# Hydroboration. 49. Effect of Structure on the Selective Monohydroboration of Representative Conjugated Dienes by 9-Borabicyclo[3.3.1]nonane

Herbert C. Brown,* Ronald Liotta,[1] and Gary W. Kramer[2]

*The Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907*

The exceptionally high sensitivity toward structure exhibited by 9-borabicyclo[3.3.1]nonane (9-BBN) in the hydroboration of simple olefins and nonconjugated dienes carries over to conjugated dienes with one major difference. Conjugation markedly decreases the reactivity of the system toward hydroboration. For example, a nonconjugated diene, such as 1,4-hexadiene, is selectively hydroborated by 9-BBN in the presence of a related conjugated diene, such as 1,3-pentadiene. Moreover, this deactivation of the system by conjugation often causes the second stage of the hydroboration to be considerably faster than the first, making it difficult to control the reaction to achieve monohydroboration. Thus, treatment of 1,3-butadiene with 9-BBN in a 1:1 molar ratio gives approximately 50% residual 1,3-butadiene and 50% of the 1,4-diborabutane derivative. On the other hand, in cases where the two olefinic centers of the diene possess structures which differ considerably in reactivity toward 9-BBN, clean monohydroboration can be achieved. Thus, *trans*-1,3-pentadiene is readily converted into the monohydroboration product, *B*-(*trans*-3-penten-1-yl)-9-BBN. In certain dienes, the initial reaction product is the allylic, rather than the more usual homoallylic, derivative. In such cases, 1,3-cyclohexadiene and 2,5-dimethyl-2,4-hexadiene, the reaction is more easily controlled to achieve monohydroboration. A knowledge of the relative reactivities of simple olefin structures is helpful in predicting and rationalizing the behavior of these conjugated dienes toward hydroboration with 9-BBN.

In previous studies, it has been pointed out that 9-borabicyclo[3.3.1]nonane (9-BBN) is an interesting hydroboration agent which exhibits unusual regio-[3] and stereospecificity[4] and remarkable sensitivity to the structures of olefins.[5] With such valuable characteristics, it appeared appropriate to examine the utility of this reagent for the hydroboration of representative nonconjugated dienes,[6] conjugated dienes (present study), allenes,[7] and acetylenes.[8]

The study of the hydroboration of representative nonconjugated dienes[6] established that the relative reactivities of simple olefinic structures toward hydroboration with 9-BBN[5] could be carried over to predict reliably the course of the reaction. Such regularity greatly facilitates applying hydroboration of nonconjugated dienes with 9-BBN as a synthetic route in organic synthesis. Consequently, we undertook a study of the hydroboration of conjugated dienes by 9-BBN in order to ascertain whether these structures would reveal a similar regular pattern of reactivity.
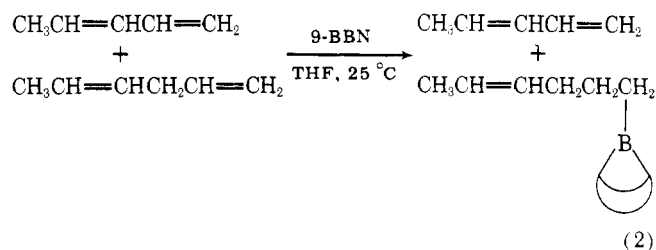
## Results and Discussion

The reaction procedure was identical to that used for the nonconjugated dienes.[6] It involved the addition of a standard solution of 9-BBN in tetrahydrofuran (THF) to an equivalent amount of the diene. The reaction mixture was 0.5 M in each component. An internal standard suitable for GC analysis was introduced. The reaction was allowed to proceed to completion, usually at 25 °C. The reaction product was then oxidized with alkaline hydrogen peroxide in the usual manner.[9] GC examination for residual diene was used to establish the extent of monohydroboration (0% diene = 100% monohydroboration; 50% diene = 0% monohydroboration). The mono-ol and diol products revealed the point or points of attack. In some cases, prior to the oxidation the boron intermediate was treated with acetone to convert reactive allylic 9-BBN derivatives to alcohol derivatives suitable for GC analysis.[13]

**Symmetrical Acyclic Conjugated Dienes.** The reaction of 9-BBN with a symmetrical nonconjugated diene, such as 1,5-hexadiene, in a 1:1 molar ratio proceeds in an essentially statistical manner, giving approximately 25% residual diene, 50% monohydroboration product, and 25% dihydroboration product.[6] However, a conjugated diene, 1,3-butadiene, behaves quite differently. Here the reaction product consists of equal amounts of residual diene and 1,4-dihydroboration product (eq 1).



$$H_2C=CHCH=CH_2$$

$$\text{THF, 0–25 °C} \quad | \quad \text{9-BBN}$$

(1)

48%          48%          trace (<0.1%)
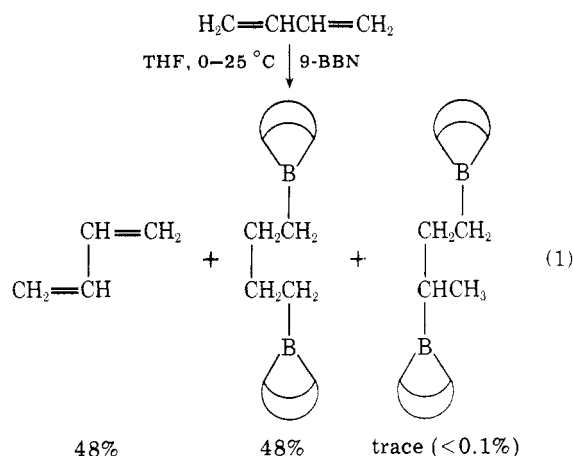
It was observed previously that conjugation in dienes greatly decreases their reactivity towards hydroboration, either by diborane[10] or by disiamylborane.[11] The results with 1,3-butadiene are consistent with such a deactivating conjugation. Thus, the first hydroboration should produce *B*-(3-buten-1-yl)-9-BBN. Here the homoallylic double bond should possess a reactivity comparable to that of 1-butene, far more reactive than the conjugated double bonds of the parent diene. Accordingly, the second stage should be much faster than the first stage, and the dihydroboration product will dominate (eq 1).

