Table II. Comparison of Thermodynamic Parameters of Activation in Aqueous Buffered Solution and Anionic AOT Reversed Micelle[a]

environment	E_{act}, kcal/mol	$\Delta G^{\ddagger}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
aq soln (pH 5)	22.85	22.02	22.26	+0.81
0.2 M AOT/0.6 M H_2O/hexane	22.34	24.95	21.75	−8.75

[a] $[1] = 1.0 \times 10^{-5}$ M.

increase in the viscosity of the micellar core. Increasing the *R* values in the reversed micellar system, of course, brings about a decrease in the microscopic viscosity[11,17-21] and an increase in the microscopic polarity of the water pool, subsequently resulting in an increase in the thermocoloration rate (Table I). In order to make the point clearer, we determined the thermodynamic parameters of activation for the present reaction from an Arrhenius plot, where the most reliable linear correlations were attained in both the aqueous and reversed micellar systems. Clearly, from the results listed in Table II, the difference in the entropy term in the reaction rate between the two systems is brought about by means of restricting the freedom of molecular motion (Figure 3).

It may be reasonablly concluded, thus, that the rate deceleration of the thermocoloration of **1** in the reversed micellar core must be caused by the restriction of the mobility and internal rotation of **1** in a highly viscous environment. Furthermore, through kinetic studies on the thermocoloration process in various media, it was found that the photobleached species being at a higher energy level has a longer lifetime in the restricted field provided by reversed micelles than in the homogeneous regular solutions. In addition, present results suggest that the photochromism of spiropyran serves as a good kinetic probe for exploring the microenvironmental effect of the reaction field.

Acknowledgment. The support of the Ministry of Education, Science, and Culture (Grants-in-Aid No. 447068 and 56550594) is gratefully acknowledged.

Registry No. 1, 82352-70-3; 2, 82352-71-4; 2′, 82352-72-5; *N*-(2-hydroxybenzylidene)aniline, 779-84-0; 1,3,3-trimethyl-2-methyleneindoline, 118-12-7.

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[21] Also, from the ^{13}C NMR T_P measurements of glycine encapsulated in the water pool of dodecylammonium propionate reversed micelles, it is confirmed that the microscopic viscosity of the micellar core increases with a decrease in *R* values; Tsujii, K., Sunamoto, J. and Fendler, J. H., unpublished results.

Hydroboration Kinetics. 4. Kinetics and Mechanism of the Reaction of 9-Borabicyclo[3.3.1]nonane with Representative Haloalkenes. The Effect of Halogen Substitution upon the Rate of Hydroboration[1]

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Abstract: The rates of hydroboration of several haloalkenes have been investigated. The kinetics parallel those observed for the parent alkenes in that the faster reacting haloalkenes show kinetics which are first order in $(9\text{-BBN})_2$, while the slower reacting ones display kinetics which are three-halves order—first order in haloalkene and one-half-order in $(9\text{-BBN})_2$. Because of these kinetics, the relative reactivities were established by competitive reactions. These studies reveal the effect of the halogen substituent: 1-hexene, 100; allyl iodide, 7.1; allyl bromide, 4.6; allyl chloride, 4.0. Thus, the effect of an allylic chlorine is to reduce the rate of hydroboration at the γ-position by a factor of 25. In the systems in which hydroboration is directed to the β-position, the rate reduction is less: 2-methyl-2-butene, 100; 1-chloro-3-methyl-2-butene, 57; 1-bromo-3-methyl-2-butene, 54. In these latter cases, hydroboration is followed by rapid elimination and rehydroboration. A vinylic chlorine has a much more dramatic effect of forcing the hydroboration to the 2-position as well as greatly reducing the rate of hydroboration: 1-hexene, 100; *cis*-1-chloro-1-butene, 0.0093.

Introduction

The hydroboration reaction is a method of easily obtaining many organoboranes which are very useful in organic synthesis.[2] While many interesting reactions have been discovered and applied in syntheses, details of the mechanism of hydroboration are still not known.[3] An excellent way of obtaining information concerning the mechanism of a reaction is via kinetic studies. However, in the past, a major difficulty in studying the kinetics of hydroboration has been in finding a suitable hydroborating agent whose kinetics can be easily followed.

