# Hydroboration. 46. The Regio- and Stereochemistry of the Hydroboration of Representative Cyclic Olefins with 9-Borabicyclo[3.3.1]nonane

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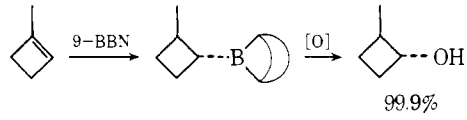
**Abstract:** The hydroboration of cyclic olefins with 9-borabicyclo[3.3.1]nonane (9-BBN) proceeds with exceptionally high regio- and stereoselectivity. Such hydroborations of 1-substituted cycloalkenes cleanly produce the *trans*-2-alkylcycloalkyl-9-BBN. Similarly, treatment of 3- or 4-alkyl substituted, 1,4-dialkyl substituted, or exocyclic olefins with 9-BBN affords predominantly those products arising from addition to the least hindered side of the double bond. For example, 4-*tert*-butylcyclopentene yields *trans*-3-*tert*-butylcyclopentyl-9-BBN (99%), while 4-methylcyclopentene gives 3-methylcyclopentyl-9-BBN (95%). In the hydroboration of 3-methylcyclopentene, as well as 3-methylcyclohexene, no detectable amounts of *cis*-2-methylcycloalkyl-9-BBN adducts are observed. Attack on norbornene occurs solely (99.5%) from the exo direction. In contrast, the addition to 7,7-dimethylnorbornene proceeds almost exclusively (97%) from the endo side. Hydroboration-oxidations of $\alpha$- and $\beta$-pinene give quantitative yields of isopinocampheol and *cis*-myrtanol, respectively. The remarkable selectivity of 9-BBN is compared, when possible, with other hydroborating agents, and plausible explanations are offered to account for the results.

9-BBN exhibits remarkable regioselectivity in the hydroboration of acyclic olefins. Terminal olefins are cleanly converted to the corresponding 1-substituted *B*-alkyl-9-BBN derivatives. Hydroboration-oxidation of 1-hexene with 9-BBN yields 99.9% 1-hexanol.[2] Similarly, internal olefins afford the least sterically hindered *B*-alkyl-9-BBN derivatives. Treatment of *cis*-4-methyl-2-pentene preferentially places boron at the 2 position. Oxidation produces 99.8% 4-methyl-2-pentanol, with only a trace amount of 2-methyl-3-pentanol.[2] In view of this exceptional behavior with acyclic olefins, it seemed desirable to examine the selectivity of 9-BBN toward cycloalkenes. The results of this study are presented in this paper.

## Results and Discussion

**1-Substituted Cycloalkenes.** Small ring 1-methylcycloalkenes are hydroborated quantitatively to produce an organoborane with the boron attached to the less hindered terminal of the double bond. The addition of B-H occurs cis. Consequently, the product from 1-methylcyclobutene and 9-BBN is the *B-trans*-2-methylcyclobutyl-9-BBN (eq 1). Oxidation

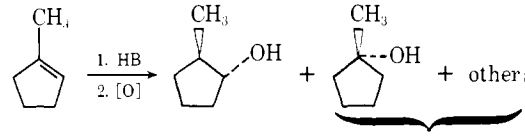



99.9% (1)

with alkaline hydrogen peroxide proceeds with retention[3] to give the corresponding *trans*-2-methylcyclobutanol (eq 1).

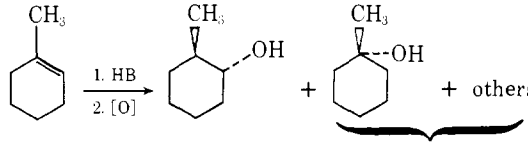
Since the oxidation procedure is a simple quantitative transformation of the organoborane into the corresponding alcohol, readily isolated and identified, we adopted this procedure to establish the stereochemistry of the hydroboration product. The formation of minor amounts of isomeric products in these reactions (eq 2, 3) may be a result of the higher reactivity and lower selectivity of diborane as compared to 9-BBN (in the hydroboration stage).

