170. MNDO Analysis of Regio- and Stereoselectivity in Hydroboration

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The origin of regioselectivity in hydroboration of olefins has been analyzed by MNDO methodology. With a standard transition structure derived from full MNDO optimizations, a linear correlation between calculated and experimental regioselectivities has been found. A similar approach applied to asymmetric inductions of hydroboration with chiral hydroborating agents lead also to an acceptable linear correlation between calculated and experimental results. The MNDO method has been used for a search of alternative hydroborating agents.

The observation by *H. C. Brown* that hydroboration of symmetrical olefins with chiral mono- and dialkylboranes followed by oxidation yields optically active alcohols has gained increasing attention [1] [2]. Due to the high enantiomeric purity which can be achieved by optimization of reaction conditions, asymmetric syntheses of natural products and other chiral compounds with hydroboration as the key step are no longer unusual [3] [4]. Apart from the remarkable results by *Masamune*, asymmetric hydroboration often makes use of alkylboranes which are derived from (+)-α-pinene [5]. In continuation of our experimental and theoretical studies, we have analyzed the factors which may control selectivity in hydroboration with the aim to design new reagents with high asymmetric induction [6].

According to the mechanistic investigations by *H. C. Brown*, an olefin reacts in the rate-determining step with BH_3 which is formed by dissociation of a $BH_3 \cdot Me_2S$ or $BH_3 \cdot THF$ complex prior to reaction with the olefin [7]. As a first approximation, solvent effects on the addition can, therefore, be ignored, and computer calculations for the gas phase can be used for the reaction in solution. Expensive optimizations of geometry parameters of solvent molecules, which are only approximately known, can thus be avoided [8]. In most cases, hydroboration of di- or trisubstituted olefins is performed in a temperature range in which the primarily formed addition products do not isomerize to the more stable alkylboranes, where the B-atom is located at a terminal C-atom [9]. Based on *ab-initio* calculations by *Lipscomb* [10], *Schleyer* [11], and *Nagase* [12], the structural features of the reaction of ethylene with BH_3 can be described in detail: The addition occurs by a π-complex and leads *via* a four-centre transition state to the products in a highly exothermic reaction.

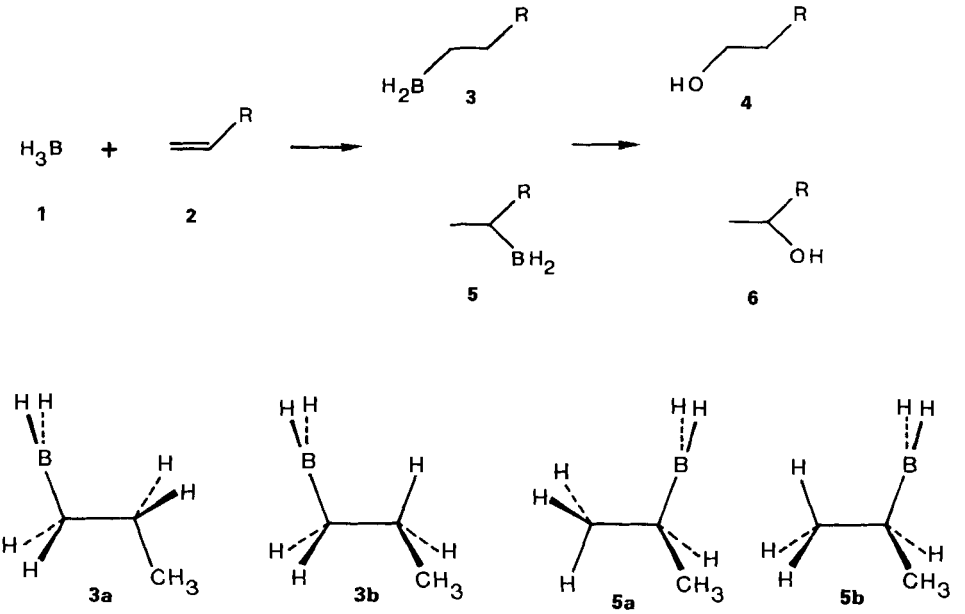
White showed that stereoselective hydroboration of sterically hindered cyclohexenes can be reproduced rather well by calculations based on a special force field [13]. Asymmetric hydroboration of alkenes and olefins with chiral substituents has been studied by *Houk* [14]. Using a combination of MM2-force-field and *ab-initio* calculations, the enantio- and diastereoselectivity could be well described by transition structures. The force-field methods used by *White* and *Houk* allow very fast computations, even on a

personal computer, but are not well suited for searching transition-state structures because they ignore electronic phenomena and calculations with most heteroatoms because of lack of parameters. *Ab-initio* calculations of structures like isopinocampheylborane ((Ipc)BH_2) with large basis sets, full optimization of geometry, and inclusion of electron correlation, necessary for the study of a transition state, are still beyond the capacity of present-day computers [15]. In our view, *Houk*'s method of first optimizing the transition-state geometry of a structure with *Allinger*'s MM2 force field [16] and then estimating the energy by an *ab-initio* (3-21G) method is not sufficiently reliable. In *ab-initio* calculations, even small changes in geometry may lead to large differences in energy and, therefore, the *ab-initio* energy of a MM2-transition structure will probably be very different from the energy of a fully optimized *ab-initio* transition state [15].