Recently it was discovered[3] that 9-borabicyclo[3.3.1]nonane, $(9\text{-BBN})_2$, is an excellent candidate for the investigation of the mechanism and kinetics of hydroboration for many reasons. (1) It has high thermal stability and purity.[4] (2) It is easier to handle compared to other boranes because of its lower sensitivity to oxygen and water vapor.[4] (3) With one reaction center per boron, its overall reaction with an alkene involves only one dissociation step and one hydroboration step. This can be contrasted to that of

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[1] Presented in part at the 180th National Meeting of the American Chemical Society, Las Vegas, NV, Aug 1980; American Chemical Society, Washington, DC, 1980; ORGN 316.

[2] Negishi, E.; Brown, H. C. *Synthesis* **1974**, 74.

[3] (a) Brown, H. C.; Scouten, C. G.; Wang, K. K. *J. Org. Chem.* **1979**, *44*, 2589–2591. (b) Brown, H. C.; Wang, K. K.; Scouten, C. G. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 698–702. (c) Wang, K. K.; Brown, H. C. *J. Org. Chem.* **1980**, *45*, 5303–5306.

[4] (a) Brown, H. C.; Knights, E. F.; Scouten, C. G. *J. Am. Chem. Soc.* **1974**, *96*, 7765–7770. (b) Brown, H. C.; Mandal, A. K.; Kulkarni, S. U. *J. Org. Chem.* **1977**, *42*, 1392–1398.

borane (BH_3)—three consecutive addition reactions, three redistribution equilibria, and five monomer–dimer equilibria.[5] (4) $(9\text{-BBN})_2$ exists in only one isomeric form.[3] This eliminates complications in the kinetics such as with the dimer of disiamylborane, which has five isomers.[6] (5) Its reaction can be studied in certain solvents such as carbon tetrachloride, cyclohexane, and benzene in which 9-BBN exists exclusively as the dimer. This eliminates complexation with solvent and simplifies the kinetics. This is much more favorable than the situation with BH_3 in THF in which formation of the $BH_3 \cdot THF$ complex, as well as the possible THF complexes of the borane intermediates, would need to be considered.[7] (6) 9-BBN is highly regio- and stereoselective;[4,8] thus, we are usually assured of studying only one reaction. (7) Lastly, it was recently discovered that its hydroboration reaction could be easily followed by monitoring via IR the disappearance of its bridging B–H bonds.[3b]

For these reasons, the kinetics of the reaction of $(9\text{-BBN})_2$ with many alkenes were investigated,[3] clearly determining that this hydroboration reaction proceeds via dissociation of the dimer (eq 1) and subsequent reaction of the monomer with alkene (eq 2).

$$(9\text{-BBN})_2 \rightleftharpoons 2\,9\text{-BBN} \qquad (1)$$

$$9\text{-BBN} + \text{alkene} \rightarrow B\text{-alkyl-9-BBN} \qquad (2)$$

Therefore, the observed kinetic order is dependent upon the reactivity of the alkene. If the alkene is reactive enough, the rate-determining step is the first step, and kinetics which are first order in $(9\text{-BBN})_2$ and zero order in alkene are observed. For less reactive alkenes, the second step is rate determining, and the kinetics displayed are three-halves order—first-order in alkene and one-half order in $(9\text{-BBN})_2$.

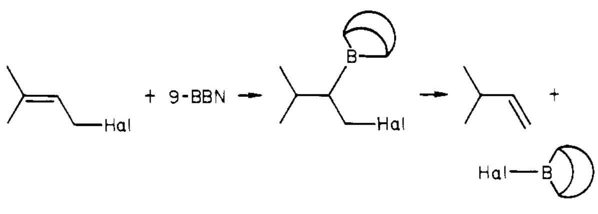
An excellent way to obtain valuable information in the areas of both mechanistic and synthetic chemistry is to investigate the effects of substituents in alkenes upon the rate of hydroboration. The effect of the substituent to donate, withdraw, or polarize electrons in the double bond should provide valuable information about the mechanism, while the relative rates of hydroboration of substituted double bonds will provide synthetic chemists with an improved means of predicting the selective hydroboration of one functionality in the presence of another. Much work in this latter area has already been carried out.[9]

The success of the investigation of the kinetics of the reaction of $(9\text{-BBN})_2$ with alkenes[3] increased our desire to explore further its mechanism and synthetic utility. Therefore, we decided to use $(9\text{-BBN})_2$ in our studies of the effects of alkene substitution. The general interest in haloalkenes prompted us to choose the halogens as our first series of substituents. Accordingly, we have investigated the hydroboration of a number of representative haloalkenes by using $(9\text{-BBN})_2$.