In order to test this interpretation, we undertook a competitive hydroboration of an equimolar mixture of a nonconjugated diene, 1,4-hexadiene (cis and trans), and a related conjugated diene, *cis*-1,3-pentadiene, with 1 equiv of 9-BBN (eq 2). Nearly all of the *cis*-1,3-pentadiene remained uncon-



$$CH_3CH=CHCH=CH_2$$
$$+$$
$$CH_3CH=CHCH_2CH=CH_2$$

$$\xrightarrow[\text{THF, 25 °C}]{\text{9-BBN}}$$

$$CH_3CH=CHCH=CH_2$$
$$+$$
$$CH_3CH=CHCH_2CH_2CH_2$$

(2)

sumed in the reaction mixture following utilization of the 9-BBN. Following oxidation of the product, GC examination

revealed only a trace amount of cis-3-penten-1-ol attributable to the hydroboration of cis-1,3-pentadiene (see below).

1,4-Diphenyl-1,3-butadiene, representative of dienes with even more extensive conjugation, proved to be remarkably resistant toward hydroboration with 9-BBN. An equimolar solution of 9-BBN and this diene failed to react to any significant extent, even after 12 days in refluxing THF. Analysis of the reaction mixture revealed the presence of 85% residual diene with only 15% of dihydroborated derivatives (not identified) (eq 3).
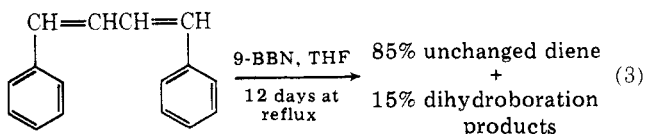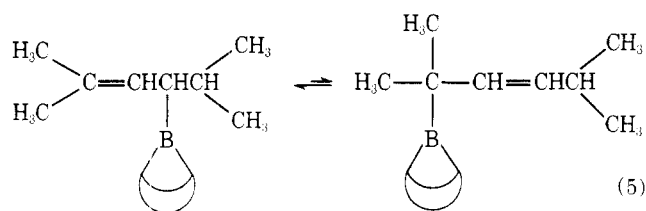


On the other hand, the hydroboration of 2,5-dimethyl-2,4-hexadiene with 9-BBN proceeds relatively rapidly to the monohydroboration product (eq 4). It should be noted that
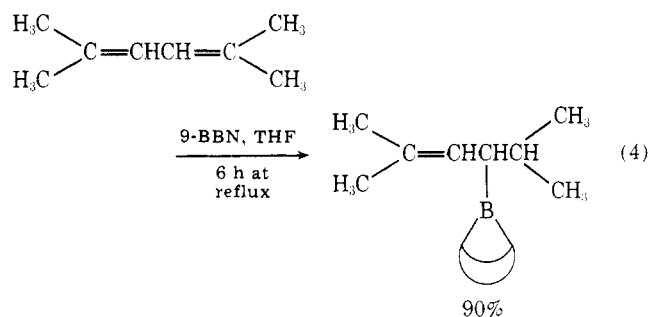


in this case the influence of the geminal methyl groups directs the boron atom to the allylic position, in contrast to the homoallylic position taken by 9-BBN in the initial hydroboration of 1,3-butadiene. Possibly the large steric requirements of the 9-BBN moiety in the allylic position resists a second hydroboration which would place a second 9-BBN moiety in the adjacent, relatively crowded position.

It is probable that the allylic boron intermediate is in equilibrium with its isomer (eq 5). However, it would be an-



ticipated that the boron atom would prefer to be attached to the secondary rather than the tertiary center, so that the product would consist predominantly of the secondary isomer.[12] Indeed, oxidation with alkaline hydrogen peroxide gives the corresponding secondary alcohol, 2,5-dimethyl-4-hexen-3-ol. On the other hand, acetone reacts with allylic rearrangement to produce 2,3,3,6-tetramethyl-4-hepten-2-ol in 80% yield (eq 6).[13]
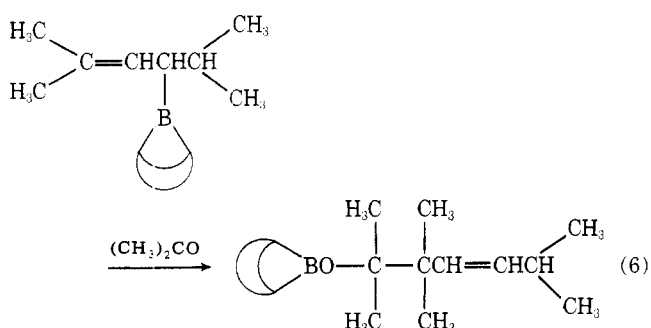


The hydroboration of the related isomeric 2,4-hexadienes is more complex and discussion of these results will be deferred until later in the paper.