For our investigations, we prefer the MNDO method [17] because this quantum-chemical procedure yields optimized geometries, energies, and electronic structures simultaneously and implicitely considers electron correlation. The MNDO method is fast in comparison with *ab-initio* calculations and gives results which are comparable with (6-31G) calculations [15a]. MNDO and CNDO studies of the mechanism of the hydroboration have been reported [18] [19].

Results and Discussion. – 1. *Regioselectivity.* Although the mechanism of hydroboration indicates that the addition of BH_3 (**1**) to olefins **2** is strongly exothermic [7] [10–12], it is of interest whether the regioselectivity is related to the products formed. According to our MNDO results, the most stable conformations of 1-propyl- (**3a**) and isopropylborane (**5a**) differ by 3.3 kcal/mol. An energy difference of 1.5 kcal/mol was found for conformers **3b** and **5b** which contain an ecliptic CH_3 and a planar BH_2–C group and might resemble the transition states of the addition more closely.

In comparison with the experimental results that propanol (**4**) and isopropyl alcohol (**6**) are formed by hydroboration/oxidation in a ratio of 94:6 [1], the calculated energy



difference for the regioisomeric alkylboranes **3a** and **5a** is too large[1]). The energy difference between **3b** and **5b** is closer to the expectation value, but appears to be unreliable in view of the highly exothermic reaction. Based on this and similar results for other olefins (where in some cases the computed ratio of regioisomers is inverse as compared with the experimental result), it may be concluded that the regioselectivity is related to activation energies rather than heats of reaction.

The subsequent MNDO simulation of the addition of BH_3 to ethylene gave a reaction profile which closely resembles the *ab-initio* (6-31G**//4-31G/SCF) results [12] *(Fig. 1)*. The formation of the π-complex *(Fig. 1, b)* prior to the transition state is well reproduced by the MNDO method. In both methods, the bond distance d(B···C) of the transition structure is very similar, whereas the MNDO angle $\sphericalangle$(H···B···C) is 15° larger. The small deformation of the olefin in the transition state (*Fig. 1, c*; $\alpha = 18.2°, \beta = 21.9°$) is in qualitative accord with the secondary isotope effect [21]. The activation energy of 2.7 kcal/mol is to be compared with the *ab-initio* value of 6.7 kcal/mol which appears to be too high by a factor of 2 [12]. An activation enthalpy of 2 ± 3 kcal/mol has been measured for the reaction between BH_3 and ethylene in the gas phase [22].

For analysis of the regioselectivity, the transition states of addition of BH_3 to the olefins **7** (see *Table 2*) have been fully optimized by the gradient method [23]. From these structures, which have very similar dimensions and differ slightly from *Houk*'s data [14a], average bond angles and bond distances for the central H···B···C⁻⁻⁻C fragment were

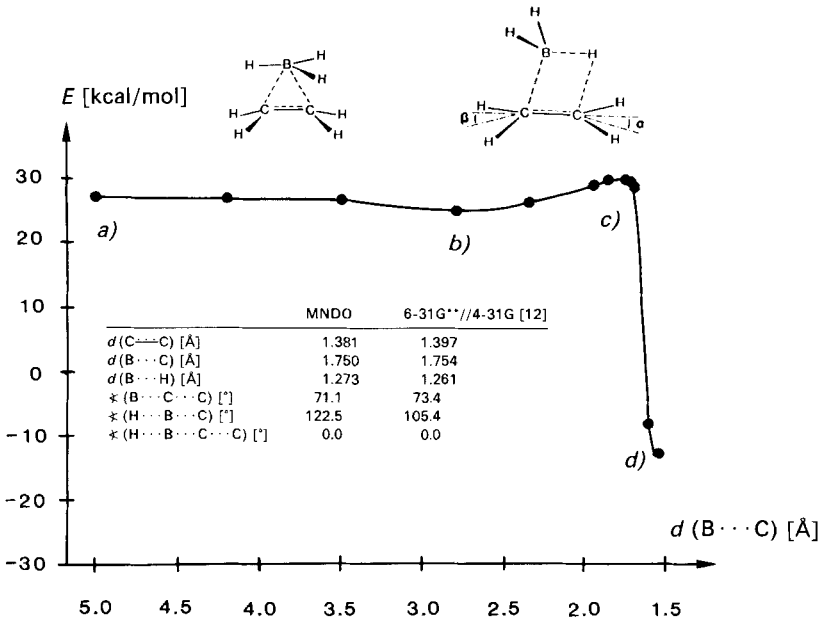
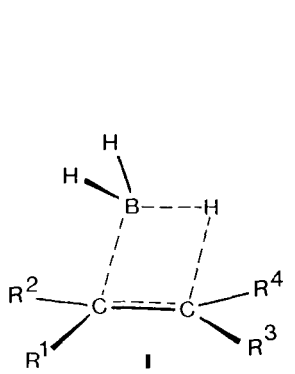


