness at the boron atom in *B*-alkyl-9-BBN derivatives has been exploit-

ed in base-induced cyclization reactions leading to cyclopropanes[20] and *B*-cycloalkyl-9-BBN derivatives.[21] Finally, our preliminary work[1] indicated that the parent compound, 9-borabicyclo[3.3.1]nonane, was a highly selective hydroborating agent. Accordingly, we have undertaken a detailed study of the preparation of 9-BBN and of its properties and reactions.

Results and Discussion

Preparation and Isolation of 9-BBN. Recent studies[22] on the hydroboration of dienes indicate that the hydroboration of 1,5-cyclooctadiene (COD) proceeds largely—if not entirely—in a cyclic manner. The addition of COD to an equimolar amount of borane in THF, followed by oxidation, yields *cis*-1,4- and *cis*-1,5-cyclooctanediols in the ratio 28:72. Only traces of other diol products were detected by glpc. Methanolysis of the hydroboration mixture, followed glpc analysis, revealed the presence of *B*-methoxy-9-borabicyclo[4.2.1]nonane and *B*-methoxy-9-borabicyclo[3.3.1]nonane in 91% overall yield. Unfortunately, the exact ratio of the two products could not be obtained from the glpc analysis. These results were explained in terms of a simple cyclic hydroboration (eq 1). Thus, it appeared that if conditions
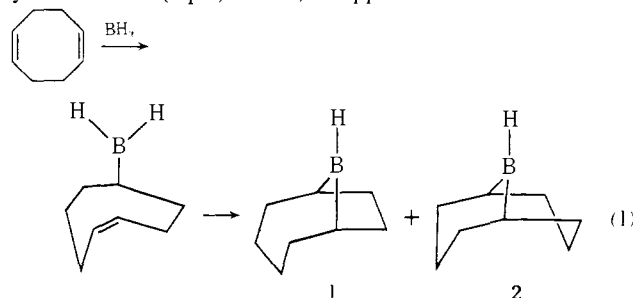
for isomerization of the 1,4-adduct (1) to the desired 1,5-adduct (2) could be found, a direct route to 9-BBN would result. Previously, several B-substituted 9-BBN derivatives had been prepared *via* pyrolysis of various cyclooctylboranes,[23] and Köster[24] had prepared 9-BBN, itself, by heating a mixture of *B-n-*propyl-9-BBN with tetra-*n*propyldiborane. The COD–borane adducts were, therefore, distilled (bp 195° (12 mm)), yielding a white solid, which gave very pure *cis*-1,5-cyclooctanediol upon oxidation.

Subsequently, we discovered that complete isomerization could be effected under milder conditions. Simply heating the THF solution of 1 and 2 under reflux for an hour effected complete conversion to the 1,5-adduct (2) as indicated by oxidation to pure *cis*-1,5-cyclooctanediol (eq 2).
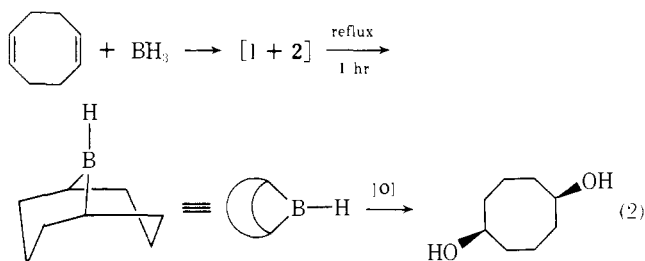
When the reaction mixture was cooled at this point, very pure (>99%) 9-BBN precipitated and was isolated in 70–80% yield. The material was characterized by analysis of active hydride by methanolysis (>99.5% H_2), glpc analysis of the methoxyborane produced (95% yield), and by satisfactory elemental analyses (C, H, B).

The infrared spectrum of 9-BBN exhibits a strong absorption at 1567 cm^{-1}, either as a mineral oil mull of the solid, or in solution (THF, benzene, hexane). This indicates the presence of a boron–hydrogen bridge, hence, 9-BBN must exist as the dimer (3), both in solution and in the solid state.[25]

3
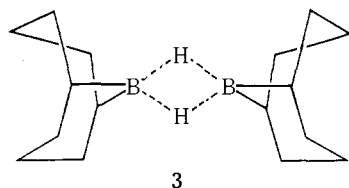
The chair–chair conformation for 3 is selected in analogy to bicyclo[3.3.1]nonane, which exists in that conformation, according to the X-ray analysis of Laszlo.[26] It has been reported that the C-3 and C-7 methylenes of bicyclo[3.3.1]nonanes will interact in the chair–chair conformation, giving rise to a characteristic infrared absorption at 1490 cm^{-1}.[27] Such an absorption was observed in the spectrum of 9-BBN.[28]