In contrast to diborane, 9-BBN achieves clean formation of the *trans*-2-methylcycloalkanyl derivatives even in the larger ring olefins (eq 4, 5). On the other hand, hydroboration of 1-methylcyclooctene under normal conditions yields a mixture of organoborane intermediates, oxidized into a mixture of isomeric methylcyclooctanols (eq 5). This difference in the behavior of the diborane and 9-BBN derived intermediates is attributed to the much lower rate of isomerization exhibited by *B*-alkyl-9-BBN.[8]



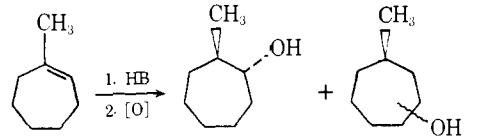

(2)

| | | |
|---|---|---|
| 9-BBN | >99.9% | ~0% |
| $BH_3$[4] | 98.5% | 1.5% |
| $HBCl_2$[5] | >99.8% | <0.2% |



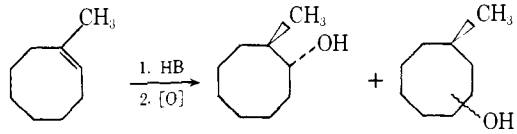

(3)

| | | |
|---|---|---|
| 9-BBN | >99.9% | ~0% |
| $BH_3$[6] | 98.0% | 2% |




(4)

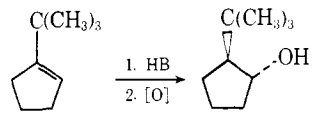
| | | |
|---|---|---|
| 9-BBN | 98% | 2% |
| $BH_3$[6] | 97% | 3% |




(5)

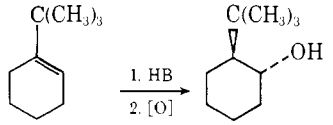
| | | |
|---|---|---|
| 2 h at 25°C 9-BBN | 98% | 2% |
| 5 min at −15°C $BH_3$[7] | 95% | 5% |
| 0.5 h at 0°C $BH_3$[7] | 60% | 40% |
| 2 h at 0°C $Sia_2BH$[7] | 60% | 40% |

The hydroboration of 1-*tert*-butylcyclopentene with 9-BBN produces the trans product stereospecifically (eq 6). Similarly,




9-BBN 99.9% (6)

1-*tert*-butylcyclohexene is also converted into the corresponding trans product (eq 7).

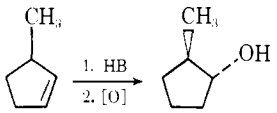



(7)

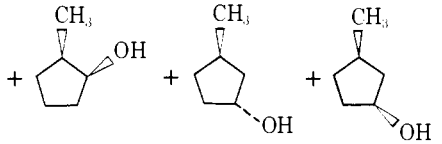
9-BBN 99.9%

It is now possible to prepare *trans*-alkyl-(9-BBN)-cycloalkanes in extremely high isomeric purity, even with highly bulky alkyl groups.

**3-Substituted Cycloalkenes.** The hydroboration of 3-methylcyclopentene with 9-BBN gives the highest regioselectivity of several common boron hydrides (eq 8, 9). Interestingly, no cis 1,2 derivative was observed in the hydroboration with 9-BBN.

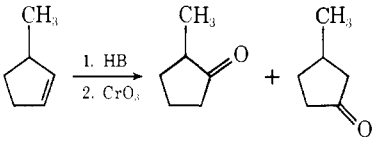



9-BBN 25%




(8)

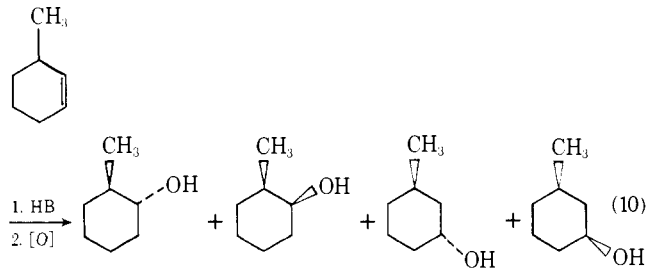
0% 25% 50%




(9)

| | | |
|---|---|---|
| 9-BBN | 22% | 78% |
| $IPC_2BH$[9] | 30% | 70% |
| $Sia_2BH$[10] | 40% | 60% |
| $BH_3$[4] | 45% | 55% |

The hydroboration of 3-methylcyclohexene with 9-BBN results in comparably high regio- and stereoselectivity (eq 10).

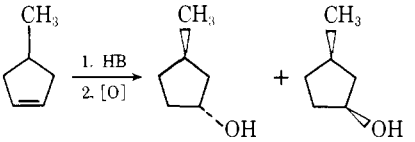



(10)

| | | | | |
|---|---|---|---|---|
| 9-BBN | 20% | 0% | 40% | 40% |
| $Sia_2BH$[11] | 30% | 18% | 25% | 27% |
| $BH_3$[12] | 34% | 16% | 32% | 18% |

As shown by the alcohol products (eq 10), the 9-BBN hydroboration realizes an 80:20 preference for the 3 position in 3-methylcyclohexene over the 2 position. The other two boron hydrides exhibit little or no discrimination between the two terminals of the double bond, in each case giving about 50/50 of the epimeric mixtures of 2- and 3-methylcyclohexanols. No *cis*-2-methylcyclohexanol was obtained from the hydroboration–oxidation reaction with 9-BBN. However, significant amounts of this isomer were produced with the disiamylborane (18%) and with the diborane (16%) hydroboration–oxidation reaction (eq 10).