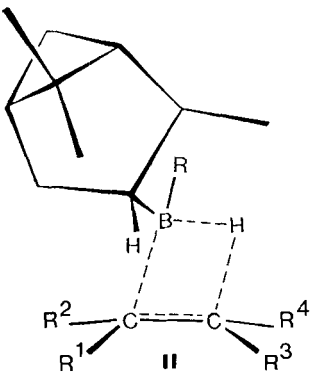
Fig. 1. *MNDO-energy profile for the reaction of BH_3 with CH_2=CH_2 and structural data for the transition state.* Heats of formation (kcal/mol) are given. *a:* CH_2=CH_2 and BH_3 in a distance of 5 Å; *b:* π-complex; *c:* transition state; *d:* ethylborane in the most stable conformation.

[1]) Throughout this paper, it is assumed that the alcohols obtained from olefins by hydroboration/oxidation are formed in kinetically controlled reactions and that no isomerisations have occurred during oxidative workup of the alkylboranes [20].

Table 1. *Parameters Used for Standard Transition Structure of Hydroboration of Olefins.* **I** with BH_3; **II** with (1*R*,2*S*,3*R*,5*R*)-(Ipc)BH_2 (**8a**) and ((1*R*,2*S*,3*R*.5*R*)-Ipc)$_2$BH (**8b**).



I

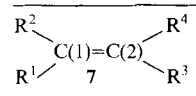


II

	I	II
d(B···H)	1.21 Å	1.20 Å
d(B···C)	1.71 Å	1.78 Å
d(C···C)	1.45 Å	1.43 Å
∢(H···B···C)	117°	117°
∢(B···C ⋯ C)	72.5°	72.5°
∢(H···B···C ⋯ C)	0°	0°

calculated (*Table 1*, **I**). In the subsequent calculations, all substituents were optimized according to the method of *Davidon, Fletcher,* and *Powell* (DFP method [24]), while the averaged parameters of the central H···B···C ⋯ C structure were kept constant. The energies and geometries of these transition structures, requiring much less computer time, hardly differ from the fully optimized MNDO transition states (see below).

Table 2. *Ratios of Regioisomeric Alkylboranes from* **7** *and* BH_3



	R^1	R^2	R^3	R^4	$\Delta\Delta H^{\neq}$ [a] [kcal/mol]	Ratio of products calc.[b]	exp.[c]	$c_1^2:c_2^2$[d]
a	CH_3	H	CH_3	CH_3	1.16	88:12	98:2	0.44:0.41
b	CH_3	H	H	CH_2Cl	–3.65	< 1:99	1:99	0.41:0.45
c	H	H	CH_3	CH_3	1.85	96:4	99:1	0.46:0.42
d	CH_3	CH_3	Cl	H	–3.28	< 1:99	1:99	0.37:0.38
e	H	H	H	$(CH_3)_3C$	1.48	93:7	94:6	0.47:0.45
f	H	H	H	CH_2Cl[e]	0.86	81:19	60:40	0.47:0.45
g	CH_3	CH_3	H	$(CH_3)_3C$	–0.39	34:66	2:98	0.41:0.42
h	CH_3	H	H	$(CH_3)_2CH$	0.24	58:42	57:43	0.44:0.44

[a]) Difference of MNDO-activation enthalpies.
[b]) Product ratios calculated for $\Delta H^{\neq}$ using the *Eyring* equation [25] for the temperature of the experimental hydroboration.
[c]) Calculated from the alcohols isolated [1].
[d]) HOMO coefficients of the olefin from MNDO calculations.
[e]) Synplanar conformation.

Therefore, regioselectivities in hydroboration can reliably be obtained by a procedure in which the transition-state structures *(Fig. 1, c)* are approximated and which is computationally much faster. From the difference in activation energies for the formation of regioisomeric alkylboranes, relative rates and product ratios can be obtained[1][2] *(Tab. 2)*. In this way, an acceptable linear relationship ($r = 0.79$) between computed and experimental rates has been obtained for the regioselectivity in hydroboration of simple olefins *(Fig. 2)*. In order to evaluate the influence of entropy on the product distribution, the activation entropies have been calculated for the olefins **7** of *Table 2* and incorporated into the relative rates. In comparison with the experimental results, a smaller r-factor ($r = 0.69$) was found. This may indicate that the MNDO method is more reliable for activation energies than for entropies. Together with the fact that entropies can be calculated by the MNDO programs used [17] [26] only after full gradient optimization, the method of using standard geometries for transition structures and evaluation of selectivities as used here is to be preferred.