The mass spectrum of 9-BBN exhibits a prominent cluster of peaks at *m/e* 242, 243, and 244 in the approximate ratio of 1:8:16. Both the mass and the observed relative intensities of these peaks correspond to those expected for the molecular ion derived from 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.[29] Simple dialkylboranes evidently dissociate and distill as the monomer, whereas 9-BBN must distill as the dimer. Presumably, dissociation would be accompanied by an increase in the C–B–C angle from 111.8° [28] to 120°. Such an increase could be readily accommodated in the acyclic dialkylborane but would be resisted in the rigid bicyclic structure. The unusual stability of the dimeric form, 3, is reflected in the chemistry of 9-BBN.

Stability of 9-BBN. The thermal stability of 9-BBN is remarkable. A sample of pure 9-BBN in a sealed, evacuated capillary was heated repeatedly to 160° without any noticeable change in the melting point. Samples of 9-BBN were heated under N_2 to 200° for 24 hr, either as the solid or in the presence of hydrocarbons (*e.g.*, tetradecane) with only minor loss of hydride activity. In sharp contrast, disiamylborane undergoes isomerization at 75°,[30] and dicyclohexylborane is reported[31] to decompose at 180–200°, yielding cyclohexene and a polymeric borane.

The stability of pure 9-BBN toward air oxidation is unique among dialkylboranes and is comparable to that of lithium aluminum hydride. Even so, some loss of purity attends exposure to the atmosphere. Consequently, for quantitative studies it is recommended that manipulations of solid 9-BBN be carried out—as much as possible—under a nitrogen atmosphere, in order to maintain the maximum hydride activity and purity. Solutions of 9-BBN, on the other hand, are highly reactive toward both oxygen and water and should be rigorously protected from these reactants for both preparative and quantitative studies.

From a practical standpoint, 9-BBN is stable at room temperature. The reagent can be stored, either as the solid or in THF solution, for indefinite periods (>2 years) without any noticeable change in activity, provided that an inert atmosphere is maintained.[32]

Reactions of 9-BBN with Hydroxylic Compounds. The reactions of 9-BBN in THF at 25° with water and simple alcohols (methanol, *tert*-butyl alcohol) afford quantitative yields of hydrogen and the corresponding *B*-hydroxy- and *B*-alkoxy-9-BBN derivatives. However, these reactions are by no means instantaneous, requiring 10–60 min for complete evolution of hydrogen. This is much slower than the comparable solvolysis of disiamylborane.

The rates of reaction of disiamylborane with various alcohols have been studied[33] by adding the alcohol to a THF solution containing 4 equiv of disiamylborane at 0°. Hydrogen was instantaneously evolved with methanol and *tert*-butyl alcohol; however, no hydrogen evolution was observed when 3-ethyl-3-pentanol was added. Evidently steric hindrance prevents reaction with the bulky disiamylborane in this case. Yet, when tri-*n*-butylcarbinol, which is clearly more hindered than 3-ethyl-3-pentanol, was added to a fourfold excess of 9-BBN in THF at 25°, reaction was complete in 60 min. Hence, it would appear that 9-BBN is less sterically hindered than disiamylborane. In that case, the slower rates of reaction of 9-BBN with simple alcohols appear anomalous.

It was previously pointed out that 9-BBN exists as an exceptionally tightly bound dimer. It is now suggested that the sluggishness with which 9-BBN reacts with the simple alcohols may be a reflection of the unusual stability of the boron–hydrogen bridge in the 9-BBN dimer.

Finally, it has been observed that no hydrogen is evolved on treatment of 9-BBN with 2,6-di-*tert*-butyl-4-methylphenol at 145° for 21 hr.[34] Apparently, in this case massive steric hindrance by the two ortho *tert*-butyl groups is sufficient to prevent coordination with boron. In contrast, reaction with 2,6-diisopropylphenol in THF at only 50° is complete in 20 min.