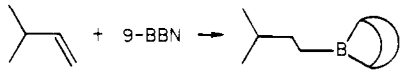
Results

Allylic haloalkenes containing a terminal double bond undergo hydroboration primarily at the 1-position. However, all other haloalkenes examined (Table II) underwent hydroboration β to the halogen substituent. By this, we mean the boron atom was attached β to the halogen substituent. These products immediately underwent elimination of B-halo-9-BBN, followed by rapid rehydroboration of the now unsubstituted terminal double bond. An example of this is given in eq 3.

In these cases, reaction of one equivalent each of haloalkene and 9-BBN leads to equal amounts of the B-halo-9-BBN and the B-alkyl-9-BBN, as observed by ^{11}B NMR spectroscopy. In no case was any B-haloalkyl-9-BBN detected. Oxidation of the reaction mixture and GC analysis revealed only cyclooctanediol and the alcohol corresponding to the B-alkyl-9-BBN.



(3a)



(3b)

The kinetics for the reactions of the haloalkenes proved to be the same type as for the unsubstituted alkenes with the order of the reaction depending upon the reactivity of the substrate. The kinetic results for the haloalkenes and their unsubstituted "parent" compounds are shown in Table I. In general, terminal haloalkenes with an unhindered end of the double bond were faster reacting, and these displayed first-order kinetics. Most of those having an internal double bond were found to follow kinetics of three-halves order—first-order in haloalkenes and one-half order in $(9\text{-BBN})_2$. Several of them did not fit into either category but displayed intermediate kinetic behavior.

Like the other slower reacting haloalkenes, the first hydroboration of the compounds which underwent rapid elimination and rehydroboration displayed three-halves-order kinetics. Apparently, the first hydroboration is rate determining with elimination and rehydroboration occurring at a much faster rate. When these last two steps are added, the total reaction sequence for these few cases is shown in eq 4–7.

$$(9\text{-BBN})_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,9\text{-BBN} \qquad (4)$$

$$9\text{-BBN} + \text{haloalkene} \xrightarrow{k_2} B\text{-haloalkyl-9-BBN} \qquad (5)$$

$$B\text{-haloalkyl-9-BBN} \xrightarrow{\text{fast}} \text{alkene} + B\text{-halo-9-BBN} \qquad (6)$$

$$9\text{-BBN} + \text{alkene} \xrightarrow{\text{fast}} B\text{-alkyl-9-BBN} \qquad (7)$$

Fortunately, we found the kinetics of these reactions could still be calculated as follows.

For the rate of hydroboration of the compounds which experience elimination and rehydroboration to be compared with that of the other haloalkenes, we must determine the rate of the first hydroboration step (eq 5). We can do this by using the above equations to obtain the kinetic expression

$$\frac{-d[(9\text{-BBN})_2]}{dt} = k_1[(9\text{-BBN})_2]\left(\frac{k_2[\text{haloalkene}]}{k_{-1}[9\text{-BBN}] + k_2[\text{haloalkene}]}\right) \qquad (8)$$

If $k_2[\text{haloalkene}] \gg k_1[9\text{-BBN}]$, eq 8 reduces to

$$\frac{-d[(9\text{-BBN})_2]}{dt} = k_1[(9\text{-BBN})_2] \qquad (9)$$

which is the same first-order rate expression as obtained for the unsubstituted alkenes.[3] However, if $k_2[\text{haloalkene}] \ll k_{-1}[9\text{-BBN}]$, eq 8 reduces to

$$\frac{-d[(9\text{-BBN})_2]}{dt} = \left(\frac{k_1}{k_{-1}}\right)^{1/2} k_2[(9\text{-BBN})_2]^{1/2}[\text{haloalkene}] \qquad (10)$$

Rewriting this in terms of the three-halves-order rate expression obtained for unsubstituted alkenes[3] yields eq 11, where $k_{3/2}$ is the

$$\frac{-d[(9\text{-BBN})_2]}{dt} = 2k_{3/2}[(9\text{-BBN})_2]^{1/2}[\text{haloalkene}] \qquad (11)$$

three-halves-order rate constant for hydroboration of unsubstituted alkenes. When the equations and approximations given above are used, the three-halves-order rate expressions for the substituted and unsubstituted cases differ only by a factor of 2. Thus, we

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[5] Pasto, D. J.; Lepeska, B.; Balasubramaniyam, V. *J. Am. Chem. Soc.* **1972**, *94*, 6090–6096.

[6] Brown, H. C.; Klender, G. J. *Inorg. Chem.* **1961**, *1*, 204.

[7] Elliott, J. B.; Roth, W. L.; Roedel, G. P.; Boldebuck, F. K. *J. Am. Chem. Soc.* **1952**, *74*, 5211–5212.