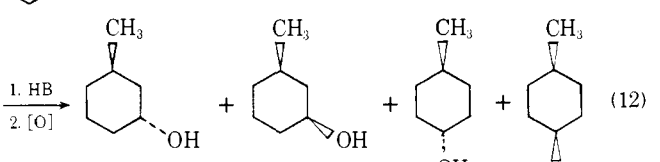
**4-Substituted Cycloalkenes.** The hydroboration of 4-methylcyclopentene with diborane produces largely the trans adduct (83%).[13] The stereoselectivity of the reaction is significantly increased by conducting the hydroboration with 9-BBN (eq 11).




(11)

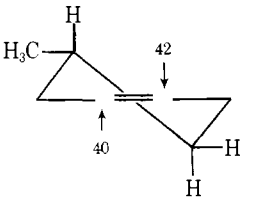
| | | |
|---|---|---|
| 9-BBN | 95% | 5% |
| $BH_3$[13] | 83% | 17% |

The hydroboration of 4-methylcyclohexene with diborane is neither stereoselective nor regioselective (eq 12). All four possible isomeric products are formed in approximately the same amounts. The 9-BBN reaction is likewise not regioselective. There are equal amounts (50/50) of 3- and 4-methylcyclohexanols. However, the hydroboration of 4-methylcyclohexene with 9-BBN is somewhat stereoselective. *trans*-4-Methylcyclohexanol is produced in 42% yield and *cis*-3-methylcyclohexanol is formed in 40% yield. Evidently, attack by boron at the positions shown by arrows (**1**) is favored on steric grounds. The trans-3 and the cis-4 positions are shielded by an axial methine and methylene hydrogen, respectively. Therefore, only slight amounts (~10% each) of *trans*-3-methylcyclohexanol and *cis*-4-methylcyclohexanol are produced.



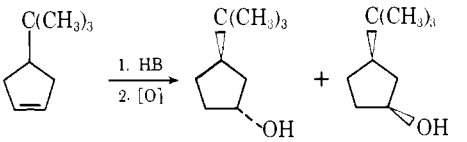

(12)

| | | | | |
|---|---|---|---|---|
| 9-BBN | 10% | 40% | 42% | 8% |
| $BH_3$[15] | 27% | 28% | 25% | 20% |




1

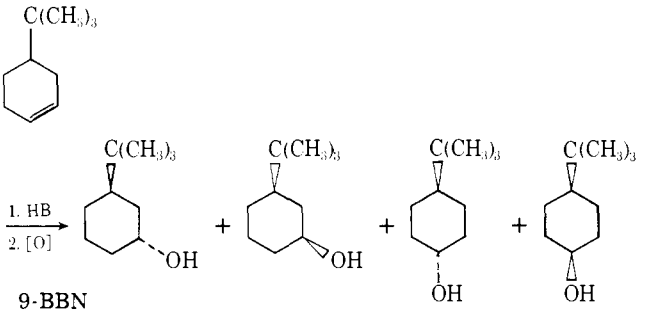
The hydroboration of 4-*tert*-butylcyclopentene with 9-BBN proceeds with high stereospecificity (eq 13), higher than that realized in 4-methylcyclopentene (eq 11). The attack of 9-BBN is from the side opposite to the *tert*-butyl group. Upon oxidation of the organoborane intermediate, *trans*-3-*tert*-butylcyclopentanol is formed.




(13)

9-BBN >99% trace

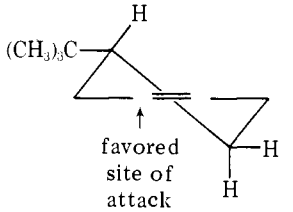
On the other hand, the hydroboration of 4-*tert*-butylcyclohexene with diborane,[12] like that of the 4-methyl analogue, is neither regio- nor stereospecific. However, treatment of this same olefin with 9-BBN, and, to a lesser extent, thexylborane,[12] favors production of one isomer (eq 14). The favored product is the *cis*-3-*tert*-butylcyclohexyl adduct. It is suggested that the *tert*-butyl group forces the hydrogen (bound to C-4) out over the double bond, shielding this side of the molecule from attack by 9-BBN (**2**). Attack on C-1, cis to the 4-*tert*-butyl group, is hindered by the axial methylene hydrogen on



| 9-BBN | | | | |
|---|---|---|---|---|
| $BH_3$[12] | 8% | 62% | 20% | 10% |
| thexyl-borane[12] | 20% | 32% | 25% | 23% |
| | 6% | 52% | 30% | 6% |

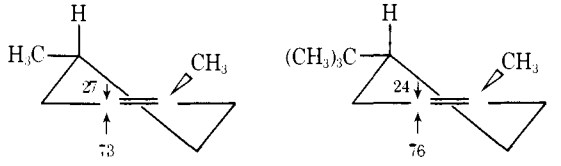
(14)

C-5. This leaves C-2, cis to the 4-*tert*-butyl group, as the preferential site for reaction.