The Hydroboration of Olefins with 9-BBN in THF. Previous workers[31,35] have observed that dialkylboranes are significantly more selective in the hydroboration of unsymmetrical olefins than is diborane itself. Thus, the hydroboration of 1-hexene with disiamylborane[35] gave only 1% of the alkyl group containing boron at the 2-position, compared to 6% with diborane. As previously noted, 9-BBN is distinctly less sterically hindered than disiamylborane in its reactions with bulky alcohols. Therefore, it was surprising that the

hydroboration of 1-hexene with 9-BBN in THF at 25° was even more selective than with disiamylborane.[36.] After oxidation of the intermediate organoborane, less than 0.1% of 2-hexanol was found. Similarly, the hydroboration-oxidation of cis- 4-methyl-2-pentene with 9-BBN produced only ~0.2% of the more hindered alcohol, 2-methyl-3-pentanol, compared to 3% with disiamylborane, and almost no selectivity with diborane. Indeed, the selectivity obtained with 9-BBN is generally higher than that previously realized with 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	Hydroborating agent	Product distribution, %[c]		
		1-ol	2-ol	3-ol
1-Hexene	BH₃	94	6	
	Sia₂BH	99	1	
	9-BBN	>99.9		
Styrene	BH₃	80	20	
	Sia₂BH	98	2	
	9-BBN	98.5	1.5	
cis-4-Methyl-2-pentene	BH₃		57	43
	Sia₂BH		97	3
	9-BBN		99.8	0.2

[a] H. C. Brown and G. Zweifel, J. Amer. Chem. Soc., **82**, 4708 (1960). [b] Reference 35. [c] Total yields of products were 95 ± 5%. The organoboranes were converted to alcohols by oxidation in situ with alkaline hydrogen peroxide.

We have carried out experiments to establish the time required to achieve essentially complete hydroboration for olefins of different structural types.[38] In general, the hydroborations of terminal olefins with an equimolar amount of 9-BBN in THF were complete in 2 hr at 25°. Internal olefins varied widely in reactivity. For example, cyclopentene required only 2 hr for complete hydroboration, while 2,3-dimethyl-2-butene was not completely hydroborated after 3 days.[39] These results are summarized in Table II.

Table II. Reaction of Various Olefins with 9-BBN in THF at 25°

Olefin[a]	Olefin reacted, %		
	2 hr	4 hr	24 hr
1-Hexene	100		
3,3-Dimethyl-1-butene	100		
Styrene	94	100	
2-Methyl-1-pentene	100		
cis-3-Hexene	81	92	100
cis-4,4-Dimethyl-2-pentene	77	90	99
2-Methyl-2-butene	91		
2,3-Dimethyl-2-butene	11	15	33
Cyclopentene	100		
Cyclohexene	30	46	88
Cycloheptene	100		
Cyclooctene	100		
Norbornene	100		

[a] Olefin concentration was 0.4 M. An equivalent amount of 9-BBN was used.

Considerably shorter reaction times were achieved at higher temperatures. With 1 equiv of 9-BBN in refluxing THF, even the most sluggish olefin studied, 2,3-dimethyl-2-butene, was completely hydroborated in 8 hr. Essentially quantitative yields (>95%) of alcohols were obtained in each case after the usual oxidation. Only in the case of 2,3-dimethyl-2-butene was there identified a trace (<0.5%) of the primary alcohol, possibly derived from an isomerized organoborane. The results are summarized in Table III.

Table III. Products from the Hydroboration–Oxidation of Representative Olefins with 9-BBN in THF[a]

Olefin	Time, hr	Temp, °C	Product distribution, %
1-Hexene	2	25	1-Hexanol, >99.9
3,3-Dimethyl-1-butene	2	25	3,3-Dimethyl-1-butanol, >99.7
			3,3-Dimethyl-2-butanol, <0.3
Styrene	4	25	1-Phenylethanol, 98.5
			2-Phenylethanol, 1.5
2-Methyl-1-pentene	2	25	2-Methyl-1-pentanol, >99.8
cis-3-Hexene	1	65	3-Hexanol, 100
cis-4-Methyl-2-pentene	1	65	4-Methyl-2-pentanol, 99.8
			2-Methyl-3-pentanol, 0.2
cis-4,4-Dimethyl-2-pentene	1	65	4,4-Dimethyl-2-pentanol, 99.9
			2,2-Dimethyl-3-pentanol, 0.1
2-Methyl-2-butene	1	65	3-Methyl-2-butanol, >99.8
Cyclopentene	2	25	Cyclopentanol, 100
Cycloheptene	2	25	Cycloheptanol, 100
Cyclooctene	2	25	Cyclooctanol, 100
Norbornene	2	25	exo-Norborneol, 99.5
			endo-Norborneol, 0.5
Cyclohexene	1	65	Cyclohexanol
1-Methylcyclohexene	8	65	trans-2-Methylcyclohexanol, >99.8
2,3-Dimethyl-2-butene	8	65	2,3-Dimethyl-2-butanol, 99.5
			2,3-Dimethyl-1-butanol,[b] 0.5

[a] Analysis by glpc. The combined yield of alcohols was >97% except for 2,3-dimethyl-2-butene, where a yield of 95% was indicated. [b] Probably formed via isomerization of the B-alkyl-9-BBN.