**Symmetrical Cyclic Conjugated Dienes.** 1,3-Cyclopentadiene is readily monohydroborated by disiamylborane[11] or by diisopinocampheylborane[14] to give the homoallylic derivatives (eq 7). Unfortunately, hydroboration with 9-BBN
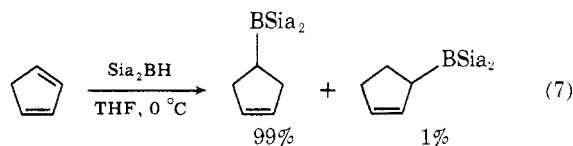


is slower, and dimerization of the 1,3-cyclopentadiene competes with the hydroboration, yielding complex products.

On the other hand, hydroboration of 1,3-cyclohexadiene proceeds smoothly to the monohydroboration stage. In agreement with this result, tests revealed that in the reaction with 9-BBN under identical conditions, 1,3-cyclohexadiene is indeed more reactive than cyclohexene. For example, 1,3-cyclohexadiene reacts completely with 1 equiv of 9-BBN in 6 h at 5 °C, whereas the corresponding reaction with cyclohexene is only 88% complete in 24 h.[3]

Either conjugation between the two double bonds is much less effective in 1,3-cyclohexadiene than in 1,3-butadiene in deactivating the system toward hydroboration, or the unusual inertness of cyclohexene toward hydroboration[3,5] is responsible for this capability exhibited by the reaction to stop at the monohydroboration stage. The product of the reaction is exclusively the allylic derivative, with none of the homoallylic derivative detected (eq 8).
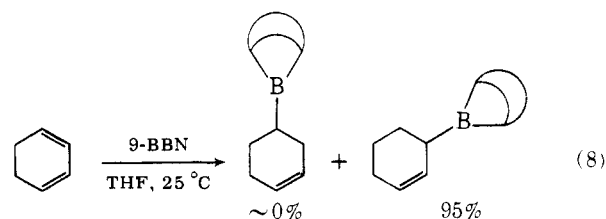


It was previously suggested that this difference in the position taken by boron in the hydroboration of 1,3-cyclopentadiene and 1,3-cyclohexadiene with disiamylborane might be the result of differences in the steric requirements of the planar C-5 ring and the puckered C-6 ring.[11] The same explanation may be utilized for 9-BBN.

In the case of 2,5-dimethyl-2,4-hexadiene, discussed earlier, the directive influence of the terminal methyl substituents directs the 9-BBN moiety to the allylic position (eq 4). Here the reaction can also be controlled to yield the monohydroboration product predominantly. It was suggested that further hydroboration would be resisted since it would place the second 9-BBN moiety in the crowded adjacent position. Possibly the same explanation may hold for the cyclohexenyl intermediate (eq 8). Irrespective of the precise explanation of the phenomenon, the fact is that the reaction readily proceeds cleanly to give the allylic derivative. Such allylic derivatives are quite reactive, readily adding to the carbonyl group of aldehydes and ketones.[13]

Recently, we had occasion to synthesize a series of tertiary alcohols with the structure 1-aryl-1-($\Delta^2$-cyclohexenyl)ethanol. Apparently, it is not feasible to convert 1-chloro- or 1-bromo-2-cyclohexene into the corresponding Grignard reagents. The synthesis was successfully accomplished by treating the corresponding acetophenone derivatives with the 9-BBN adduct (eq 9).[15]

In contrast to the behavior of 1,3-cyclohexadiene, 9-BBN reacts with 1,3-cyclooctadiene to give predominantly dihy-

(9)
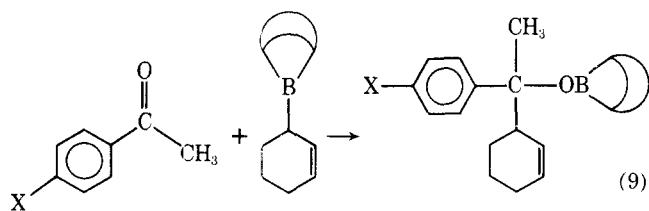
droboration products (not characterized). Thus, the second stage must be considerably faster than the first (eq 10).



(10)

45%      50%
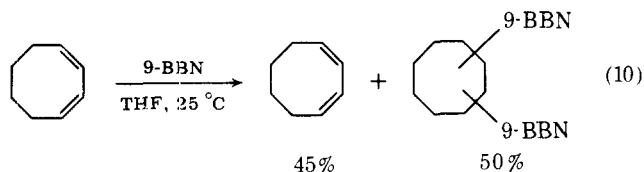
This behavior contrasts with that of the nonconjugated 1,5 derivative. Here the monohydroboration product is readily synthesized[6] (eq 11).



(11)

85%
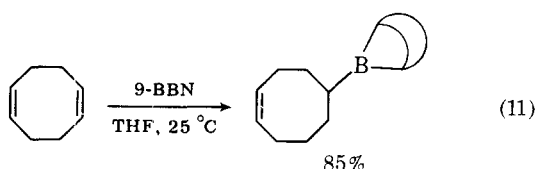
**Unsymmetrical Acyclic Conjugated Dienes.** Unlike 1,3-butadiene, the next higher homologues, *cis-* and *trans-* 1,3-pentadiene, are readily converted into the corresponding monohydroboration derivatives (eq 12, 13).