When applied to the hydroboration of bridgehead substituted norbornenes, this procedure gave results consistent with the experimental regioselectivities [6] [27].

We had earlier proposed that regioselectivity in hydroboration can qualitatively be described by the ratio of the squared coefficients of HOMO ($(c_\mu^2 : c_\nu^2)_{HOMO}$) in the olefinic double bond [6][3]. The small energy gap between the π-complex and the transition state as

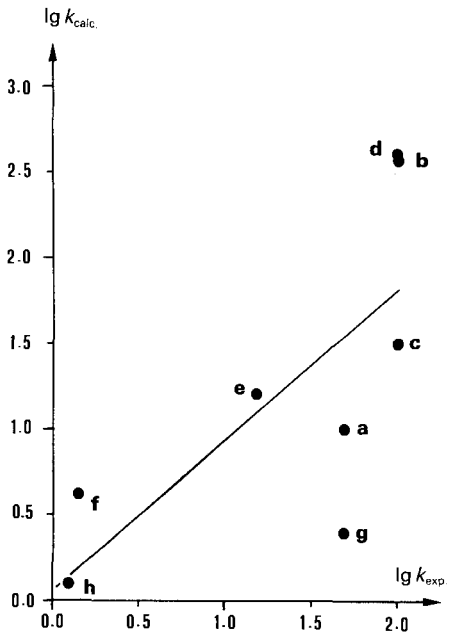
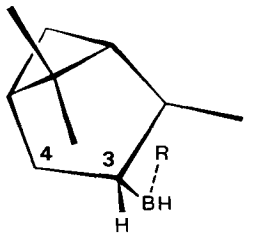


Fig. 2. *Correlation between experimental and calculated regioselectivities of selected olefins* **7** *in hydroboration with* BH_3 *(cf. Table 2).* $\lg k_{calc.} = 0.932 \lg k_{exp.} + 0.08$ ($r = 0.79$).

[2]) Relative rates $k_{calc.}$ were calculated *via* the *Eyring* equation [25]; the values of $k_{exp.}$ were calculated from the ratios of alkohols for the temperature of the hydroboration reaction.

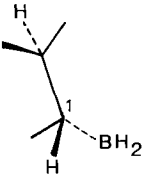
[3]) According to intermolecular perturbation theory [28], the ratio $(c_\mu^2 : c_\nu^2)_{HOMO}$ – and not $(c_\mu : c_\nu)_{HOMO}$ as suggested by *Nelson* and *Cooper* [29] – is directly related to ratios of interaction energies.

well as the small deformation from planarity in the olefin between structure *b* and *c* (see *Fig. 1*) are in support of this notion *(cf. Table 2)*. Recently, *Nelson* and *Cooper* provided evidence that the relative rates of the hydroboration of olefins with 9-borabicyclo-[3.3.1]nonane correlates with the energy levels of HOMO in the alkenes as determined by the first ionisation potential and MNDO calculations [29].



8a R = H
b R = Isopinocampheyl

9



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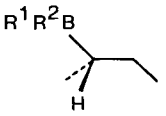
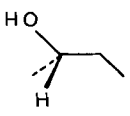
2. *Asymmetric Induction.* In recent years, considerable progress has been made in optimization of stereoselective and asymmetric hydroboration [2] [4]. This is mainly due to the preparation of optically pure hydroborating agents (*e.g.* **8**–**9**), separation of diastereoisomeric dialkylboranes prior to oxidation, and the synthesis of new hydroborating agents (*e.g.* **9**) with high asymmetric induction [5].

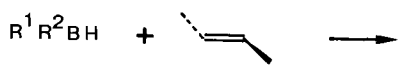
First, we consider the reaction of (1*R*,2*S*,3*R*,5*R*)-isopinocampheylborane (**8a**) with (*E*)-2-butene (**11**) which leads *via* (*Si*)-attack to (*S*)-**12a** and subsequent oxidation to (*S*)-2-butanol (**13**). (*R*)-2-Butanol (**15**) is formed *via* the alkylborane (*R*)-**14a**. Subsequently, the reactions with (*Z*)-2-butene and those of di[(1*R*,2*S*,3*R*,5*R*)-isopinocampheyl]borane (**8b**) and (2*R*,5*R*)-2,5-dimethylborolane (**9**) with the same olefins are analyzed.