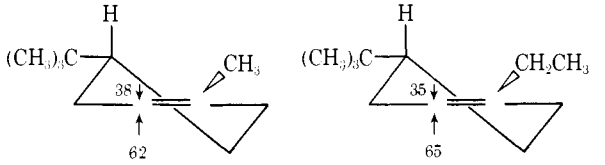
2

**1,4-Disubstituted Cycloalkenes.** The hydroboration of 1,4-dimethylcyclohexene and 1-methyl-4-*tert*-butylcyclohexene with 9-BBN reveals a similar stereoselectivity (**3a,b**).



3a with 9-BBN 3b with 9-BBN

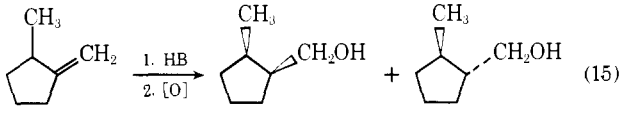
This result is consistent with the fact that the steric environment around the double bond for each olefin is about the same (**3a,b**). The diborane hydroboration[12] of 1-alkyl-4-*tert*-butylcyclohexene is not as stereoselective as the 9-BBN reaction (**4a,b**). Undoubtedly, the lower stereospecificity of the



4a with diborane 4b with diborane

diborane reaction (**4**), compared with the hydroboration with 9-BBN (**3**), can be attributed to the lower steric requirements of diborane. Replacement of the methyl group (**4a**) with an ethyl group (**4b**), as expected, has little effect on the stereochemical course of the reaction.

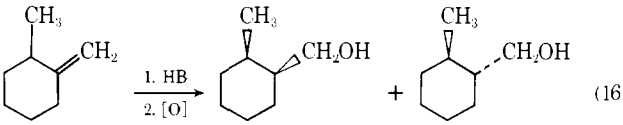
**Alkyl-Substituted Exocyclic Olefins.** The hydroboration of 2-methyl-1-methylenecyclopentane with 9-BBN produces the less thermodynamically stable product to the extent of 78% (eq 15). Apparently, the methyl group plays an important role in



9-BBN 78% 22% (15)

directing the incoming hydroborating reagent. Thus the kinetic cis product which results from trans attack is predominantly formed.

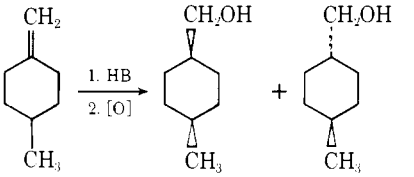
The hydroboration of 2-methyl-1-methylenecyclohexane with 9-BBN is less stereoselective than the corresponding reaction for the cyclopentane derivative (eq 16). The equatorial



9-BBN 60% 40% (16)

substituent in the 2 position of a methylenecyclohexane is nearly eclipsed to the exocyclic double bond. Thus, the methyl group, which, for the most part, lies in the same plane as the double bond, plays a small role in directing the incoming boron hydride. So it is reasonable that the cis isomer (product of trans attack) is produced in slight excess.

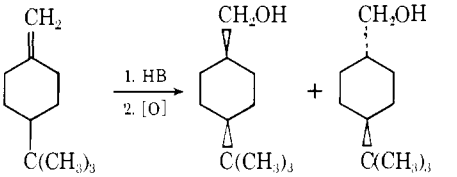
The hydroborations of 4-methyl-1-methylenecyclohexane with 9-BBN, dichloroborane, and diborane produce amazingly similar product distributions (eq 17).



| 9-BBN | 61% | 39% |
|---|---|---|
| $HBCl_2$[15] | 68% | 32% |
| $BH_3$[15] | 66% | 34% |

(17)

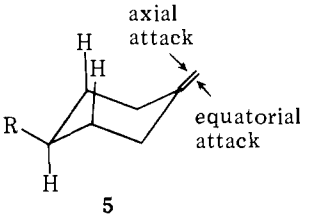
The 4-methyl group is too far removed from the reaction site to have any steric influence in the attack by boron. The function of the alkyl substituent is to hold the ring in the preferred conformer (**5**). Further evidence for this is revealed by hydroboration–oxidation of 4-*tert*-butyl-1-methylenecyclohexane (eq 18).