Hydroboration of Olefins with 9-BBN in Benzene and Hexane.

While convenient procedures were available for the hydroboration of olefins with 9-BBN in THF, recent developments in our laboratory made it desirable to have a direct route to B- alkyl-9-BBN derivatives in nonether solvents.[18] Accordingly, we have investigated the hydroboration of representative olefins with 9-BBN in benzene and hexane.

Hydroborations in these solvents were found to be somewhat slower than in THF. In general, treatment of a modest (10%) excess of the olefin with 9-BBN in the refluxing solvent for 8 hr effected complete hydroboration. After oxidation, the anticipated alcohols were obtained in essentially quantitative yield based on 9-BBN.

A longer reaction time, 12 hr, was required for complete hydroboration of 1-methylcyclohexene. The very recalcitrant olefin, 2,3-dimethyl-2-butene, was not completely hy-
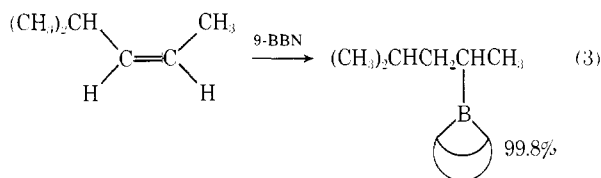
Table IV. Products from the Hydroboration–Oxidation of Representative Olefins with 9-BBN in refluxing Benzene and Hexane Solvents

| Olefin	Product	Yield (%)[a,b]	
		Benzene	Hexane
1-Hexene	1-Hexanol	>99.5	>99.5
	2-Hexanol	<0.5	Trace
3,3-Dimethyl-1-butene	3,3-Dimethyl-1-butanol	>99.5	>99.5
	3,3-Dimethyl-2-butanol	Trace	Trace
Styrene	2-Phenylethanol	98	98
	1-Phenylethanol	2	2
cis-3-Hexene	3-Hexanol	100	100
2,3-Dimethyl-2-butene[c]	2,3-Dimethyl-2-butanol	99.5	99.5
		0.5	0.5
Cyclopentene	Cyclopentanol	100	100
Cyclohexene	Cyclohexanol	100	100
1-Methylcyclohexene[d]	trans-2-Methylcyclohexanol	>99.5	>99.5
	Cyclohexanemethanol	Trace	Trace
Norbornene	exo-Norborneol	99.5	99.5
	endo-Norborneol	0.5	0.5

[a] Glpc analysis. Reaction times were 8 hr, except as noted. [b] Total yields of 93–100% were obtained, except as noted. [c] Reaction time of 12 hr. Total yield of alcohols was 71% in benzene and 40% in hexane. [d] Reaction time of 12 hr.

droborated, even after 12 hr. In this case after 12 hr, 2,3-dimethyl-2-butanol was obtained in yields of 71 and 40% in refluxing benzene and hexane, respectively. Significantly, no more than a trace of isomerization was observed in these reactions. The results are summarized in Table IV.

Regio- and Stereospecificity. As was pointed out earlier, 9-BBN exhibits a remarkable regiospecificity in the hydroboration of many alkenes. Thus, 1-hexene yields 99.9% of the 1-isomer and the disubstituted olefin (Table I), cis-4-methyl-2-pentene, reacts to place 99.8% of the boron at the less hindered of the two carbon atoms of the double bond (eq 3).
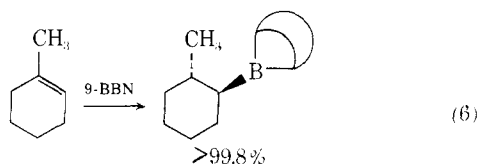
$$(CH_3)_2CH \qquad CH_3$$
$$\diagdown C=C \diagup \qquad \xrightarrow{\text{9-BBN}} \qquad (CH_3)_2CHCH_2CHCH_3 \qquad (3)$$
$$H \diagup \qquad \diagdown H$$

with B, 99.8%

Norbornene reacts to give the exo isomer predominantly (eq 4). On the other hand, 7,7-dimethylnorbornene reacts to

$$\xrightarrow{\text{9-BBN}} \qquad 99.5\% \qquad + \qquad 0.5\% \qquad (4)$$
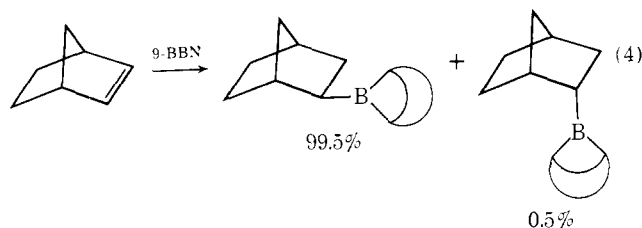
give the endo isomer preferentially (eq 5).[40] Finally, 1-