[8] Brown, H. C.; Liotta, R.; Scouten, C. G. *J. Am. Chem. Soc.* **1976**, *98*, 5297–5301.

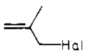
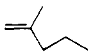
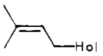
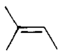
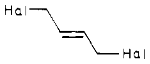
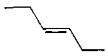
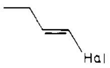
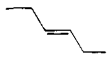
[9] Wang, K. K. Ph.D. Thesis, Purdue University, 1979.

Table **I.** Relative Reactivities and Rate Constants for the Hydroboration of Haloalkenes and Their Parent Compounds in CCl_4 and in THF at 25 °C

			10^4k_1, s^{-1}, or $10^4k_{3/2}$, $M^{-1/2}$ s^{-1}		
compd no.	alkene	rel reactivities	CCl_4	THF	
1	2-methyl-1-pentene[a]	196	1.53	14.3	first-order kinetics
2	1-hexene[a]	100	1.54	14.2	
3	methallyl chloride	13.6	1.65	13.5	
4	allyl iodide	7.1	1.63	13.6[b]	
5	allyl bromide	4.6	1.57	12.0[b]	
6	allyl chloride	4.0	1.55	12.3[b]	
7	2-methyl-2-butene[a]	1.13	*b*	6.91[b]	intermediate kinetics
8	*cis*-3-hexene[a]	0.68	*b*	4.53	
9	1-chloro-3-methyl-2-butene	0.64		3.34	
10	1-bromo-3-methyl-2-butene	0.61		2.90	
11	*trans*-3-hexene	0.32		2.65	
12	*cis*-1,4-dichloro-2-butene	0.0144	0.161	0.218	
13	*cis*-1-chloro-1-butene	0.0093		0.115	
14	2,3-dimethyl-2-butene[a]	0.0061	0.020	0.049	three-halves-order kinetics
15	*trans*-1,4-dichloro-2-butene	0.0033	0.024	0.048	
16	*trans*-1-chloro-1-butene	0.0031		0.029	

[a] Results for these compounds are from ref 3. [b] This reaction displays at least some intermediate behavior in the solvent indicated.

Table **II.** Effect of Halogen Substitution on the Relative Reactivity of Alkenes in Hydroboration with $(9\text{-}BBN)_2$

				factor by which rel reactivity of haloalkene is lowered		
haloalkene	parent	type of halogen	positn of hydroboratn rel to halogen	Cl	Br	I
		allylic	γ	25	21.7	14.1
		allylic	γ	13.6		
		allylic	β	1.77	1.85	
		allylic	β,γ	48		
		allylic	β, γ	100		
		vinylic	β	73		
		vinylic	β	103		

can calculate the rate constant of the first hydroboration step for the compounds which undergo rapid elimination and rehydroboration.

Originally we had hoped to establish the effect of halogen substituents on the rate of hydroboration by comparing the actual rate constants. Unfortunately, this did not prove possible. Some of the compounds of interest reacted through first-order kinetics, giving the same rate constant. We did measure rate constants for the reactants exhibiting three-halves-order kinetics, and here we could establish the relative reactivity through a comparison of the rate constants. Finally, a few of the compounds exhibited complex kinetics, lying somewhere between first order and three-halves order.

Because the reactions of many of the compounds displayed first-order or intermediate kinetics, no information about their relative reactivities could be obtained from the kinetic studies. Consequently, we had to rely primarily on competitive methods to establish the effect of halogen on the rate of reaction. Good agreement was realized for the relative reactivities determined by comparison of the $k_{3/2}$ values and the relative reactivities established by the competitive experiments.

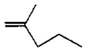
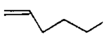
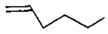
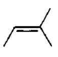
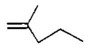
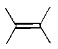
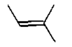
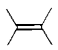
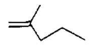
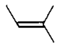
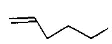
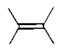
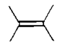
The relative reactivities and kinetic data for the alkenes are shown in Table I. When the relative reactivity of a haloalkene is compared with that of its parent compound, the effect of the halogen substituent can be determined (Table II).

Our results indicate that the rate of 9-BBN hydroboration of an alkene is governed by two major influences: (1) steric hindrance and (2) electron availability at the site of hydroboration. The steric requirements of an alkene effect not only the rate but also the regiochemistry of hydroboration. For example, alkenes having one end of the double bond unsubstituted usually react via a fast first-order reaction with hydroboration occurring at the less hindered site. On the other hand, the highly hindered tetramethylethylene reacts very slowly through the three-halves-order mechanism.