95%      (12)



85%      (13)
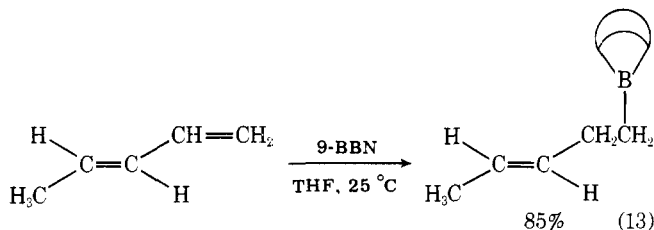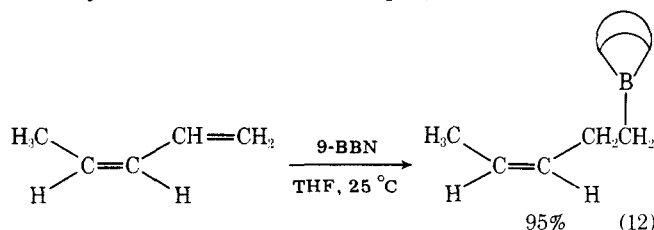
A simple terminal olefin is considerably more reactive toward 9-BBN than a related internal olefin. Thus, 1-hexene is about 100 times as reactive as *cis*-2-pentene.[6] This decreased reactivity of internal olefins is evidently sufficient to allow satisfactory yields of the monohydroboration products (eq 12, 13).

Similarly, 5,5-dimethyl-1,3-hexadiene undergoes clean conversion to the monohydroboration product (eq 14).



(14)

99%
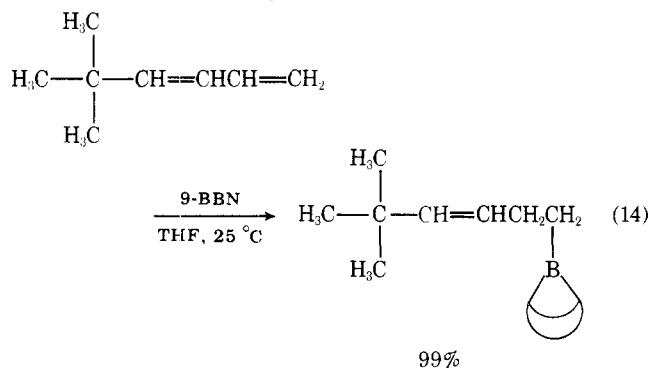
Isoprene, which undergoes significant monohydroboration with disiamylborane,[11] does not do so with 9-BBN (eq 15).



(15)

(50%)      46%
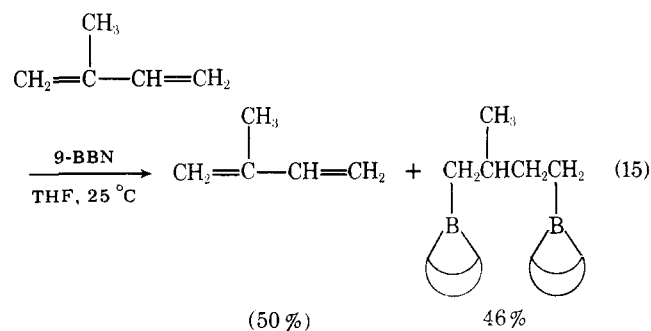
Evidently, this is a consequence of the difference in the behavior of the two reagents toward the structures $RCH=CH_2$ and $RC(CH_3)=CH_2$. Disiamylborane is far more reactive towards the former than the latter, whereas 9-BBN is actually somewhat more reactive towards the 2-methyl-1-alkene structure.[6]

With *gem*-dimethyl substituents introduced into the 4 position of the isoprene molecule, monohydroboration again becomes feasible (eq 16).



(16)

99%
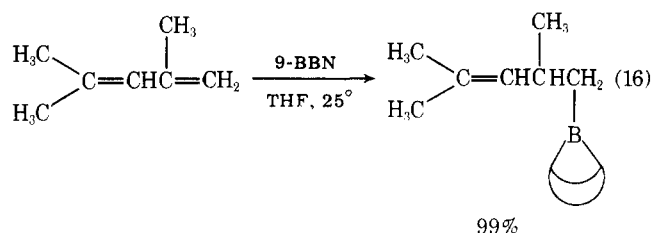
**The 2,4-Hexadienes.** The hydroboration of the isomeric 2,4-hexadienes exhibits both interesting features and complexities which make it desirable to consider them as a separate group.

In the case of 1,3-butadiene, the monohydroboration product is evidently the homoallylic product, which is rapidly consumed by a second hydroboration to give the 1,4-dibora-butane derivative (eq 1). On the other hand, the monohydroboration of 2,5-dimethyl-2,4-hexadiene proceeds to place



34%   66%          42%   58%
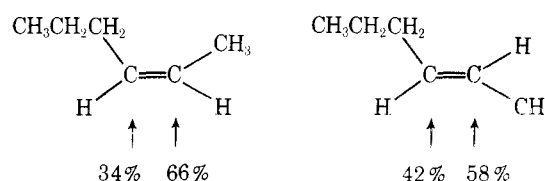
the boron in the allylic position (eq 4) with little dihydroboration. The structure of 2,4-hexadiene is halfway between these two extremes, and the hydroboration exhibits features common to both.

The reaction of 9-BBN with *cis-* and *trans*-2-hexene proceeds to place boron at both C-2 and C-3. Accordingly, it was anticipated that the monohydroboration of *cis,cis-*, *cis,trans-*, and *trans,trans*-2,4-hexadiene with 9-BBN would produce both the allylic and homoallylic 9-BBN derivatives (eq 17). The *B*-allyl-9-BBN component would undergo the usual fast allylic rearrangement,[12,13] providing an equilibrium mixture of the two allylic boranes (eq 17).