| 9-BBN | 61% | 39% |
|---|---|---|
| $BH_3$[15] | 68% | 32% |

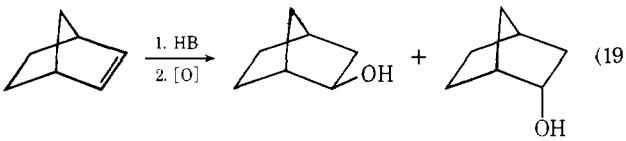
(18)

The 4-*tert*-butyl derivative gives rise to the same product distribution as that found for the 4-methyl analogue. The equatorial side is the less sterically hindered direction of attack on the chair exocyclic methylene (**5**). Therefore, the production of the cis isomer is favored.



5

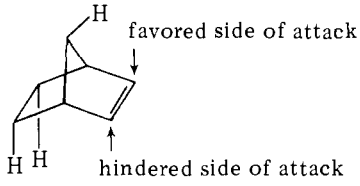
**Bicycloalkenes.** The hydroboration of norbornene with monochloroborane[5] and with 9-BBN[16] proceeds stereospecifically to give essentially quantitative yields of the exo product (eq 19).



| $ClBH_2$[15] | 99.8% | 0.2% |
|---|---|---|
| 9-BBN[16] | 99.5% | 0.5% |
| $Sia_2BH$[11] | 87.0% | 13.0% |

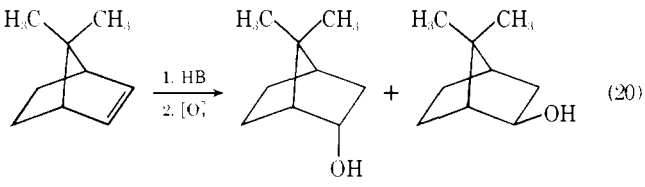
(19)

The reason for the high exo attack by boron is attributed to the more openness of this face of the molecule. There are two endo methylene hydrogens (on C-5 and C-6) which block the bottom of the double bond from attack and only one methylene hydrogen (on C-7) to block attack from the top (**6**). Hydro-




**6**

boration of 7,7-dimethylnorbornene with 9-BBN reveals that the steric hindrance caused by the replacement of a hydrogen with a methyl group reverses the stereochemical course of the reaction (eq 20).

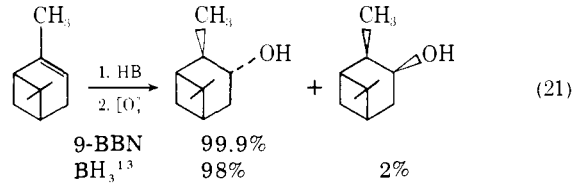



(20)

9-BBN 97% 3%

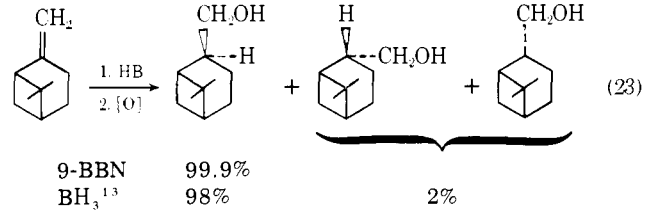
Similar results have been observed in the reaction of 9-BBN with *syn*- and *anti*-7-*tert*-butylnorbornene. The anti isomer hydroborates to give the exo 9-BBN derivative. The syn isomer reacts much slower and yields the endo adduct.[17] Now the favored side of attack is from the endo direction.

Both $\alpha$- and $\beta$-pinenes are hydroborated stereospecifically and in quantitative yields to their respective organoborane intermediates. Upon oxidation, alcohols of high purity are obtained (eq 21, 22).




(21)

9-BBN 99.9%
$BH_3$[13] 98% 2%




(23)

9-BBN 99.9%
$BH_3$[13] 98% 2%

## Conclusion

The hydroboration of 1-alkylcycloalkenes with 9-BBN produces the corresponding *trans*-2-alkylcycloalkyl-9-BBN in essentially quantitative yields. The thermal isomerization (at room temperature) of the initially formed *B*-alkyl-9-BBN derivative is found in only two cases (1-methylcycloheptene and 1-methylcyclooctene) and to only a small extent. This is in sharp contrast to diborane and disiamylborane, where, for example, as much as 40% of the organoborane initially derived from 1-methylcyclooctene isomerized in 0.5 h at 0 °C.[7] Thus, the hydroboration of 1-alkylcycloalkenes with 9-BBN represents the only method currently available for the preparation of the corresponding trans isomer in high isomeric purity.