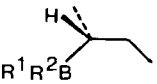
(*S*)-**12a,b**

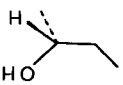


(*S*)-**13**



8a,b **11**





a R^1 = Ipc, R^2 = H
b $R^1 = R^2$ = Ipc

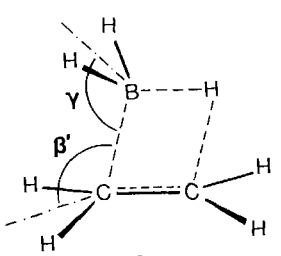
(*R*)-**14a,b**

(*R*)-**15**

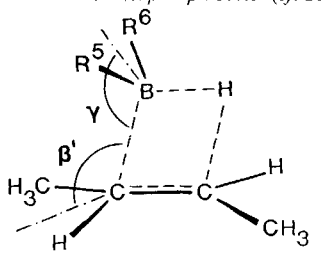
A standard geometry for the transition structures was extracted from the fully optimized diastereoisomeric transition states for the reactions mentioned above (**8a,b** + **18**; see *Table 1*, **II**)[4]). In comparison with the transition structure **I** used for addition of BH_3 to olefins, the distance $d(B\cdots C) = 1.78$ Å is slightly longer; whereas the elongation of the

[4]) For B in transition states with **8a** resp. **8b**, only (*Si*)-topicity (*cf. Table 1*) is considered [14a].

Table 3. *Geometry Parameters Found in Transition Structures* **16** *and* **17a,b**. $\beta' = \beta + 107.5°$ (*cf. Table 1*).



16



17a R^5 = Ipc, R^6 = H
b $R^5 = R^6$ = Ipc

	16	**17a**	**17b**
β'	135.5°	137.2°	144.3°
γ	121.6°	126.3°	136.2°

olefinic double bond is smaller. The angles β' resp. γ between the quasi-ecliptic substituents at the B- and the adjacent C-atom increase with sterically demanding substituents (see **16** and **17**, *Table 3*).

In the reaction of (*E*)-2-butene (**11**) with (Ipc)BH_2 (**8a**), (*Si*)-attack leads to a transition structure with a dihedral angle ω(H–B–C(3)–C(4)) of *ca.* 60° (*Fig. 3a*). Rotation of the isopinocampheyl moiety around the B–C bond gives rise to two conformational minima at *ca.* 175 and 330° with energies 2.9 and 2.13 kcal/mol, respectively, above the one of the transition structure (*Fig. 3a*)[5]). Likewise, three conformational minima are found for (*Re*)-attack, when the isopinocampheyl group is rotated (*Fig. 3b*). The minima at *ca.* 50 and 320° hardly differ in their energy, whereas the conformer with a dihedral angle of *ca.* 200° lies 1.89 kcal/mol above the transition structure. The energy of the transition structure being 1.07 kcal/mol higher than for (*Si*)-attack is consistent with the experimental observations of hydroboration of (*E*)-2-butene with (Ipc)BH_2 (**8a**; *Table 4*).

In the reaction of (Ipc)BH_2 (**8a**) with (*Z*)-2-butene, very similar energies were obtained for the transition structures of (*Si*)- and (*Re*)-attack, respectively. This result is compatible with the 60:40 mixture of 2-butanols, found experimentally (*Table 4*). In both cases, the dihedral angle ω(H–B–C(3)–C(4)) is close to 40°. Rotation of the isopinocampheyl group around the B–C bond gives rise to two more conformational minima at *ca.* 190 and 340° with energies 1.53 and 0.92 kcal/mol, respectively, above the one of the transition structure. Similarly, for (*Re*)-attack, two additional conformers were found which are less stable by 1.43 and 1.5 kcal/mol, respectively, than the corresponding transition structure. The quasi-ecliptic arrangement of the substituents at the B-atom and the adjacent C-atom of the double bond, the large angles β' and γ found in transition structures **II** (see *Table 3*), those for attack of $(Ipc)_2BH$ (**8b**), and the strong rotational dependency indicate that the asymmetric induction is due to steric repulsions. In view of this concept, the extraordinarily high asymmetric induction obtained by *Masamune* in the reaction of (*Z*)-2-butene with (2*R*,2*R*)-2,5-dimethylborolane (**9**) is informative [5]: In the transition structure for (*Si*)-attack, the shortest H···H distances

[5]) The conformational changes of the olefinic CH_3 groups were small.