Unlike the previously discussed case of 2,5-dimethyl-2,4-hexadiene, the monohydroborated products from 2,4-hexadiene should readily react further with 9-BBN since the remaining double bonds are not highly sterically encumbered.

### Table I. Monohydroboration of 2,4-Hexadienes with 9-BBN[a]

| Isomer | Registry no. | Solvent | Residual diene,[b] % | Allylboranes, % | | | Diols,[c] % |
| | | | | Total | I + III[h,i] | II + IV[h,j] | |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Cis,cis | 6108-61-8 | Pentane[d] | 30[f] | 36 | 60 | 40 | 36 |
| Cis,cis | | THF[e] | 19[g] | 41 | 60 | 40 | 33 |
| Trans,trans | 5194-51-4 | Pentane[d] | 33[f] | 16 | 60 | 40 | 50 |
| Trans,trans | | THF[e] | 23[g] | 19 | 60 | 40 | 45 |
| Cis,trans | 5194-50-3 | THF[e] | 18[g] | 29 | 60 | 40 | 43 |

[a] Registry no.: 9-BBN, 280-64-8. [b] Residual diene isomer was identical to starting diene isomer. [c] 2,4-Hexanediol was the major component (>90%) in each case; diols were analyzed as bis(TMS) derivatives. [d] Reaction time, 10 days. [e] Reaction time, 55.5 h. [f] Analysis before oxidation. [g] Analysis after oxidation; some diene probably lost during oxidation. [h] See eq 18; allylboranes analyzed as their acetone derivatives. [i] Equal amounts of product from I and III were found. [j] Equal amounts of product from II and IV were found.
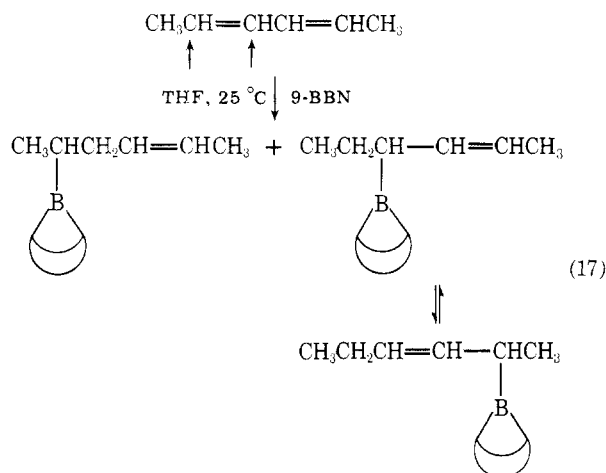


Assuming that a significant amount of allylborane is formed, the permanent allylic rearrangement should result in a mixture of four isomers (two cis/trans pairs) (eq 18). In
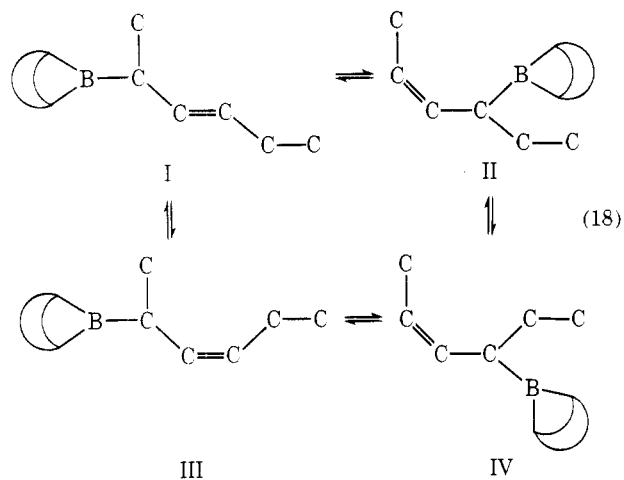


such equilibrium mixtures, boron generally prefers the least hindered position.[12] Consequently, we would expect that I and III will predominate in the mixture since in these isomers boron is flanked by a methyl group instead of an ethyl group. However, the difference in steric requirements of methyl, in I or III, vs. ethyl, in II or IV, is not large; the preference for I and III should not be great. If the permanent allylic rearrangement is important, the same isomer distribution of allylboranes, or their derivatives, should be found irrespective of which isomer of 2,4-hexadiene is hydroborated.

On the other hand, the amount of homoallylic derivative formed should depend somewhat on the particular isomer of 2,4-hexadiene hydroborated. Accordingly, we examined the hydroboration of all three isomeric 2,4-hexadienes. The cis,cis- and trans,trans isomers were hydroborated in pentane with 9-BBN, and all three isomers were hydroborated in THF with

the reagent. Following completion of the hydroborations, the reaction products were first treated with excess acetone to convert the allylic boranes into the corresponding tertiary alcohol derivatives[13] and then oxidized with alkaline hydrogen peroxide to convert any homoallylic product into the corresponding homoallylic alcohol.[9] The experimental results are summarized in Table I.

With one exception, the results are in good agreement with expectations based upon the considerations presented. Dihydroboration is competitive with monohydroboration. The product distribution depends upon the particular diene used. However, the same mixture of allylboranes is formed from the three isomers. The products derived from I and III are found in larger amounts (~60%, 50% from I and 50% from III) than those from II and IV (~40%, 50% from II and 50% from IV).