While 9-BBN is less sterically hindered than some hydroborating agents such as disiamylborane,[3] it is more sensitive to the steric factor than borane. Because of this, 9-BBN exhibits much more selectivity than borane, giving usually only one product rather than a mixture of products. Because of the sensitivity of 9-BBN to electronic factors, the influence of substituents on 9-BBN reaction rates can be dramatic. Nevertheless, it is still necessary to separate the steric effects from electronic effects in order to enable us to analyze the magnitude of either.

As an approximation, we shall assume that, for the compounds examined in this study, steric effects are important only when a vinylic hydrogen is replaced by a bulkier group. This seems reasonable, since it was found earlier[3,8,9] that the effect of increasing the chain length of the alkyl substituent in an alkene did not have a significant effect; the change was to increase only slightly the rate of hydroboration. This gives evidence for a small inductive effect rather than a steric one. Therefore, it seems reasonable to approximate the difference in steric effects between *cis*-3-hexene and tetramethylethylene as being equal to the effects of replacing two vinylic hydrogens by methyl groups. We can also neglect the steric effects when comparing the rates of reaction

Table III. A Breakdown of the Effects of Alkyl Groups Which Influence the Change in Reaction Rate in Alkenes

alkyl-substituted compd	parent	factor by which rel reactivity changes	type	hyperconjugative effects of additional alkyl group(s) at positn rel to site of hydroboratn		inductive effects on π bond	steric effects of additional alkyl group(s) at positn rel to site of hydroboratn	
				α	β		α	β
		↑1.96	A	0	1	1	0	1
		↑1.77						
		↓156	B	1	0	1	1	0
		↓173						
		↓185						
		↓3.21×10^4	2 of B	2	0	2	2	0
		↓88.5	1 of A and 1 of B	1	1	2	1	1
		↓105						
		↓1.64×10^4	2 of B and 1 of A	2	1	3	2	1

of compounds such as 1-hexene and allyl chloride for the same reason.

Discussion

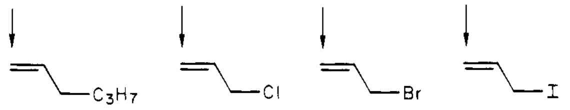
A. Alkenes. The relative magnitudes of the effects of steric hindrance, induction, and conjugation are difficult to sort out. Initial attempts to do this were made through studying the hydroboration of acyclic alkyl substituted alkenes with $(9\text{-BBN})_2$. In Table III we have listed some of the substituted and parent alkenes investigated along with the respective changes in the relative reactivity brought about by substitution. In these systems, the most important factors influencing the rate of hydroboration are probably the steric, inductive, and hyperconjugative effects.

From Table III, it is immediately obvious that the effects upon reaction rate which are brought about by alkyl substitution are cumulative and highly regular. Here we have listed pairs of alkenes which have been investigated. Each pair will differ in that one will have more alkyl groups attached to the double bond than the other. By comparing the relative reactivity of this pair of alkenes, we can observe the effect of one or more additional alkyl groups upon the relative rates of hydroboration. Therefore, the relative reactivity of each pair of compounds compared reflects the steric, inductive, and hyperconjugative effects of the additional alkyl group relative to hydrogen. The effect of the alkyl group will obviously be different if it is α to the site of hydroboration than if it is β. Finally, in some cases, more than one alkyl group has been added. These cases merely represent combinations of the types of individual alkyl groups involved. From our data, we can draw a few empirical rules which might prove useful. An alkyl substituent α to the site of hydroboration (type B) has an effect of decreasing the rate of reaction by an average of about 170. On the other hand, a methyl substituent β to the site of hydroboration (type A) has an effect of increasing the reaction rate by a factor of about 1.87.

An example of applying these empirical rules should serve to demonstrate the regularity of the effects. If one wanted to calculate the effect of addition of three alkyl substituents—two α and one β to the site of hydroboration—he would figure this effect as (α effect)^2(β effect) = ↓171^2/↑1.87 = ↓1.56×10^4 (rate reduction). This estimate is in good agreement with the experimentally observed effect of ↓1.64×10^4 (rate reduction) in comparing the relative reactivity of tetramethylethylene with that of 1-hexene.

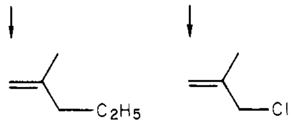
B. Allyl Halides. The situation in the haloalkenes is somewhat simplified. As stated earlier, when comparing these systems with their parent systems, we can neglect the steric effects with only a small error being introduced. Therefore, in these compounds, we can attribute any changes in the reaction rates to the electronic effects of the halogens.