$$\xrightarrow{\text{9-BBN}} \qquad 3\% \qquad + \qquad 97\% \qquad (5)$$
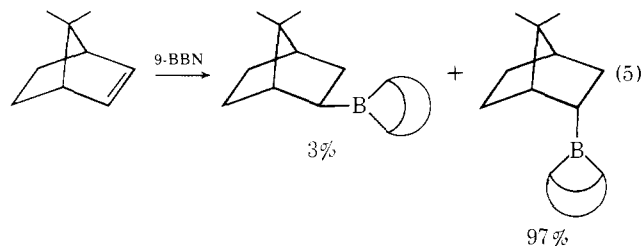
methylcyclohexene provides >99.8% of the trans isomer (eq 6).

$$\xrightarrow{\text{9-BBN}} \qquad >99.8\% \qquad (6)$$

Conclusions

A simple, direct synthesis of 9-BBN, via the cyclic hydroboration of COD, has been developed. The product can be stored indefinitely at room temperature, either as the solid or in solution, provided that an inert atmosphere is maintained.

The product exists almost entirely as the dimer, (9-BBN)$_2$, whether in the solid or vapor states or in solution in THF, benzene or hexane.

Treatment of an olefin with 9-BBN at 65–80° in THF, benzene, or hexane provides a general method for the preparation of B-alkyl-9-BBN derivatives. Extremely high regioselectivity is obtained in these reactions.

Experimental Section

The organoboranes were always handled under an atmosphere of prepurified nitrogen (Airco) with careful exclusion of both oxygen and water.[41,42] All glassware, syringes, and needles were oven-

dried at 150° before use. The glassware was assembled while hot and cooled under a flow of nitrogen. When the assembled apparatus was cool, and had been thoroughly flushed with nitrogen, the injection port of the reaction flask was capped with a rubber serum stopple. A small positive pressure of nitrogen was maintained thereafter, using a mercury bubbler as a pressure relief valve. Syringes were assembled and fitted with needles while hot, then cooled as assembled units. Pmr, ir, and mass spectra were obtained with a Varian T-60, a Perkin-Elmer 700, and a Hitachi RMU-6A, respectively. Boron-11 nmr spectra were obtained with a Varian XL-100-15 spectrometer. Glpc analyses of alcohols and olefins were carried out using a Varian Model 1200 F.I.D. chromatograph, equipped with the indicated column. When analyzing organoborane products, a Hewlett-Packard 5752B chromatograph, equipped with the indicated column, was employed. In order to avoid decomposition of the organoboranes, the column was treated with Silyl-8 (Pierce Chemical Co.) before use. Diol diacetates were analyzed using a Perkin-Elmer Model 226 F.I.D. chromatograph, equipped with the indicated Golay column. Microanalyses were performed by the Purdue Microanalytical Laboratory.

Materials. The preparation of borane solutions in THF was carried out as described previously.[43] 1,5-Cyclooctadiene (Columbian Carbon) (bp 45–48° (19 mm), n^{20}D 1.4938) was distilled from lithium aluminum hydride. Styrene (J. T. Baker) (bp 36° (19 mm), n^{20}D 1.5474) was distilled immediately before use. The other olefins were obtained commercially and used after checking the refractive indices and verifying the purity by glpc analyses ($\frac{1}{8}$ in. × 6 ft, 10% SE-30 on Varaport 30, 60°, and $\frac{1}{8}$ in. × 6 ft, 20% adiponitrile on Varaport 30, 40°). The n-alkanes (Phillips), employed as internal standards, were used as received. Technical grade pentane and hexane were stirred over fuming sulfuric acid to remove any olefinic impurities, washed with aqueous base, dried over anhydrous magnesium sulfate, and distilled under nitrogen from lithium aluminum hydride. Benzene (Mallinckrodt SpectrAR) was distilled under nitrogen from lithium aluminum hydride.

Thermal Isomerization of the COD–Borane 1:1 Adducts. A 300-ml flask with an injection port was equipped with a magnetic stirring bar and a gas inlet tube connected to a nitrogen source. The flask was cooled in an ice-water bath and charged with 100 ml of 1 M borane in THF. To the stirred borane solution was added 12.4 ml of COD (100 mmol) via syringe over a period of 10 min. The mixture was allowed to stir for 1 hr to ensure complete reaction, then the ice bath was removed. The gas inlet tube was removed and the flask was fitted with a short path distillation head, the receiver of which was cooled in a Dry Ice-acetone bath. The solvent was removed, leaving a white solid (mp ~130°) in the distillation flask. The solid was distilled (bp 185–195° (12 mm)), finally leaving 1.75 g of an oily residue (14.3 mmol based on 9-BBN) in the distillation flask.