The hydroboration of 3-methylcyclopentene or 3-methylcyclohexene with 9-BBN, amazingly, produces no cis 1,2 isomer, whereas both diborane and disiamylborane form a significant amount of the corresponding cis 1,2 isomer when either of these olefins is hydroborated. This amazing selectivity exhibited by 9-BBN with regard to the hydroboration of 1-methyl- and 3-methylcycloalkenes leads us to predict that 1,3-dimethylcycloalkenes should hydroborate to exclusively form the *trans,trans*-2,*n*-dialkylcycloalkyl-9-BBN derivative (where $n \equiv$ ring size).[18]

The hydroboration of 4-methylcyclopentene with 9-BBN produces the trans 3-substituted adduct to the extent of 95%. The importance of the size of the alkyl group is revealed when the methyl group is replaced with a *tert*-butyl substituent. Only a trace of the cis isomer was observed during the hydroboration–oxidation of 4-*tert*-butylcyclopentene.

For certain olefins, 4-alkylcyclohexenes, methylenecycloalkanes, and 1,4-dialkylcyclohexenes, the treatment with 9-BBN generally affords one *B*-alkyl-9-BBN derivative in moderate yields (60–78%) with lesser amounts of other stereoisomers also produced.

The results of this work clearly indicate that the regio- and stereoselectivity of 9-BBN surpasses that obtained with other hydroborating agents. Thus, the initial findings[15] that 9-BBN is very sensitive to subtle differences in steric environment has now been definitely established.

## Experimental Section

The organoboranes were always handled under an atmosphere of prepurified nitrogen (Airco) with careful exclusion of both oxygen and water. All glassware, syringes, and needles were oven dried at 150 °C 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. $^1$H NMR, IR, and mass spectra were obtained with a Varian T-60, a Perkin-Elmer 700, and a Hitachi RMU-6A, respectively. GLC analysis of alcohols, ketones, and olefins were carried out using a Varian Model 1200 FID chromatograph, a Hewlett-Packard 5752B chromatograph, and Perkin-Elmer Model 226 FID capillary chromatograph, each instrument equipped with the appropriate column.

**Materials.** The preparation of 9-BBN in THF was carried out as described previously.[2] The *n*-alkanes (Phillips) employed as internal standards were used as received. 3-Methylcyclopentene, 3- and 4-methylcyclohexene, 1-methylcycloheptene, 1-methylcyclooctene (Chemical Samples), 4-methylcyclopentene (API Standard Reference Materials, Carnegie-Mellon University), (+)-$\alpha$-pinene (Dragoco), $n^{20}$D 1.4665, and (±)-$\beta$-pinene (Arizona Chemicals), $n^{20}$D 1.4772, were all used as supplied after checking their purity. The rest of the olefins were prepared as described below.

**1-Methylcyclobutene.** Following the method in the literature,[19,20] in a dry 100-mL two-neck flask fitted with a condenser, thermometer, and stirring bar was placed 60 mL of anhydrous ethylenediamine and the solution heated to 90–100 °C in an atmosphere of nitrogen. To this hot solution was added 1.38 g (200 mmol) of lithium. The temperature rises during the addition. The reaction mixture was stirred for an additional 2 h at 90–100 °C, then cooled to room temperature. To this solution was added 6.8 g (100 mmol) of methylenecyclobutene (Chemical Samples) and the solution kept at room temperature for 2 h after which the olefin was distilled by warming in a mild flow of nitrogen and collected in a dry ice–acetone trap to give 5.9 g (87% yield) of a mixture of 1-methylcyclobutene and methylenecyclobutene in a ratio of 86:14 from which 1-methylcyclobutene was separated by preparative GLC, using a 30% silver nitrate–ethylene glycol column 6 ft × 0.25 in. at 45 °C.

The syntheses of 1-*tert*-butylcyclopentene and 1-*tert*-butylcyclohexene were performed according to the procedure of Buhler.[21]

**4-*tert*-Butylcyclopentene.** $\beta$-*tert*-Butyladipic acid was prepared by the ammonium vanadate catalyzed nitric acid oxidation of 4-*tert*-butylcyclohexanol (Chemical Samples). Cyclization with $Ba(OH)_2$ gave 3-*tert*-butylcyclopentanone.[22] This ketone was then reduced with $LiAlH_4$ to produce a mixture of 3-*tert*-butylcyclopentanols. The epimeric alcohol mixture was converted to the tosylates[23] and treated with *tert*-butyl alcoholate to yield the desired olefin.[24] Isolation of

4-*tert*-butylcyclopentene was achieved by preparative GLC (30% silver nitrate–ethylene glycol column 6 ft × 0.25 in.).

**4-*tert*-Butylcyclohexene.** This olefin was prepared from a mixture of *cis*- and *trans*-4-*tert*-butylcyclohexanols (Aldrich Chemical Co.) in an analogous manner as described above.