The importance of the electronic effects becomes obvious when considering the rates of hydroboration of the allyl halides. The Cl, Br, or I substituent at the γ-position has a rate-reducing effect of 25, 21.7, or 14.1, respectively.



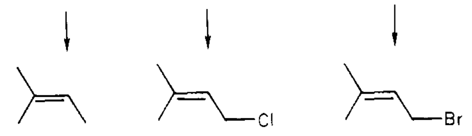
100 4.0 4.6 7.1

The order of rate reduction Cl > Br > I is the same as the increasing electron-withdrawing effect (inductive + mesomeric) of the halogen. The effect seems to be slightly reduced in methallyl chloride.



100 6.9

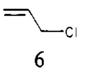
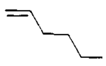
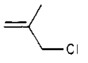
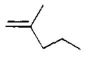
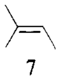
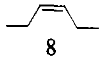
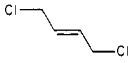
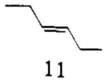
In the 1-halo-3-methyl-2-butene system, hydroboration is directed to the position β to the halogen substituent. In these cases, as described earlier, the product of hydroboration undergoes rapid elimination and rehydroboration. The rate-retarding effect of the halogen substituent upon hydroboration at the β-position is a factor of about 2, much less than in the examples above, in which hydroboration occurs at the γ-position.



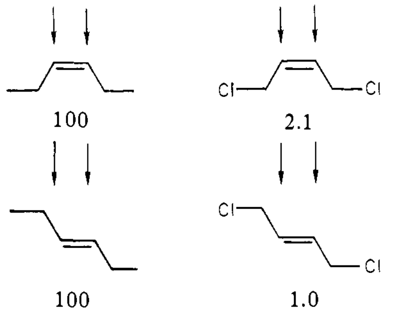
100 57 54

The 1,4-dichloro-2-butene system has two equivalent sites available for hydroboration. Either of these will result in hydroboration β to one chlorine and γ to the other. Again, hydroboration of this system is followed by rapid elimination and rehydroboration. The rate reduction in this system is rather large,

Table IV. Breakdown of the Effects of Chlorine Substituents Which Influence the Electron Availability in Allylic Chlorides

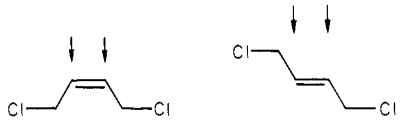
allyl chloride	parent compd	increases in indicated interactns in going from parent to substituted compd: factor by which rel reactivity is lowered	inductive interactn of Cl with π bond, $-I$	hyperconjugative effect of Cl at positn rel to chlorine: $-K_\beta$	$-K_\gamma$
 6	 2	25	1	0	1
 3	 1	13.6	1	0	1
 9	 7	1.77	1	1	0
 12	 8	48	2	1	1
 15	 11	100	2	1	1

a factor of 48 or 100, depending on which isomer is being considered.

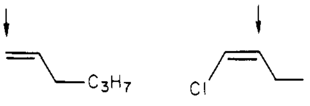


It should be noted that one could predict the cumulative effect of β- and γ-chorine substutions using the data for allyl chloride and for 1-chloro-3-methyl-2-butene (see Table IV). If we calculate this estimated rate change in the same manner as in the previous section, we obtain (↓25)(↓1.77) = ↓44. Again, this estimate is in good agreement with the experimentally observed value of ↓48. Since it was demonstrated for the alkenes in the preceding section that the effects of substituents on the rates of the hydroboration reactions are regular and cumulative, we could also expect the effects to be regular and cumulative in the allyl halides.

Last, in the 1,4-dichloro-2-butene system, 9-BBN is shown to have a small preference for the cis isomer. However, this should not be taken as a result applicable to cis–trans pairs in general.

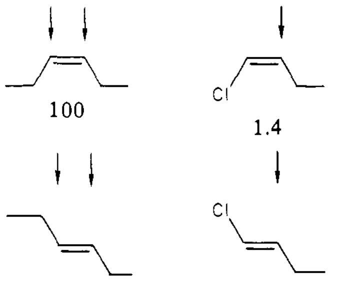


C. Vinylic Chlorides. Attaching a chlorine substituent to the terminal position of an alkene has a dramatic effect upon its reaction with 9-BBN. Hydroboration is forced to the 2-position, and the rate of reaction is decreased by a factor of more than 10^4.



