Hydroboration. 63. Kinetics and Regiospecificity of the Hydroboration of Isomeric *cis*- and *trans*-Alkenes via 9-Borabicyclo[3.3.1]nonane. Effects of 1,1- and 1,2-Dialkyl Interactions

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The kinetics of regiospecificity of the hydroboration of representative isomeric *cis*- and *trans*-alkenes via 9-borabicyclo[3.3.1]nonane (9-BBN) in THF have been studied. These compounds obey kinetics which are three-halves order, first order in alkene and half order in $(9\text{-BBN})_2$. In contrast to other hydroborating agents and contrary to previous reports, 9-BBN does not predictably hydroborate the cis nor the trans isomer selectively. Also, the selectivity displayed is rather low, being only a factor of 2 or 3. The regiospecificity of hydroboration seems to be influenced by steric and/or electronic factors which can act to increase hydroboration at a given site by increasing the favorability toward hydroboration at that site or by decreasing it at the competing site.

It was previously reported[1] that in the hydroboration of alkenes with 9-BBN a preference for the trans isomer was observed in all cases studied at that time. This result was unusual in that the other hydroborating agents investigated thus far had demonstrated a preference for the cis isomer. Based on the data available at that time, this seemed to give a general means of obtaining preferential hydroboration of the cis or trans isomer merely by the proper choice of the hydroborating agent. We now have conducted a more thorough study of the 9-BBN hydroboration of alkenes. This study encompasses the kinetics as well as the relative reactivities of the reaction of 9-BBN with several cis-trans pairs, including all of those previously covered. The results of our more complete investigation indicate that 9-BBN does *not* always preferentially hydroborate the trans isomer.

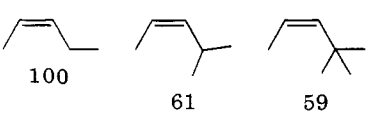
While investigating the effects of chlorine substitution in alkenes upon the kinetics of their hydroboration with 9-BBN,[2] we found these cis-trans pairs to obey kinetics which are 3/2 order, first order in chloroalkene and half order in $(9\text{-BBN})_2$. In these systems the *trans*-chloroalkenes have a lower rate constant than their cis isomers (see Table I). We have previously observed that in the 9-BBN hydroboration of unsaturates, the 3/2-order rate constants are proportional to the relative reactivities of the unsaturates.[2-6] Therefore, the previous results,[1] which indicated that the trans isomer of the unsubstituted alkenes had a higher relative reactivity, did not agree with our new findings. Accordingly, we repeated our kinetic experiments, and we also determined the relative reactivities of the chloroalkenes via competitive reactions. We obtained the same results for these compounds as before, again indicating a consistent preference for the cis isomers. Since in the former study of the unsubstituted alkenes, the relative reactivities had been determined solely on the basis of competitive reactions, we decided to repeat these reactions and to investigate the hydroboration kinetics for these compounds as well. This provides a rigorous check, since a preference for one isomer would appear in the kinetics measurements as a higher 3/2-order rate constant for that isomer.

The rate constants determined by the kinetics study of the 9-BBN hydroboration of the unsubstituted cis-trans pairs did not all agree with the results obtained from the previous study[1] of their relative reactivities. The rate constants indicated a slight trans preference in some cases and a slight cis preference in others. We then repeated the competitive reactions and found these relative reactivities to agree with the kinetic results. The rate constants and relative reactivities are all displayed in Table I. Therefore, in contrast to other hydroborating agents and contrary to previous reports, 9-BBN does not predictably hydroborate the cis or the trans isomer selectively. In addition, the selectivity is rather low, only a factor of 2 or 3.

By comparing the cis and trans isomers of alkenes containing bulky alkyl groups, we are able to discern the effects of 1,2-dialkyl steric interactions. For completion, we include examples of 1,1-dialkyl steric interaction as well.

(A) 1,2-Dialkyl Interaction. $A^{(1,3)}$ Strain.[7] The product distributions from the hydroboration-oxidation of the unsymmetrical isomeric cis-trans alkenes with 9-BBN enable several interesting observations. Bulkier groups, presumably because of their greater steric requirements, increase the amount of hydroboration at the less hindered position (see Chart I), except in the case of 1-phenylpropene. Also, this directive influence of bulky groups is less than the trans isomers of the alkenes. These points are discussed separately below.