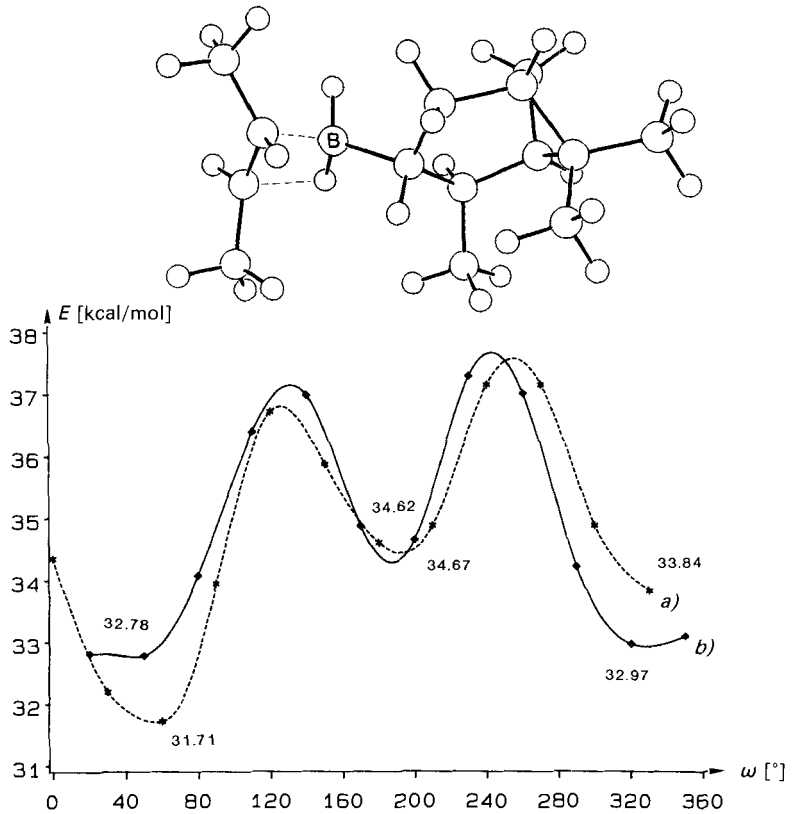


Fig. 3. *Energy of the transition structure for reaction of (1R,2S,3R,5R)-(Ipc)BH$_2$* (**8a**) *with (E)-2-butene* (**11**) *as a function of the dihedral angle ω(H–B–C(3)–C(4)H$_2$)*. Heats of formation (kcal/mol) are given. *a)* (*Si*)-attack (ORTEP-plot of the transition structure); *b)* (*Re*)-attack.

Table 4. *(S)/(R) Ratios of Chiral Alcohols*

Entry	Olefin **18**	R^1R^2BH		$\Delta\Delta H^{\neq}$ [a])	Ratio (*S*)/(*R*)	
		R^1	R^2	[kcal/mol]	calc.[b])	exp.[c])
a	(*Z*)-2-Butene	Ipc	H[d])	−0.09	46:54	60:40
b	(*E*)-2-Butene	Ipc	H[d])	1.37	91: 9	87:13
c	2-Methyl-2-butene	Ipc	H[d])	0.39	66:34	77:23
d	(*Z*)-2-Butene	Ipc	Ipc[e])	−3.57	< 1:99	1:99
e	(*E*)-2-Butene	Ipc	Ipc[e])	1.21	89:11	58:42
f	(*Z*)-2-Butene	[f])		3.37	> 99: 1	99.5:0.5
g	(*E*)-2-Butene	[f])		2.25	99: 2	99:1

[a]) Difference of MNDO-activation enthalpies for diastereoisomeric transition structures (see text).
[b]) Product ratios calculated for $\Delta H^{\neq}$ using the *Eyring* equation [25] for the temperature of the experimental hydroboration.
[c]) Calculated from the alcohols isolated [4] [5].
[d]) (1*R*,2*S*,3*R*,5*R*)-Isopinocampheylborane (**8a**).
[e]) Di[(1*R*,2*S*,3*R*,5*R*)-Isopinocampheyl]borane (**8b**).
[f]) (2*R*,5*R*)-2,5-Dimethylborolane (**9**) [5].

between the borolane ring and (*Z*)-2-butene are 2.31 and 2.45 Å and are thus much smaller than that found in addition of (Ipc)BH_2 (2.94 and 2.89 Å).

With the standard parameters (*Table 1*, **II**) for the structural fragment H···B···C$\overset{\cdots}{—}$C and full optimization of the substituents by the DFP method, relative activation energies for asymmetric hydroborations have been determined (*Table 4*). Given the limited number of substrates considered, the computed product ratios correspond rather well with the experimental results. Including MNDO results obtained for hydroboration of (*Z*)- and (*E*)-2-butene with (2*R*,5*R*)-2,5-dimethylborolane (**9**) [5] with the standard parameter set **II** (*Table 1*), a good linear relation between computed and experimental product ratios has been obtained ($r = 0.92$; *Fig. 4*). The regression line lies above the one to be expected for an exact correspondance between computed and experimental rates and has a larger slope. This indicates that the computed asymmetric inductions are slightly larger than those reported.