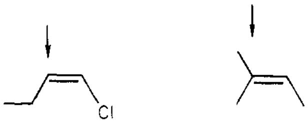
Again, hydroboration β to chlorine is followed by rapid elimination and rehydroboration.

In order to elucidate the electronic effects of chlorine in this system, it is necessary to compare the reaction rate with that of a compound such as 3-hexene, a compound which has similar steric requirements in its reaction with 9-BBN.



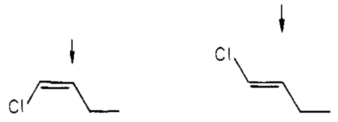
When 3-hexene is used for comparison, the electronic effects still appear to be greater in the vinylic systems than in the allylic ones. In this case, the effect of chlorine is compared to that of an alkyl group. To compare it to that of hydrogen, we must also consider the rate-accelerating effect of the alkyl group β to the site of hydroboration in 3-hexene which will not be present in the butenylic chlorides. Relative to hydrogen, the factor by which this alkyl group will accelerate the rate of hydroboration is 1.87 (see section A). This means that relative to hydrogen, the effect of a butenylic chlorine on the rate of hydroboration is to decrease it by ↓88/↑1.87 = ↓47, assuming that the steric effects of the chlorine substituent are about equal to those of hydrogen.

Note that this is not much larger than the effect of an allylic chlorine on hydroboration at the γ-position. The rate reduction by a factor of 47 indicates a large electronic effect in the butenyl chlorides at the β-position. However, the electronic effect at the position α to chlorine must be enormous, for it has been demonstrated that for 1-chloro-2-methyl-1-butene, in which the steric requirements at the position β to chlorine are very high, hydroboration still occurs mainly at that position.[10]



Evidently, electronic effects in this system must be large because they outweigh the steric effects which ordinarily force hydroboration to occur at the less substituted position.

In butenyl chlorides, 9-BBN again exhibits only a small preference for the cis isomer.



D. Theoretical. The electron availability at the site of hydroboration is affected by the electronic interactions within a given molecule. There have long been recognized two electronic modes of internal transmission of electronic interaction.[11] These are inductive, *I*, and conjugative, *K*. It seems that Ingold intended the latter cagegory to include hyperconjugation.[11]

Steric effects and the above electronic effects seem to be responsible for the relative reactivities of the alkenes. In most cases, the steric effects seem to predominate; increasing the number of substituents on the double bond decreases the reaction rate.

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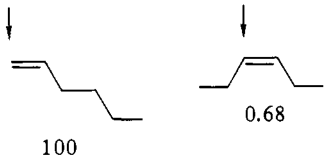
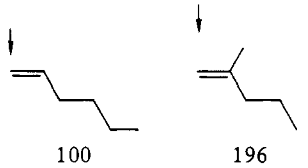
(10) (a) Chen, J. C. Ph.D. Thesis, Purdue University, 1979. (b) Brown, H. C.; Chen, J. C. *J. Org. Chem.* **1981**, *46*, 3978.

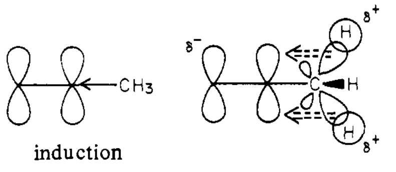
(11) Ingold, C. K. "Structure and Mechanism in Organic Chemistry", 2nd ed.; G. Bell & Sons: London, 1969.



However, this is not true in the cases in which a methyl group has been substituted β to the site of hydroboration.



The rate increase in this last example is probably due to relatively small steric effects being slightly overridden by the induction and hyperconjugation of the methyl group, which act to increase the electron availability of the system in the manners shown.

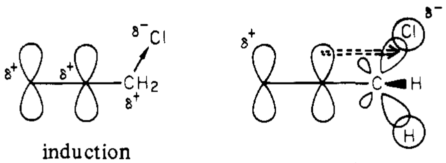


induction

hyperconjugation

It should be noted that the effect of a methyl group at C_2 to place more electron density at C_1 than at C_2 was recently reported in calculations on the reaction of borane and propylene.[12]

The rate-retarding effect of the allylic halogen substituents can be accounted for by using the traditional modes of electronic interaction which could be present: induction and hyperconjugation. Both of these effects are electron withdrawing and, therefore, rate reducing at either the β- or the γ-position.