The receiver, containing a white solid and a clear supernatant liquid, was warmed to room temperature, whereupon most of the solid dissolved. The receiver was connected to a gas meter and 8 ml of absolute ethanol (135 mmol) was added. Gas evolution amounted to 75 mmol. Oxidation was effected by adding, successively, 100 ml of ethanol, 60 ml of 3 N NaOH, and 40 ml of 30% hydrogen peroxide. After evaporation of the solvent, there was obtained 14.0 g of a viscous oil, which was crystallized from ether to give 7.94 g (55%) of cis-1,5-cyclooctanediol, mp 73.5–74.8° (lit.[44] mp 73.8–74.8°), and bis-p-nitrobenzoate, mp 180.5–181.2° (lit.[44] mp 181.4–182.8°); pmr (CDCl$_3$–TMS) δ 1.6 (broad singlet, 7 H), 3.8 (broad singlet, 2 H). The diol was converted to the diacetate (acetic anhydride–pyridine), which gave a single sharp peak upon glpc analysis (150 ft × 0.010 in., Os-138).

Preparation of 9-BBN. A 1000-ml flask with an injection port was equipped with a magnetic stirring bar and a reflux condenser. To the top of the condenser was fitted a pressure-equalized dropping funnel which was connected to a source of nitrogen. The flask was cooled to −5° in an ice-salt water bath and charged with 505 ml of 1.98 M borane in THF (1 mol). The dropping funnel was charged with 108 g of COD (1 mol), which was added dropwise over 1 hr to the stirred borane solution. The cooling bath was removed and the mixture was heated under reflux for 1 hr. The resulting clear solution was cooled slowly, without stirring, to room temperature. Cooling in an ice-water bath completed precipitation of the product. The supernatant liquid was decanted using a dou-

ble-ended 15-gauge needle.[41,42,45] The solid was washed twice with 50-ml portions of ice-cold pentane, decanting the supernatant liquid as before. After drying at 50° *in vacuo*, the yield of fine, white powder was approximately 75% (85–95 g): mp 152–155° (in a sealed, evacuated capillary); ir (THF) 1490 (w), 1567 cm⁻¹ (s); pmr (benzene-TMS) δ 1.8 (broad singlet); B¹¹ nmr (THF) δ −28 relative to external BF₃·OEt₂; (benzene) −28 relative to external BF₃·OEt₂ (broad singlet).

Anal. Calcd for $C_{16}H_{30}B_2$: C, 78.72; H, 12.39; B, 8.89. Found: C, 78.99; H, 12.54; B, 8.85.

The mass spectrum of 9-BBN, at an ionizing voltage of 70 eV, displayed a prominent cluster of peaks (*m/e* 242, 243, 244) in the approximate ratio 1:8:16. This is the ratio expected for a species containing two boron atoms, since the natural abundance of ¹⁰B is 20% and that of ¹¹B is 80%. No significant peaks were observed at higher mass numbers (to *m/e* 600).

The active hydride content of weighed samples was determined by measuring the hydrogen (>99.5% of theoretical) evolved upon methanolysis. The resulting *B*-methoxy derivative (95% yield by glpc) was found to be essentially free of its isomer, *B*-methoxy-9-borabicyclo[4.2.1]nonane, by glpc analysis (3 ft × ¼ in., 10% Apiezon on Chromosorb W-AW-DMCS).[46]

Thermal Stability. A sample of crystalline 9-BBN (mp 152–155°) was sealed under vacuum in a melting point capillary and heated to 160°. The sample solidified upon cooling and was again heated to 160° with no change in the melting point. This was repeated several times.

A 2.44-g sample of 9-BBN (20 mmol) was placed under nitrogen in a 100-ml flask attached to a gas buret. The flask was heated at 200° for 24 hr, then cooled to room temperature. Gas evolution amounted to 2 mmol at this point. Ethanol (2 ml) was added and an additional 17.4 mmol of gas was evolved. Alkaline hydrogen peroxide oxidation of the ethanolysis mixture yielded *cis*-1,5-cyclooctanediol, plus a small amount of an unidentified material. Similar tests were made in the presence of tetradecane (60 mmol) and naphthalene (60 mmol) with comparable results.

A sample of 9-BBN, which had been stored under nitrogen for over 2 years at room temperature, was opened. The melting point (151–153°) was unchanged. Similarly, a solution of 9-BBN in THF (0.67 *M*), which had been stored under nitrogen at room temperature for 2.5 years, retained greater than 98% of its hydride activity.