Unexpectedly, no homoallylic alcohol was found in the oxidized products. This means that the initial hydroboration product does not contain a significant amount of the homoallylic 9-BBN derivative (eq 17). Possibly the −I inductive effect of the double bond is sufficient to direct the boron atom preferentially into the allylic, rather than the homoallylic, position. Such a directive effect has been observed previously. Thus, Zweifel and Polston reported that conjugated diynes exhibit a similar directive influence in hydroboration with either disiamylborane or dicyclohexylborane[16] (eq 19). The corresponding enyne exhibits a similar directive effect[16] (eq 20).
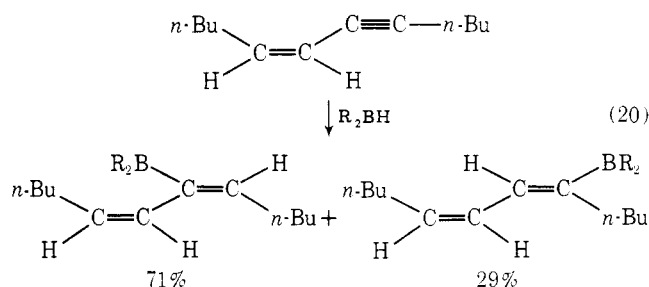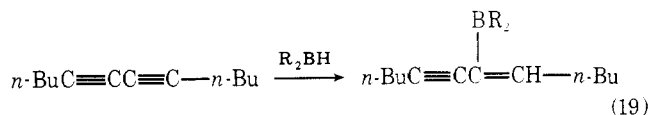


Superimposed on this directive influence favoring the formation of the allylic isomer in the monohydroboration product may be a reactivity factor, favoring the further hydroboration of the homoallylic derivative over the allylic isomer.

The diol formed is predominantly (>90%) the 2,4-hexanediol, accompanied by only a small amount of the 2,5 isomer. This would appear to require that the allylic isomers (eq 18) must resist hydroboration to place the two 9-BBN moieties in adjacent positions.

Another puzzling feature is the relative reactivities. In the reaction with 9-BBN, trans olefins are more reactive than cis.[5]

**Table II. Hydroboration–Oxidation Product Distribution in the Reaction of Conjugated Dienes with One Equivalent of 9-BBN (0.5 M) in THF at 25 °C**

| Diene | Registry no. | Residual diene,[a] % | Unsaturated alcohols (%) | Diols,[b] % |
|---|---|---|---|---|
| 1,3-Butadiene | 106-99-0 | 48 | Trace | 48 |
| 1,4-Diphenyl-1,3-butadiene | 886-65-7 | 85 | | ~15[c] |
| 2,4-Hexadiene[d] | | 18–33 | Isomeric allylic derivatives (16–41) | 33–50 |
| 2,5-Dimethyl-2,4-hexadiene | 764-13-6 | 4 | 2,5-Dimethyl-4-hexen-3-ol (90) | |
| 1,3-Cyclohexadiene | 592-57-4 | Trace | 2-Cyclohexen-1-ol (85) | 5[e] |
| 1,3-Cyclooctadiene | 1700-10-3 | 45 | | 50[e] |
| *cis*-1,3-Pentadiene | 1574-41-0 | Trace | *cis*-3-Penten-1-ol (95) | 3 |
| *trans*-1,3-Pentadiene | 2004-70-8 | 5 | *trans*-3-Penten-1-ol (85) | 8 |
| 2-Methyl-1,3-butadiene | 78-79-5 | 50[f] | 2-Methyl-3-buten-1-ol (7.4) | 46 |
| | | | 3-Methyl-3-buten-1-ol (3.7) | |
| 5,5-Dimethyl-1,3-hexadiene | 1515-79-3 | 0 | 5,5-Dimethyl-3-hexen-1-ol (99) | 0 |
| 2,4-Dimethyl-1,3-pentadiene | 1000-86-8 | Trace | 2,4-Dimethyl-3-penten-1-ol (99) | 0 |

[a] Analysis after oxidation with alkaline hydrogen peroxide. [b] Based on diene. [c] Not isolated or identified (see Experimental Section). [d] Data for isomeric 2,4-hexadienes. [e] Unresolved mixture of isomers. [f] Estimated by difference.

Yet the evidence is that the *cis,cis*-2,4-hexadiene is considerably more reactive than the *trans,trans*-2,4-hexadiene. The former reached a constant concentration (completion of reaction) within 48 h, whereas the latter required several days. Perhaps the higher reactivity arose from the lesser conjugation in the cis,cis structure, where steric interactions of the terminal methyl groups could affect the planarity of the π system. Such interactions would be absent in the trans,trans isomer.

These results for the hydroboration of 2,4-hexadienes with 9-BBN establish that it is not useful for synthetic applications. However, the system is of considerable interest theoretically, and further study is desirable to establish the precise course of the reaction and to provide a better understanding of the experimental observations.

## Conclusion

For convenience, the results are summarized in Table II.

The hydroboration with 9-BBN of conjugated dienes exhibits certain characteristics which offer promise for applying this reaction to achieve the synthesis of desired boron intermediates and to apply those intermediates for synthetic purposes. Thus, conjugation frequently reduces the reactivity of dienes to the point where it is often feasible to hydroborate a nonconjugated double bond in the presence of a conjugated diene moiety.