**2-Methyl-1-methylenecyclohexane,[25] 2-Methyl-1-methylenecyclopentane,[26] 4-*tert*-Butyl-1-methylenecyclohexane, and 4-Methyl-1-methylenecyclohexane.** These olefins were prepared following reported procedures,[26] by addition of the corresponding cycloalkanones to the ylide generated from triphenylmethylphosphonium bromide.

**1,4-Dimethylcyclohexene[28] and 4-*tert*-Butyl-1-methylcyclohexene.**[28] Addition of methyllithium to 4-methylcyclohexanone or to 4-*tert*-butylcyclohexanone followed by dehydration of the resulting alcohols with iodine afforded the desired olefins. Small amounts of exocyclic olefin present in the products were eliminated by addition of a THF solution of 9-BBN in equivalent amounts to the impurity present as determined by $^1$H NMR. The internal olefin was then separated pure by fractional distillation.

**Hydroboration of Olefins.** The hydroboration of olefins was carried out as described previously.[2] In all cases the reaction was complete in 2 h at 25 °C, except for the six-membered ring endocyclic olefins, which required heating to 50 °C for 8 h. After the usual oxidation with alkaline hydrogen peroxide, the resulting alcohol mixture was analyzed by GLC, as indicated in the following section.

## Product Studies

**Hydroboration–Oxidation of 1-Methylcyclobutene, 1-Methylcycloheptene, 1-Methylcyclooctene, 1-*tert*-Butylcyclopentene, 1-*tert*-Butylcyclohexene, 3-Methylcyclohexene, 4-Methylcyclopentene, 4-*tert*-Butylcyclopentene, 4-*tert*-Butylcyclohexene, 4-Methyl-1-methylenecyclohexene, 4-*tert*-Butyl-1-methylenecyclohexene, (+)-α-Pinene, and (±)-β-Pinene.** The composition of isomeric alcohols was determined by GLC by comparison with authentic samples.

**Hydroboration–Oxidation of 4-Methylcyclohexene.** We were not able to find a column that would show baseline separation of all four possible isomeric alcohols. The best results were obtained using a capillary column (TCEP, 150 ft × 0.125 in.), which separated the mixture into three peaks corresponding to *trans*-3-, *cis*-4-, and a mixture of *trans*-4- and *cis*-3-methylcyclohexanols. On the other hand, chromic acid oxidation of the alcohols[29] yielded a mixture of 3- and 4-methylcyclohexanones separable on GLC (quadrol or diglycerol). A combination of both analyses allowed us to estimate the product composition of alcohols.

**Hydroboration–Oxidation of 3-Methylcyclopentene.** The product mixture was analyzed on GLC (quadrol and diglycerol) and compared with a mixture of 2- and 3-methylcyclopentanols obtained via $LiAlH_4$ reduction of the corresponding ketones. This analysis showed that there was no *cis*-2-methylcyclopentanol present in the reaction mixture; however, it was not possible to get baseline separation of the remaining three isomers.

The product composition was finally determined as follows. A sample of the alcohol mixture from the reaction was oxidized with chromic acid.[29] GLC analyses of the resulting product (quadrol and diglycerol) revealed the presence of 2-methylcyclopentanone and 3-methylcyclopentanone in a 23:77 ratio.

Another sample of the reaction products was concentrated on the rotary evaporator to eliminate volatile solvents and the resulting residue repeatedly extracted with hot pentane to allow separation of the methylcyclopentanols from 1,5-cyclooctanediol present as a by-product of the oxidation of the organoborane mixture. Elimination of pentane left a residue which was used for $^1$H NMR studies, as described below.

To a 20% solution of the alcohol mixture in carbon tetrachloride, freshly sublimed $Eu(fod)_3$ was added in small increments and the $^1$H NMR spectrum of the resulting solution recorded each time. The addition was continued until the reagent would hardly dissolve. At this point, a set of three doublets (methyl groups) was clearly separated close to baseline resolution, approximate area ratios 25:50:25, $J$ = 6.75, 5.7, and 6.4 Hz, respectively. The assignment of isomers was accomplished by comparison of coupling constants obtained in a similar fashion from a commercially available sample of *trans*-2-methylcyclopentanol (Aldrich) ($J$ = 6.75 Hz) and from a sample from $LiAlH_4$ reduction of 3-methylcyclopentanone in which the cis alcohol isomer predominates[13] ($J_{cis}$ = 5.7 and $J_{trans}$ = 6.4 Hz). The assignments were corroborated by observation of the increment of methyl group areas in the $^1$H NMR spectrum upon addition of a mixture of 3-methylcyclopentanols (obtained via $LiAlH_4$ reduction of the ketone) to the reaction products.