Reactions of 9-BBN with Alcohols. A 100-ml flask with an injection port was equipped with a magnetic stirring bar and attached to a gas buret. The flask was charged with 1.22 g (10 mmol) of 9-BBN and 25 ml of THF. The alcohol, methanol, *tert*-butyl alcohol, or tri-*n*-butylcarbinol (2.5 mmol) was then added *via* syringe. The theoretical amount of hydrogen (>98%) was obtained in each case. The times required for complete evolution were: methanol (10 min), *tert*-butyl alcohol (30 min), tri-*n*-butylcarbinol (30 min). Similar results were obtained with other simple alcohols (ethanol, 1-butanol, triethylcarbinol).

Reactions of 9-BBN with Sterically Hindered Phenols. (a) 2,6-Diisopropylphenol. A 100-ml flask with an injection port was equipped with a magnetic stirring bar and a reflux condenser leading to a gas buret. The flask was charged with 1.88 g (15.4 mmol) of solid 9-BBN and 8 ml of THF. To the stirred 9-BBN solution was added 2.74 g (15.4 mmol) of 2,6-diisopropylphenol. The theoretical amount of hydrogen (106%) was evolved in 20 min.

(b) 2,6-Di-*tert*-butyl-4-methylphenol (BHT). A 100-ml flask was charged with 11.7 g of 9-BBN (97 mmol), equipped with a magnetic stirring bar and a reflux condenser, and attached to a gas meter. After flushing the apparatus with nitrogen, 21.2 g of BHT (97 mmol) was added in ∼30 ml of THF. The reaction mixture was stirred for 30 min at room temperature, then heated under reflux for 14 hr. No hydrogen evolution was observed. The solvent was removed under reduced pressure, and the reactants were heated as a melt at 145° for 21 hr. Still, no hydrogen was evolved. The mixture was cooled to 50°, and 10 ml of THF was added. Then, 17.1 g (96 mmol) of 2,6-diisopropylphenol was added dropwise. The evolution of hydrogen was complete (>98%) 15 min after the phenol had been added.

Hydroboration of Olefins with 9-BBN in THF. (a) Rate Studies. A 50-ml flask with an injection port was fitted with a magnetic stirring bar and a gas inlet tube connected to a nitrogen source. The flask was charged with 10.0 ml of a 0.5 *M* solution of 9-BBN

(5 mmol) in THF and brought to the indicated reaction temperature. The olefin (5 mmol) and an appropriate *n*-alkane (0.5 ml as internal standard) were then added as 2.5 ml of a THF solution. Samples were removed periodically, injected into a vial containing methanol to destroy residual hydride, and analyzed for unreacted olefin by glpc (6 ft × ⅛ in., 20% adiponitrile on 100–120 mesh Varaport 30, or 6 ft × ⅛ in., 10% SE-30 on 100–120 mesh Chromosorb W-AW-DMCS). The results are summarized in Table II.

(b) Product Studies. The hydroborations were carried out as above. After allowing sufficient time for complete reaction, the organoboranes were oxidized by adding, successively, 3 ml of ethanol, 1 ml of 6 *N* NaOH, and 2 ml of 30% hydrogen peroxide. The mixture was heated for 1 hr at 50°, then cooled to room temperature. The aqueous layer was saturated with potassium carbonate. The organic layer was separated, dried over anhydrous potassium carbonate, and analyzed by glpc (6 ft × ⅛ in., 10% Carbowax 400 on 100–120 mesh Varaport 30 or 1.5 in. × ⅛ in., 10% Carbowax 20M on 100–120 mesh Chromosorb W-AW-DMCS). The yields of alcohols obtained are given in Table III.

Hydroboration of Olefins with 9-BBN in Benzene and Hexane Solutions. Stock solutions of 9-BBN were prepared in benzene (0.73 *M*) and in hexane (0.38 *M*) by dissolving the solid reagent. The solutions were standardized by measuring the hydrogen evolved upon methanolysis. A 50-ml flask with an injection port was equipped with a magnetic stirring bar and a reflux condenser connected to a low pressure (mercury bubbler) nitrogen source. The flask was charged with 5 mmol of 9-BBN in the appropriate solvent and heated to reflux. The olefin (5.5 mmol) and a suitable *n*-alkane (0.5 ml as internal standard) were then added. In general, the olefins were added neat, *via* syringe. The solid olefin, norbornene, was dissolved in a small amount of the solvent and added as the solution. After heating under reflux for the indicated time period, the organoboranes were oxidized by adding, successively, 3 ml of ethanol, 1 ml of 6 *N* NaOH, and 2 ml of 30% H₂O₂. The mixtures were heated at 50° for 1 hr to ensure complete oxidation, then cooled to room temperature. The aqueous layer was saturated with potassium carbonate. The organic layer was separated and the aqueous layer was washed with 5 ml of solvent. The combined organic layers were dried over anhydrous potassium carbonate and analyzed for alcohols by glpc (6 ft × ⅛ in., 10% Carbowax 400 on 100–120 mesh Varaport 30 or 1.5 in. × ⅛ in., 10% Carbowax 20M on 100–120 mesh Chromosorb W-AW-DMCS). The results are summarized in Table IV.

