Revisiting the Stereoselectivity in Organoborane Rearrangement

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Abstract

Hydroboration of 1,2-dimethylcyclohexene (**A**) and successive rearrangements yield not only tertiary alkylboranes but also primary and secondary ones. In addition, nontypical *anti*-addition products are detected, whose formation mechanism is not apparent. Herein, we revisit three mechanisms proposed in the literature: an elimination and readdition, an intramolecular process involving an intermediate π-complex, and an intramolecular migration. According to our computations, the formation of all products starts from the tertiary alkylborane obtained by hydroboration of olefin **A**. This alkylborane then undergoes a sequence of further retrohydroborations and hydroborations in a *syn* fashion. Interestingly, the conformational changes on the ring affect these transformations and decide the rearrangement mechanism. Free olefin intermediates are generated during these reactions, which are then rehydroborated from their opposite faces, explaining the formation of *anti*-addition products. Moreover, the temperature effect on the rearrangement reactions is also analyzed.

Introduction

In 1957, Brown and Rao reported the use of diborane as a reducing agent for organic compounds,[1] which eventually led to the discovery of the alkene hydroboration reaction. The stereochemistry of hydroboration is explained through the *syn*-addition of borane to olefins in the anti-Markovnikov fashion via the formation of a π-complex followed by a four-membered ring transition state (4MR-TS), *i.e.*, hydrogen and BH_2 bind to the same π-face of the alkene.[2–9]

However, Brown and Rao observed as early as 1957 that, upon heating, products resulting from the hydroboration/oxidation of 2-pentene, 2-hexene, and a mixture of 2-, 3-, 4-, and 5-decenes are primary alcohols![2] This was explained by an elimination followed by the readdition of borane in the corresponding organoborane (Figure 1). They also indicated that borane migrates to a less sterically hindered carbon,[3] resulting from the displacement of a double bond from inside the carbon chain to a terminal position,[4] even organoboranes with steric hindrance in the boron moiety rearranged faster.[5] Ten years later, Rosi and co-workers suggested a π-complex intermediate to explain this alkylborane rearrangement.[10]

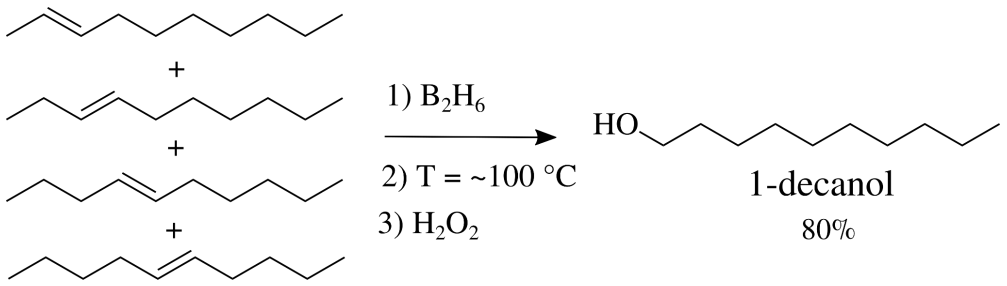

Figure 1. Hydroboration/oxidation of a mixture of 2-, 3-, 4-, and 5-decenes affords 1-decanol in good yield.[2]

Another oddity was reported in the hydroboration/oxidation of 1,2-dimethylcyclohexene (**A**), where only tertiary alcohols should be expected, but in 1971, Wood and Rickborn noted the formation of primary alcohols from this cyclic alkene.[11] In

subsequent work in 1983, these authors extended the study to 2-methyl-1-methylenecyclohexane (**B**) and 1,6-dimethylcyclohexene (**C**) and attempted to understand their rearrangements to secondary and primary alkylboranes at 373.15 K (Figure 2).[12] To this end, they proposed an intramolecular rearrangement via a π-complex intermediate, ruling out the mechanism suggested by Brown.[5]

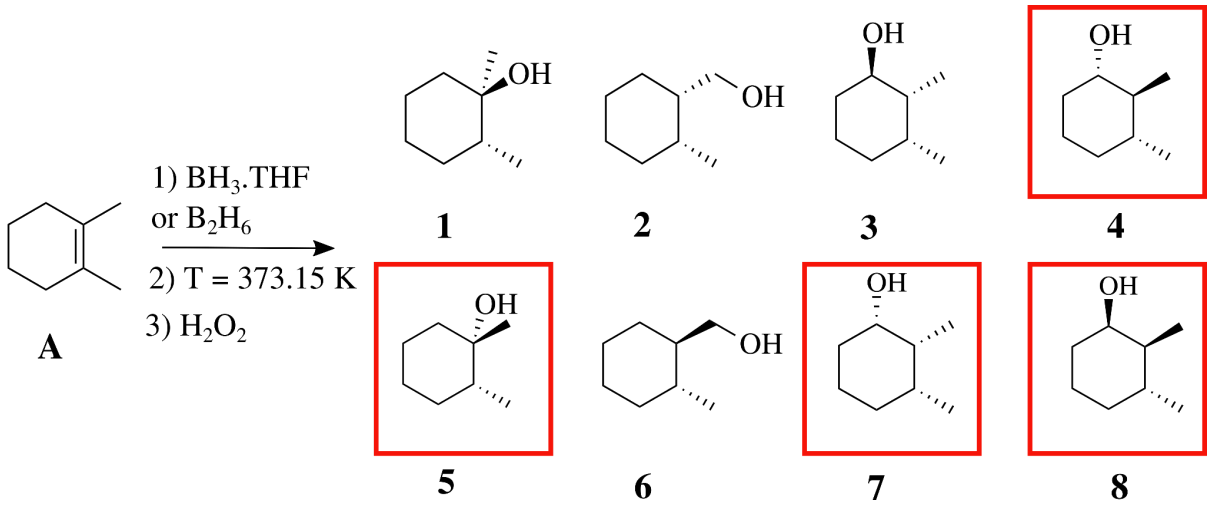

Figure 2. Hydroboration/oxidation products of 1,2-dimethylcyclohexene (**1**) obtained by Wood and Rickborn.[12] The *anti*-addition products are in red boxes.