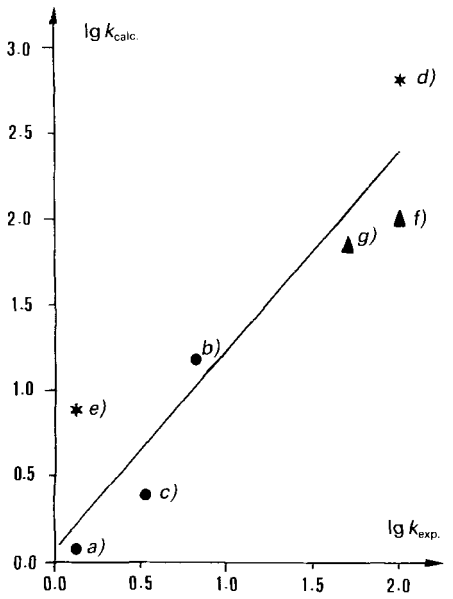


Fig. 4. *Correlation between experimental and calculated asymmetric inductions in hydroboration of some olefins* (*cf. Table 4*); $\lg k_{calc.} = 1.129 \lg k_{exp.} + 0.142$ ($r = 0.92$)

3. *Search for Alternative Hydroborating Agents.* The successful MNDO simulation of the regioselectivity and asymmetric induction lead to a search for hydroborating agents which may enhance selectivity. *Brown* had shown that regioselectivity and stereoselectivity can be improved when olefins are hydroborated with haloboranes like BH_2Cl, BH_2Br, or $BHBr_2$ instead of BH_3 [30]. Using model **I** (*Table 1*), our MNDO results indicate that the regioselectivity indeed increases, when **7a** and **7h** are reacted with BH_2Cl instead of BH_3. It was, therefore, of interest to explore whether asymmetric induction could also be improved using chiral haloboranes. When (Ipc)BHX with X = F, Cl, Br, or CH_3O instead of (Ipc)BH_2 was added to (*Z*)-2-butene, the enantiomeric ratio computed with model **II** (*Table 1*) increased considerably (*Table 5*)[6]).

[6]) For use of (Ipc)BX_2(X = F,Br) as catalyst for asymmetric *Diels-Alder* reactions, see [31].

Table 5. *Substituent Effects in Asymmetric Hydroboration*

Olefin	R^1R^2BH		$\Delta\Delta H^{\neq}$ [a] [kcal/mol]	Ratio (*S*)/(*R*) [b]
	R^1	R^2		
(*Z*)-2-Butene	Ipc	F	2.45	99: 1
	Ipc	Cl	1.86	96: 4
	Ipc	Br	2.13	97: 3
	Ipc	CH_3O	4.62	> 99: 1
(*E*)-2-Butene	Ipc	F	1.23	89:11
	Ipc	Cl	1.69	95: 5
	Ipc	Br	1.94	93: 3
	Ipc	CH_3O	1.65	94: 6
(*Z*)-2-Butene	[c]	H	−0.24	40:60
		F	3.21	> 99: 1
		Cl	1.42	92: 8
		CH_3O	3.63	> 99: 1
(*E*)-2-Butene	[c]	H	0.25	60:40
		F	0.30	63:37
		Cl	0.40	66:34
		CH_3O	−0.20	42:58

[a] Difference of MNDO-activation enthalpies.
[b] Ratios obtained from $\Delta H^{\neq}$ using the *Eyring* equation for $T = 25°$ [25].
[c] R^1 = (*R*)-1,2-Dimethylpropyl (see **10**).

For (*E*)-2-butene, the computed e.e. was in the same range as with (Ipc)BH_2 itself. The origin of this result became apparent when the bond distances and nonbonded interactions in the fully optimized transition structures of (*Si*)-attack were compared: With (Ipc)BH_2 (**8a**), d(B···C), ∢(H···B···C), and ∢(B···C⋯C) are 1.76 Å, 114°, and 72°, respectively, whereas with (Ipc)BHF, the values 1.75 Å, 110°, and 78°, respectively, are observed *(cf. Table 3)*, while the smallest H···H distances are 2.83 and 2.71 Å for **8a** and (Ipc)BHF, respectively. Surprisingly, in the case of (Ipc)BHF, the central H···B···C⋯C fragment is no longer planar, the torsional angle being 10°. When isopinocampheylborane (**8a**) in the reactions with (*E*)- and (*Z*)-2-butene was replaced by (*R*)-(1,2-dimethylpropyl)borane (**10**) which contains the same structural features, the asymmetric induction was found to be of the same order (*cf. Table 4* and *5*). Rotation of the 1,2-dimethylpropyl group in the transition structures of (*Si*)- and (*Re*)-addition to (*E*)-2-butene gives each rise to two additional conformers *(Fig. 5a,b)*.