As shown in Chart I, methyl substitution at the 4-position increases the amount of 2-ol produced. One reason for this is probably that increasing the steric requirements at the 3-position actually *reduces* the rate at which the precursor to the 3-ol (and to a lesser extent, that to the 2-ol) is produced. This idea is supported by the decrease in the rate of hydroboration which accompanies methyl substitution at the 4-position. Apparently, the steric effect



and hyperconjugation by the methyl group, which would tend to direct hydroboration to the 3-position, are outweighed by the steric effects of the larger alkyl group.

(1) Brown, H. C.; Liotta, R.; Scouten, C. G. *J. Am. Chem. Soc.* **1976**, *98*, 5297-301.
(2) Nelson, D. J.; Brown, H. C. *J. Am. Chem. Soc.* **1982**, *104*, 4907-12.
(3) Brown, H. C.; Scouten, C. G.; Wang, K. K. *J. Org. Chem.* **1979**, *44*, 2589-91.
(4) Wang, K. K.; Brown, H. C. *J. Org. Chem.* **1980**, *45*, 5303-5306.
(5) Wang, K. K.; Scouten, C. G.; Brown, H. C. *J. Am. Chem. Soc.* **1982**, *104*, 531.
(6) Nelson, D. J.; Blue, C. D.; Brown, H. C. *J. Am. Chem. Soc.* **1982**, *104*, 4913-7.
(7) (a) Johnson, F. *J. Am. Chem. Soc.* **1965**, *87*, 5492. (b) Johnson, F. *Chem. Rev.* **1968**, *68*, 375.

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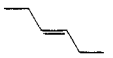
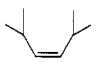
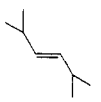
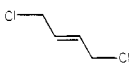
Table I. Relative Reactivities and Rate Constants for the Hydroboration via 9-BBN of Several Cis-Trans Pairs at 25 °C in THF Solvent

alkene	structure	rel react. (1-hexene = 100)	k_{cis}/k_{trans}	$k_{3/2}$(cis)/ $k_{3/2}$(trans)	$10^4 k_{3/2}$, $M^{-1/2}$ s^{-1}
1-hexene		100			14.3 (1st order)
cis-3-hexene		0.68	2.1	1.7	4.53
trans-3-hexene		0.32			2.65
cis-4-methyl-2-pentene		0.53	3.3	3.3	4.20
trans-4-methyl-2-pentene		0.16			1.28
cis-1-phenylpropene		0.024	0.39	0.39	0.227
trans-1-phenylpropene		0.062			0.579
cis-2,5-dimethyl-3-hexene		0.0017	0.076	0.60	0.0110
trans-2,5-dimethyl-3-hexene		0.022			0.183
cis-1,4-dichloro-2-butene		0.0144	4.4	2.3	0.218
trans-1,4-dichloro-2-butene		0.0033			0.096
cis-1-chloro-1-butene		0.0093	3.0	2.0	0.115
trans-1-chloro-1-butene		0.0031			0.058

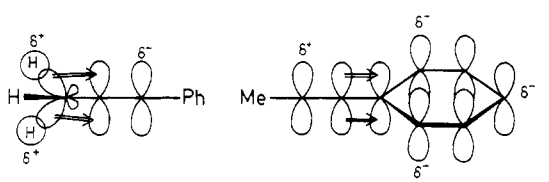
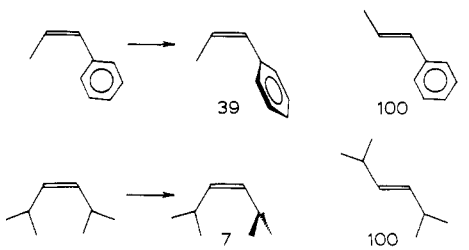


Figure 1. Diagram to show combined effects of phenyl conjugation (–K) and methyl hyperconjugation (+K) in 1-phenylpropene.

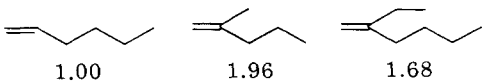
The preferred site of hydroboration in 1-phenylpropene, the site to which boron becomes attached, is the 1-position (vide supra). This is not what one would expect on the basis of steric effects. One possible explanation for this is the combined effects of phenyl conjugation (–K) and methyl hyperconjugation (+K) which act to decrease the amount of electron density at the 2-position and to increase it at the 1-position (Figure 1). Evidently these mesomeric effects are strong enough to override the steric effects of the phenyl group.