Certain symmetrical conjugated dienes, such as 2,5-dimethyl-2,4-hexadiene and 1,3-cyclohexadiene, can be monohydroborated to give the corresponding allylic derivatives. However, others, such as 1,3-butadiene and 1,3-cyclooctadiene, afford dihydroborated products.

In the case of unsymmetrical dienes, it is possible to take advantage of substantial differences in the reactivities of the two olefin moieties constituting the diene to achieve monohydroboration at the more reactive site. Thus, unsymmetrical dienes, such as 1,3-pentadiene, 5,5-dimethyl-1,3-hexadiene, and 2,4-dimethyl-1,3-pentadiene, are readily monohydroborated with 9-BBN to yield the homoallylic 9-BBN derivatives.

Such homoallylic and hindered allylic 9-BBN derivatives can be oxidized to the corresponding alcohols[9] or utilized for the many reactions which organoboranes undergo.[9] In addition, the allylic 9-BBN derivatives can be utilized for additions to the carbonyl groups of aldehydes, ketones, and other carbonyl derivatives.[13]

It follows that the selective hydroboration with 9-BBN of dienes, both conjugated and nonconjugated,[6] provides a valuable entry to the conversion of such dienes into synthetically valuable intermediates.

## Experimental Section

**General Comments.** In general, the techniques described in Chapter 9 of ref 9 were employed. All glassware, syringes, and needles were oven-dried at 150 °C for 4 h before use, assembled hot, and cooled under a stream of prepurified nitrogen. Syringes were assembled and fitted with needles while hot and then cooled as assembled units. They were flushed with nitrogen immediately before use. All reactions were stirred magnetically and were carried out under a static pressure of nitrogen.

**Materials.** The *n*-alkanes (Phillips) employed as internal GC standards were used as received. Technical grade pentane was stirred over concentrated sulfuric acid to remove any olefinic impurities, washed with aqueous base, dried over anhydrous magnesium sulfate, and distilled under nitrogen from lithium aluminum hydride. THF was distilled from lithium aluminum hydride prior to use. All conjugated dienes used in this study, except 1,3-cyclooctadiene (Cities Service), were purchased from Chemical Samples Co. and were used after checking their ^{1}H NMR spectra, indices of refraction, and GC analyses. 2,3-Hexanediol and 3,4-hexanediol were synthesized according to known procedures.[17,18] Other diols and alcohols used for identification purposes were either commercial materials, were available from previous studies,[10-13] or were isolated by preparative GC from the oxidized reaction mixtures. 9-BBN (mp 151–153 °C) was prepared and purified, and its solutions were standardized as reported previously.[4,5,9,12]

**Hydroboration of 1,3-Butadiene.** The determination of the stoichiometry of the reaction of 1,3-butadiene with 9-BBN offered difficulties because of the volatility of the diene. A detailed description of the procedure is provided to facilitate the work of others who may wish to do quantitative work in this area. To an oven-dried, nitrogen-flushed, flamed-out, 50-mL flask fitted with a reflux condenser, septum inlet, and magnetic stirring bar was added 9.26 mL of 0.540 M 9-BBN in THF (5.00 mmol) and 0.50 mL of *n*-tridecane (2.05 mmol; standard for GC analysis). The mixture was cooled to 0 °C (with crystallization of 9-BBN). The 1,3-butadiene, Phillips special purity (122.6 mL of gas at 23 °C, 753 mmHg, 5.00 mmol), was bubbled in slowly utilizing a gas-tight syringe.[9] The reaction mixture was allowed to come to room temperature with stirring. After 1 h, GC analysis indicated that the amount of residual diene was constant (48%). After a further 24 h, 0.37 mL of acetone (5.0 mmol) was added to react with any allylic intermediates, and the mixture was stirred for an additional hour. The reaction mixture was then treated with 1.73 mL of 2.89 M aqueous sodium hydroxide (5.0 mmol) and the organoborane intermediates oxidized with 1.8 mL of 34% hydrogen peroxide at 50 °C, maintaining the temperature there for 2 h. Excess potassium carbonate (9.0 g) was added to facilitate recovery of the diols.[10] The THF layer was separated, and the aqueous layer was extracted with THF (3 × 10 mL). The combined extracts were dried over anhydrous magnesium sulfate, followed by crushed 3Å molecular sieves. Samples were analyzed on a HP 5752B gas chromatograph, using a 6 ft × 0.25 in 10% XE-60 column, for ene-ols, including the acetone adduct 2,3-dimethyl-4-penten-2-ol. None were found. An aliquot of the dried extracts, 0.2 mL, was treated with 0.3 mL of BSTFA + 1% trimethylchlorosilane. This was heated for 3 h at 50 °C. The resulting bis(TMS) derivatives of the diols were analyzed on a Perkin-Elmer 226 gas chromatograph on a 150 ft × 0.01 in Golay column coated with OS-138. Only 1,4-butanediol (48%) and *cis*-

1,5-cyclooctanediol (96%), along with a trace (<0.1%) of 1,3-butanediol (as their TMS ethers), were detected.

**Hydroboration of Conjugated Dienes.** The following dienes were hydroborated, oxidized, and analyzed in the same manner: 2,4-dimethyl-1,3-pentadiene, 5,5-dimethyl-1,3-hexadiene, 2,5-dimethyl-2,4-hexadiene, *cis*-1,3-pentadiene, and *trans*-1,3-pentadiene.