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Chemistry of Benzenesulfinyl Azides. Reactions with Sulfoxides[1]

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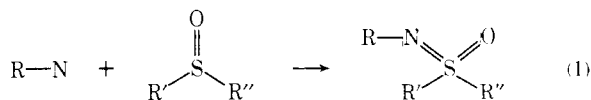
Abstract: The preparation and decomposition of some benzenesulfinyl azides are reported. They undergo ready first-order decomposition with loss of nitrogen to give products which generally are consistent with a dipolar sulfinylnitrene intermediate. Unlike carbonyl and sulfonyl azides, the benzenesulfinyl azides do not undergo the Curtius rearrangement or react with C–H bonds. In unreactive solvents like 1,2-dimethoxyethane and acetonitrile, the sulfinyl azide reacts with itself. Sulfinyl azides react with dipolar and nucleophilic compounds to give products which are quite unlike those obtained from carbonyl and sulfonyl azides. The reactions of benzenesulfinyl and p-toluenesulfinyl azides with dimethyl, diphenyl, methyl phenyl, and methyl p-tolyl sulfoxides yield sulfimide products rather than sulfoximides. The stereochemistry of the reaction was investigated with optically active methyl p-tolyl sulfoxide to give a sulfimide possessing a high degree of retention of configuration. Sulfinylsulfoximides were excluded as intermediates in the reaction. The evidence supports a mechanism where a delocalized sulfinylnitrene intermediate combines with sulfoxide via a 1,2-dipolar cycloaddition.

The organic chemistry of the azido group has been reviewed extensively in recent years,[2-5] and, with the exception of sulfonyl azides, very little has been reported on the chemistry of the azido group bonded to sulfur. Attempts to isolate sulfenyl azides have been unsuccessful.[6] Benzenesulfinyl azide was first proposed as an intermediate in the deoxygenation reaction of benzenesulfonyl azide by triphenylphosphine in acetonitrile or chloroform.[7] Purrington[8] and Kobayashi and Yamamoto[9] independently attempted the preparation of p-toluenesulfinyl azide but were not able to isolate it without decomposition.

Furthermore, nitrene and nitrenoid intermediates have often been proposed for azide decomposition reactions, for which sulfoxides have been perhaps the most effective of trapping reagents. In every case, the sulfoxide adduct has been a sulfoximide. Photolysis or thermolysis of acyl[10-12] or sulfonyl azides[10,11] and azidoformates[13] normally gives low yields of sulfoximides, and probably involves free nitrenes. The copper-catalyzed reaction of sulfonyl azides with sulfoxides proceeds in high yields but involves complexation of the reactants.[14,15]

Other important routes to sulfoximides include reactions of sulfoxides with (1) N-aminolactams[16,17] or sulfonamides[18] and lead tetraacetate, (2) sulfonoxy sulfonamides

and triethylamine,[19] (3) chloramine-T[20] at 140° or chloramine-B[21] and copper at 80°, (4) hydrazoic acid and sulfuric acid in a Schmidt reaction,[22,23] (5) 3-substituted 1,4,2-dioxazolidin-5-ones[24] at 150°, or (6) trityl thionitrite by deoxygenation with triphenylphosphine.[25] The general reaction illustrated in eq 1 depicts a nitrene mechanism as a unifying scheme; however, no statement regarding the exact mechanism is intended.

$$R\text{—}N \quad + \quad \underset{R'}{\overset{O}{\underset{\|}{S}}}\text{—}R'' \quad \longrightarrow \quad \underset{R'}{\overset{R\text{—}N}{\underset{}{S}}}\underset{R''}{\overset{O}{}} \qquad (1)$$

Previously, no sulfinyl azide had been isolated. Therefore, our objectives in this study were to prepare them and determine how they compared with other acyl azides. Particular objectives were to determine whether thermal decomposition of sulfinyl azides led to a Curtius rearrangement or intermolecular nitrene reactions. Sulfoxides were chosen as trapping reagents because of their prior effectiveness with other nitrenes.

Results

Preparation of Sulfinyl Azides. Sulfinyl azides were pre-