As was stated earlier, the influence of the bulkier group in directing hydroboration to the less hindered position is apparently decreased in the *trans*-alkenes. The reason for this may be that in the cis isomers large alkyl groups, being on the same side of the double bond, experience some 1,2-dialkyl steric interaction. Such steric interaction between substituents in the allyl system, even with relatively small alkyl groups, has been reported in the case of substituted cyclohexenes, and there it has been termed $A^{(1,3)}$ strain.[7] This steric strain is relieved by rotation of the groups so that they project above and below the plane of the carbon–carbon double bond. This effect would not be present in the trans isomers. Therefore, in their reaction with 9-BBN, the cis isomers would display an enhanced steric effect due to this nonplanar geometry. Thus, in compounds such as 1-phenylpropene and 2,4-dimethyl-3-hexene, in which the bulkiness of the groups is relatively large, the trans isomer reacts at a faster rate than the corresponding cis compound.



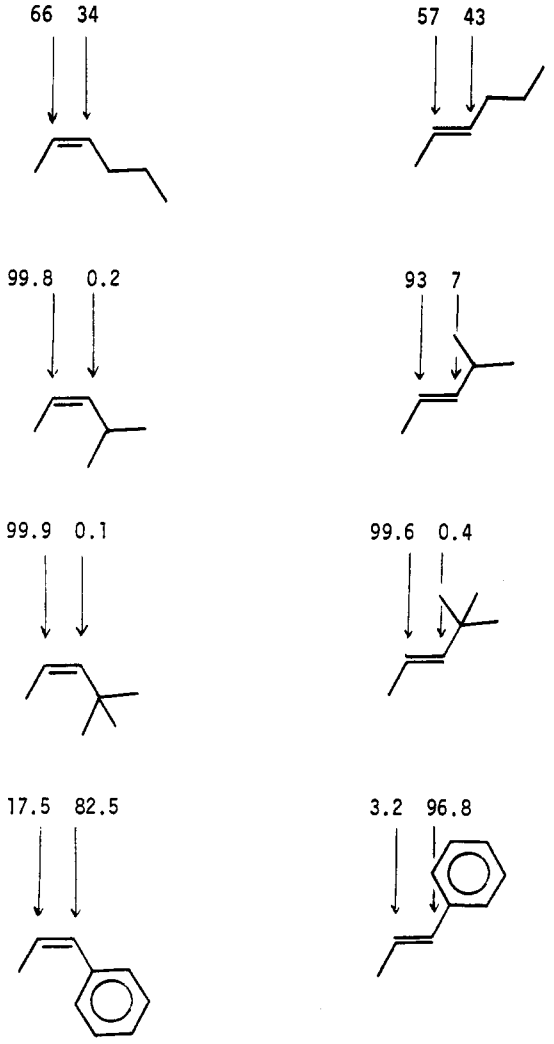
Rotation of the phenyl group out of the plane of the π system in *trans*-1-phenylpropene is also supported by a greater amount of hydroboration at the 2-position (17.5%) than in the cis isomer (3.2%). Greater electron availability at C-2 would be expected from disruption of phenyl conjugation. However, since hydroboration occurs largely to place boron α to phenyl, it is understandable that rate-retarding steric effects of phenyl rotation prevail.

(B) 1,1-Dialkyl Interactions. $A^{(1,2)}$ Strain.[7] It has long been known that 2-methyl substitution in the reaction of terminal alkenes[8] with 9-BBN increases the relative reactivity by a factor of about 2.[4,5] This was attributed to hyperconjugative effects.[2]

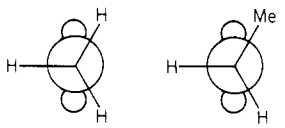


(8) This rate increase upon α-methyl substitution is also observed for vinylcyclopropane (2.8).[1] In the case of 2-butene, α-methyl substitution was reported to decrease the rate by 1.1.[1] However, this value may not be reliable because of the high volatility of 2-butene.