**General Reaction Procedure.** An oven-dried, 100-mL flask equipped with a septum inlet, magnetic stirring bar, and reflux condenser was connected to a mercury bubbler. The system was purged with nitrogen and the inert atmosphere maintained until the oxidation stage. Normally, 10.0 mmol of olefin was added via syringe along with 3 mmol of a suitable internal standard. 9-BBN (0.5 M in THF), 10.0 mmol, was added to the reaction flask slowly via syringe. After sufficient time for complete reaction, the mixture was oxidized. Aqueous sodium hydroxide (3 M, 3.3 mL) was injected into the flask followed by the dropwise addition of hydrogen peroxide (30% solution, 3.3 mL) over 10–15 min. The reaction mixture was maintained at 50 °C for 1 h and then cooled to room temperature. The aqueous layer was saturated with anhydrous potassium carbonate, and the organic layer was separated and dried over anhydrous magnesium sulfate. The aqueous layer was extracted with 15 mL of pentane, dried over magnesium sulfate, and combined with the first extract. A small aliquot (~3 mL) was further dried over 3Å molecular sieves and used for GC analyses. Pentane (25–50 mL) was added to the remaining organic fraction to precipitate *cis*-1,5-cyclooctanediol. The pentane was decanted from the diol, which appeared as a viscous oil or a crystalline solid on the bottom of the flask. Preparative gas chromatography (10% XE-60, 5 ft × 0.5 in column) of the organic mixture afforded essentially pure >98% unsaturated alcohol. ^{1}H NMR (Varian T-60) and IR (PE-137 and PE-700) spectra were taken to confirm the structure of the product.

2-Methyl-1,3-butadiene and 1,3-cyclohexadiene were hydroborated and oxidized according to the above general procedure. However, the products were not isolated since authentic samples were available for GC analysis.

1,3-Cyclooctadiene was hydroborated and oxidized following the general procedure described above. Analysis of the oxidation products proved difficult. No conditions were found to effect complete separation of the diols. However, bis(TMS) derivatives were partially resolved into two peaks (10:1 ratio) on a 10% neopentyl glycol adipate (6 ft × 0.25 in) column. The structures of the products were assumed to be cyclooctanediols by comparison of their retention times (usually identical) with that of *cis*-1,5-cyclooctanediol on several columns of differing polarity (10% XE-60, 10% SE-30, 10% DC-710; all 12 ft × ⅛ in). The bis(TMS) derivatives of the cyclooctanediols were prepared as described above for the butanediol mixture.

**Hydroboration–Derivatization of the Isomeric 2,4-Hexadienes.** The isomeric dienes (*cis,cis-*, *cis,trans-*, and *trans,trans-*2,4-hexadienes) were subjected to identical reaction conditions following the general procedure described above up to the oxidation stage. After 55 h in THF, GC analysis showed no further decrease in diene concentration, and then acetone (0.74 mL, 10.0 mmol) was added. The reaction flask became warm with the addition of the acetone. After 1 h, aqueous sodium hydroxide (3 M, 3.3 mL) and hydrogen peroxide (30% solution, 3.3 mL) were added in the usual fashion followed by the normal workup procedure. The TMS derivatives were prepared in the same manner as described previously. GC analyses were performed on a Perkin-Elmer 226 capillary chromatograph using two OS-138 Golay columns in series (two 150 ft × 0.01 in). The TMS derivatives of 2,4-, 2,4-, 2,3-, and 3,4-hexanediol were

easily separated under these conditions. Attempts to separate the isomeric homoallylic alcohols (from the reaction of allylboranes I–IV with acetone) by GC, either directly or as their TMS derivatives, were unsuccessful. However, the use of NMR shift reagents [Eu(fod)$_3$ and Pr(fod)$_3$] allowed the interpretation of the ^{1}H NMR spectrum of the mixture. Product identification was based on splitting patterns and coupling constant data, while quantitation was based on the relative areas of the *gem*-dimethyl signals from the methyl groups nearest the hydroxyl moiety.[19] The product distribution of the reaction is presented in Table I.

**Competitive Hydroboration.** An oven-dried, 100-mL flask equipped with a septum inlet, magnetic stirring bar, and reflux condenser was connected to a mercury bubbler. The system was purged with nitrogen, and the inert atmosphere was maintained until the oxidation stage. *cis*-1,3-Pentadiene (0.645 g, 9.5 mmol) and a cis/trans mixture of 1,4-hexadiene (0.872 g, 10.6 mmol) were added to the flask via syringe. *n*-Nonane (0.499 g, 3.78 mmol) was added as a GC internal standard. 9-BBN, 0.5 M in THF (20.0 mL, 10.0 mmol), was added also via syringe. After 3 h at room temperature, aqueous sodium hydroxide (3 M, 3.3 mL) and hydrogen peroxide (30% solution, 3.3 mL) were added followed by the standard oxidation workup. GC analysis on a 10% SE-30 (12 ft × ⅛ in) column revealed 9.7 mmol of *cis*- and *trans*-4-hexen-1-ol, a trace amount of *cis*-3-penten-1-ol, and 8.9 mmol of *cis*-1,3-pentadiene.

**Hydroboration–Oxidation of 1,4-Diphenyl-1,3-butadiene.** The general reaction procedure was followed. The reaction was allowed to proceed at reflux in THF for 12 days. The reaction mixture was oxidized and worked up in the usual manner. 1,4-Diphenyl-1,3-butadiene, 85% by weight, was isolated unchanged after the reaction. GC analysis on a 10% SE-30 (12 ft × ⅛ in) column revealed a small amount (~15%, based on diene) of material with a high retention time characteristic of a diol. No attempt was made to isolate or further identify this material.

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