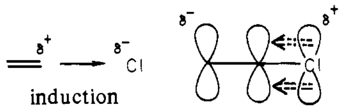


induction

hyperconjugation

relative to propene

It was observed that a vinylic chlorine substituent not only retarded the reaction rate but also directed the hydroboration to the 2-position. Thus the inductive effect of chlorine must reduce the electron availability of the π bond enough to severely retard the rate of reaction, while conjugation returns some electron density to the site β to chlorine, which then becomes the preferred site of hydroboration.



induction

conjugation

relative to ethylene

E. Solvent Effects. The rate constants for the compounds which display first-order kinetics were found to differ in THF and CCl_4 solvents. The first-order rate constant in THF solvent is found to be about ten times that in CCl_4 solvent. This catalytic effect of THF upon the hydroboration of alkenes has been noted previously.[3b] An investigation of this solvent effect is presently being carried out and will be reported later.

Conclusion

The hydroboration of haloalkenes via 9-BBN proceeds through two steps: (1) dissociation of $(9\text{-BBN})_2$ and (2) hydroboration of the haloalkene with 9-BBN monomer. The reaction steps account for the results that faster reacting haloalkenes display first-order kinetics, while slower reacting ones show kinetics which are three-halves order—first order in haloalkene and one-half order in $(9\text{-BBN})_2$. The halogen substituents were found to retard the rate of hydroboration with the rate-retarding effect being in the order Cl > Br > I.

Experimental Section

General Data. The general procedures for manipulation of boron reagents are given elsewhere.[13] The preparation of $(9\text{-BBN})_2$[4] and the distillation[13] of THF and CCl_4 have been previously described. All alkenes and haloalkenes were purchased from Chemical Samples Co., except for the following: *cis*-1,4-dichloro-2-butene, Aldrich; *trans*-1,4-dichloro-2-butene, Scientific Products. The alkenes and the haloalkenes were distilled under nitrogen from a small amount of calcium hydride and then stored under nitrogen. The alkanes which were used for internal standards were obtained from Phillips Petroleum and were used as received.

Instruments. A Wilks Scientific Corp. Model Miran-1A variable-filter infrared spectrometer was used to monitor the disappearance of the boron–hydrogen bridges of $(9\text{-BBN})_2$ by recording the absorption at 1570 cm^{-1}. The reaction mixture was pumped through a 0.10-mm Wilkes NaCl precision sealed flow-through cell at a rate of 4 mL/min.

^{11}B NMR spectra were obtained on a Varian FT-80A instrument. GC analyses were carried out on a Hewlett-Packard 5750 equipped with a thermal conductivity detector using $^1/_4$ in. × 6 ft columns or a Varian 1200 equipped with a flame-ionization detector using $^1/_8$ in. × 6 ft columns. Both chromatographs were connected to Hewlett-Packard integrators for determining peak areas. The following GC columns were used: $^1/_8$ in. × 6 ft 18% SE-30 on 100/120 mesh Chromosorb W; $^1/_4$ in. × 6 ft 10% SE-30 on 60/80 mesh Chromosorb W; $^1/_4$ in. × 6 ft 15% Carbowax 1540 on 60/80 mesh Chromosorb W.

Procedures. The procedure used for determining the kinetics of haloalkene hydroboration was the quantitative infrared method, which has been discussed in detail elsewhere.[3c] Data collection and manipulation as well as the assignment of order of reaction kinetics were carried out in the same manner as before.[3] The olefin pairs studied by competitive hydroboration include allyl chloride/1-hexene, allyl chloride/cyclopentene, allyl chloride/methallyl chloride, methallyl chloride/allyl bromide, allyl chloride/allyl bromide, allyl chloride/allyl iodide, 1-chloro-3-methyl-2-butene/*cis*-3-hexene, 1-bromo-3-methyl-2-butene/*cis*-3-hexene, *cis*-1-chloro-1-butene/methylcyclohexene, *trans*-1-chloro-1-butene/methylcyclohexene. The results are summarized in Table I.

Acknowledgment. We gratefully acknowledge support from the National Science Foundation, Grant CHE 76-20846, for support of this work. Thanks are also due to Dr. K. K. Wang for stimulating discussions.

Registry No. 1, 763-29-1; **2**, 592-41-6; **3**, 563-47-3; **4**, 556-56-9; **5**, 106-95-6; **6**, 107-05-1; **7**, 513-35-9; 8, 7642-09-3; **9**, 503-60-6; **10**, 870-63-3; **11**, 13269-52-8; **12**, 1476-11-5; **13**, 7611-86-1; **14**, 563-79-1; **15**, 110-57-6; **16**, 7611-87-2; 9-BBN, 280-64-8.

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(12) Graham, G. D.; Freilich, S. C.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1981**, *103*, 2546–2552.

(13) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975