Chart I

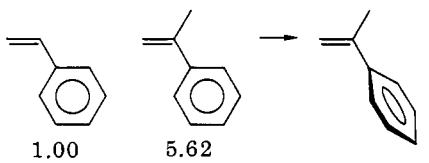


Replacing the methyl substituent by ethyl can increase the steric interaction with the 9-BBN moiety. As indicated by the following Newman projections, this change would



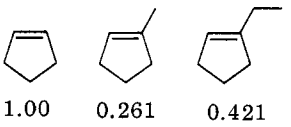
also be expected to decrease the hyperconjugative contribution.[9] Consequently, both effects should result in a reduction in the rate.

The rate-increasing effects of 2-methyl substitution are larger in the styrene system.[1] Here, $A^{(1,2)}$ strain causes

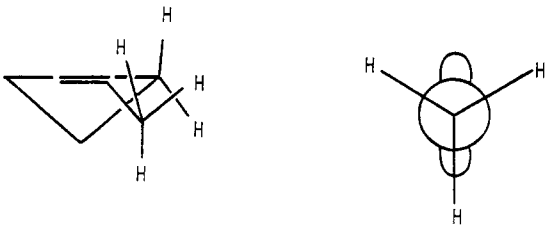


rotation of the phenyl group out of the plane of the π system, disrupting the rate-retarding phenyl conjugation. Thus, 2-methyl substitution in this system causes a larger rate increase than in 1-hexene. In this system, steric and hyperconjugative effects work together to direct hydroboration to C-1. Evidently methyl hyperconjugation (+K) and removal of phenyl conjugation (−K) act together to override the steric effects due to phenyl rotation.

On the other hand, in cyclic systems such as cyclopentene and cyclohexene similar methyl substitution re-

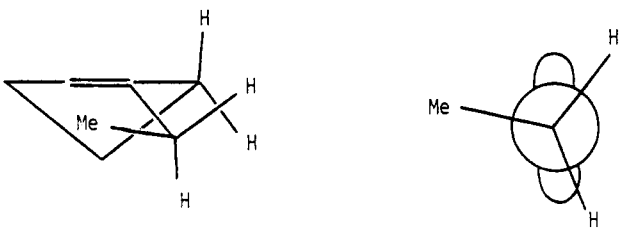


tards the rate of hydroboration.[4,5,10] In these cyclic systems, it appears that the steric retardation by methyl far outweighs the hyperconjugative contribution. Here, the 1,1-dialkyl steric interaction between the methyl group and the α-methylene unit may cause rotation of the methyl group, disrupting the hyperconjugation which would contribute to the rate enhancement. The extreme of such disruption of hyperconjugation is indicated by the two different representations below. A similar allylic steric



effect, $A^{(1,2)}$ strain, has been discussed for the cyclohexene system containing two bulky substituents. However, in our case, the interaction is between Me and H; therefore, it is not surprising that the effect is small. Nevertheless, the data indicate that it is real.

Replacing the methyl substituent by ethyl reduces the rate retardation. In part, this may be due to the greater inductive effect of ethyl. Moreover, in this case, steric interaction with the α-methylene probably causes rotation of the ethyl group so that the terminal methyl moiety is moved away. By doing so, some hyperconjugation may be gained, diminishing the rate retardation. The following diagrams indicate the kind of interactions which could be responsible for the increased hyperconjugation.



Experimental procedures have been reported in great detail in several other publications.[1,2,4-6] Alkenes were purchased from Chemical Samples Co. except for *trans*-1-phenylpropene, which came from Columbia Organic.

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Registry No. 1-Hexene, 592-41-6; *cis*-3-hexene, 7642-09-3; *trans*-3-hexene, 13269-52-8; *cis*-4-methyl-2-pentene, 691-38-3; *trans*-4-methyl-2-pentene, 674-76-0; *cis*-1-phenylpropene, 766-90-5; *trans*-1-phenylpropene, 873-66-5; *cis*-2,5-dimethyl-3-hexene, 10557-44-5; *trans*-2,5-dimethyl-3-hexene, 692-70-6; *cis*-1,4-dichloro-2-butene, 1476-11-5; *trans*-1,4-dichloro-2-butene, 110-57-6; *cis*-1-chloro-1-butene, 7611-86-1; *trans*-1-chloro-1-butene, 7611-87-2; 9-borabicyclo[3.3.1]nonane, 280-64-8.

(9) Lide, D. R., Jr.; Christensen, D. *J. Chem. Phys.* **1961**, *35*, 1374–8.

(10) If corrected statistically for the presence of two equivalent hydroboration positions in these symmetrical systems, the rate reduction upon alkyl substitution would be reduced by 50%.