**Hydroboration–Oxidation of 2-Methyl-1-methylenecyclopentane.** GLC analysis (SE-30) of the reaction mixture revealed the presence of two products in a ratio of 78:22. The minor component was identified as *trans*-2-methylcyclopentanol by comparison with an authentic sample obtained from the hydroboration–carbonylation[30] of 1-methylcyclopentene.

**Hydroboration–Oxidation of 2-Methyl-1-methylenecyclohexane.** GLC analysis (SE-30) of the reaction mixture revealed the presence of two products in a 60:40 ratio. The assignment of peaks was made possible by comparison with the product ratio of *cis*- and *trans*-1,2-dimethylcyclohexanes obtained via hydroboration–protonolysis[31] of the parent olefin.

**Hydroboration–Oxidation of 1,4-Dimethylcyclohexene.** The reaction mixture consisted of two components (GLC SE-30) in the ratio of 73:27. Hydroboration of the same olefin followed by protonolysis with propionic acid yielded a mixture of *trans*-1,3-dimethylcyclohexane and *cis*-1,3-dimethylcyclohexane (72:28).

Based on the latter result, it is established that the hydroboration–oxidation reaction yields 73% *trans,cis*-2,5-dimethylcyclohexanol and 27% of the trans,trans isomer.

**Hydroboration–Oxidation of 1-Methyl-4-*tert*-butylcyclohexene.** GLC analysis (SE-30) indicated the presence of two major components (76:24). Structures were assigned based on the $^1$H NMR spectrum which displayed the reported absorptions at 3.07 and 3.79 ppm ($CDCl_3$–$Me_4Si$) attributed to axial carbinol proton and equatorial proton, respectively,[11] with relative areas of approximately 7:2.

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# Mass Spectrometry in Structural and Stereochemical Problems. 248.[1] Stereochemical Effects in Electron Impact Induced Retro-Diels–Alder Fragmentations[2]

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**Abstract:** A series of $\Delta^7$-steroidal olefins has been synthesized in order to study the effect of stereochemistry on the electron impact induced retro-Diels–Alder (RDA) fragmentation. The mass spectra show a marked dependence upon the stereochemistry of the A/B ring juncture, in accord with orbital symmetry rules for a thermal concerted process. These results represent the first example of such apparent symmetry control in olefinic hydrocarbons. It is proposed that electron impact results in an ion in which the stereochemistry of the ring juncture is preserved and that this ion undergoes RDA fragmentation via a concerted mechanism.

Electron impact induced fragmentations which formally correspond to a retro-Diels–Alder (RDA) reaction are frequently observed in the mass spectra of six membered ring olefins and their utility in the structure elucidation of organic compounds is well established.[3] However, the mechanism of this fragmentation is still unclear and has been the subject of several recent studies. The two mechanisms which have been proposed are a stepwise cleavage initiated by electron impact or a concerted "quasi-thermal" or "quasi-photochemical" process.

Evidence for the stepwise process comes from studies of the charge distribution in the RDA fragmentation products of numerous organic compounds.[4,5] The fact that these distributions can be rationalized by consideration of the stabilities of the various possible radical and carbonium ion intermediates is taken as support for the stepwise pathway.

Dougherty[6] supports the concerted process based on theoretical considerations. The work of Elwood and Beynon[7] also would seem to support the concerted mechanism. They suggest that a correlation exists between the energy released in the metastable transitions of the RDA reaction of some gaseous bicyclic hydrocarbon ions and the ground state activation energy for the Diels–Alder reaction for formation of similar neutral molecules in solution.

If the electron impact induced RDA is concerted then it should follow the same orbital symmetry rules[8] as a thermal or photochemical RDA reaction. Mandelbaum and co-workers[9] have reported that the RDA of some cis- and trans-fused polycyclic ketones shows a dependence on the stereochemistry of the ring juncture which is in accord with the rules for a thermal concerted process. However, other studies of polycyclic compounds[10] and simple bicyclic olefins[11] have not consistently shown similar dependencies. A fortuitous observation in our laboratory[11] that the RDA of some $\Delta^7$-steroidal olefins shows a remarkable dependence on the stereochemistry ($5\beta$ series strongly favored) of the A/B ring juncture has prompted us to prepare and study a series of $5\alpha$- and $5\beta$-$\Delta^7$ steroids in order to gain further insight into the mechanistic aspects of these results, which imply the occurrence of a concerted, symmetry controlled process.

**Synthesis of $\Delta^7$ Steroids.** The hitherto undescribed $5\beta$ isomers of androst-7-ene (**8**) and pregn-7-ene (**10**) were synthe-

Scheme I