For the (*Si*)-case, the conformers with dihedral angles ω(H–B–C(1)–CH_3) *(cf. Table 3)* of 200 and 345° were 2.7 and 1.4 kcal/mol, respectively, above the transition structure *(Fig. 5a)*, whereas in the (*Re*)-addition, the conformers at 50 and 170° had energies 0.85 and 2.63 kcal/mol, respectively, larger than the corresponding transition structure *(Fig. 5b)*. The rotational profiles for addition to (*E*)-2-butene resemble closely those found for reaction of (Ipc)BH_2 *(Fig. 3a,b)*. In line with the close similarity of (*R*)-(1,2-dimethyl)propylborane (**10**) with (Ipc)BH_2 (**8a**) in asymmetric induction, substitution of one hydride in **10** by F, Cl, or CH_3O leads to an increase in the computed e.e., especially for (*Z*)-2-butene *(Table 5)*. These results indicate that asymmetric hydroborations can further be improved if substituent effects in chiral alkylboranes are considered. In order to test this concept, appropriate experiments are pursued in our laboratory.

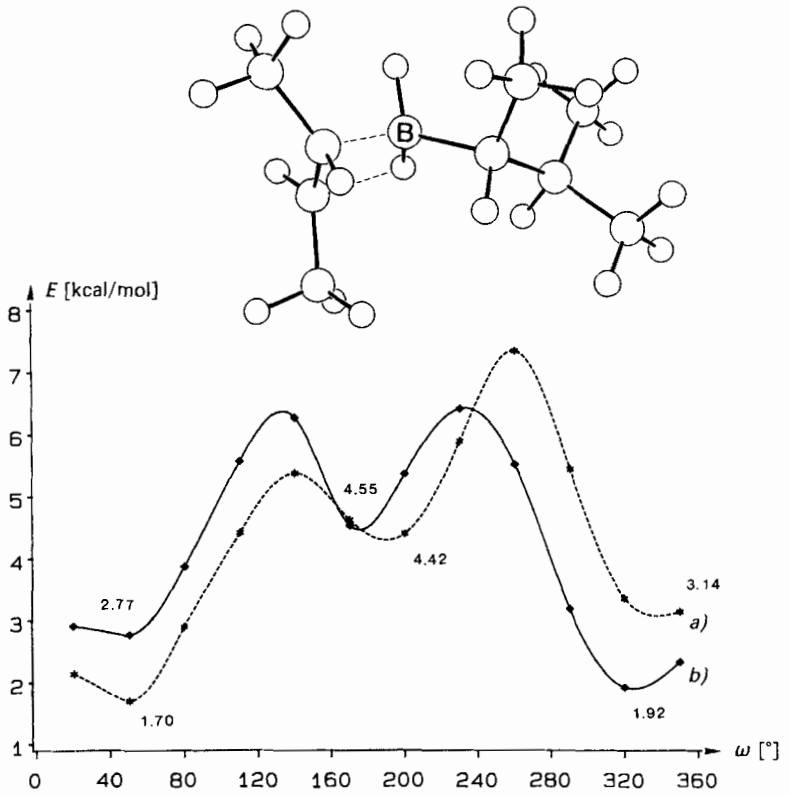


Fig. 5. *Energy of the transition structure for reaction of (*R*)-(1,2-dimethylpropyl)borane* (**10**) *with (*E*)-2-butene as a function of the dihedral angle* $\omega(H-B-C(1)-CH_3)$. Heats of formation (kcal/mol) are given. *a)* (*Si*)-attack (ORTEP-plot of the transition structure); *b)* (*Re*)-attack.

Conclusions. – The regioselectivity of reactions of BH_3 with substituted olefins is well reproduced by MNDO calculations. The asymmetric induction in reactions of symmetrical olefins with little steric hindrance has likewise been investigated. Using standard transition structures, the correlation between the computed and experimental results are hardly affected, while the computations become much faster. The full optimization of the transition state of addition of BH_3 to **7b** requires 300 sec, whereas the DFP optimization of the standard transition structure **I** *(Table 1)* for the same reaction is complete in 50 sec. In the reaction of (Ipc)BH_2 with (*Z*)-2-butene, the DFP optimization of 10 min with the standard transition structure is to be compared with 2.5 h required for the full geometry optimization[7]). The major advantage of the DFP method combined with standard transition structures becomes apparent in the search for new reagents where computer times of more than 1 h per reaction on a mainframe computer are not tolerable. Qualitatively, the regioselectivity in hydroboration is related to differences in the HOMO coefficients in the substituted olefins. For asymmetric inductions, steric interactions between the chiral substituents at the B-atom and those of the olefin play a dominant role.

[7]) For all calculations, the MNDO programs MOPAC [7] and AMPAC [26] were used on a *IBM 3090-180* at the *Bernische Datenverarbeitungs AG (BEDAG)*.

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