In 1985, Field and Gallagher[13] noted the room temperature conversion of tertiary alcohol, obtained from the hydroboration/oxidation of 1,2-dimethylcyclopentene, to a secondary one. They suggested (although not explicitly) that the Wood and Rickborn (WR) mechanism (Figure 3b) prevails under mild conditions. In contrast, the Brown and Rao (BR) alternative (Figure 3a) predominates at high temperatures. Some years later, van Eikema Hommes and Schleyer (ES)[14] found the transition state (TS) for the intramolecular rearrangement of ethylborane (Figure 3c). This TS has a B-H bond perpendicular to the C=C bond, and the imaginary frequency corresponds to the rotation of the BH_3 unit. Therefore, the ES mechanism does not involve a π-complex as an intermediate for the intramolecular rearrangement suggested by the WR mechanism. The barrier for this intramolecular process

is lower than the energy required to dissociate the complex into ethylene and borane, but at higher temperatures, the dissociation mechanism may take place, as shown by experiments.[12,13,15]

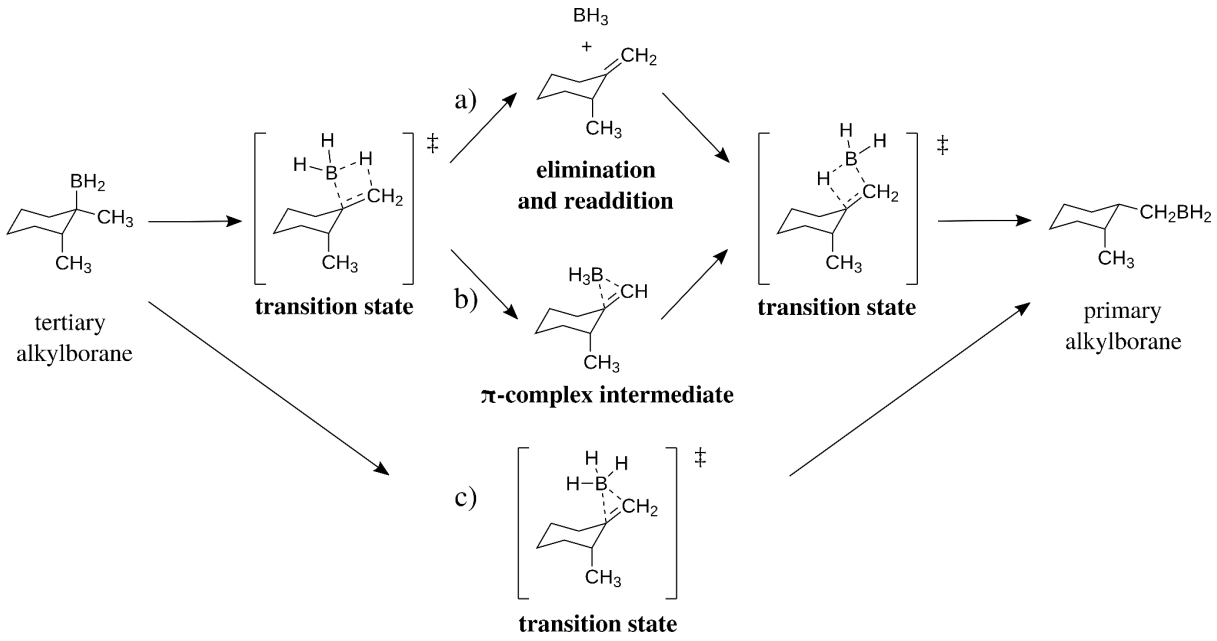

Figure 3. Proposed mechanisms for alkylborane rearrangements: a) Brown and Rao,[2] b) Wood and Rickborn,[12] and c) van Eikema and Schleyer.[14]

There is a conundrum in this story, the mechanisms of BR, WR, and ES do not explain the formation of *anti*-products (alcohols **4**, **5**, **7**, and **8**, Figure 2) synthesized by Wood and Rickborn in 1982. Even since 1961, Brown and Zweifel detected the *anti*-product (*cis*-2-methylcyclohexanol) during the hydroboration/oxidation of 1-methylcyclohexene. Around the 1990s, Fleming and Lawrence found a high stereoselectivity in favor of the *anti*-products in the hydroboration of allylsilanes with 9-BBN (9-borabicyclo[3.3.1]nonane), denoting a consecutive series of eliminations and readditions.[16–18] Hanson and co-workers studied the hydroboration of androst-4-enes and observed that allylic hydroxyl groups carry a facial selectivity towards the β-face even with steric hindrance,[19] opposite to the expected α-face hydroboration. The proposed mechanism alludes to a borane elimination to form a

3-ene, followed by the attack of a second borane molecule to the *trans* face due to the formation of bulky borate complexes from the alcohol. In 1999, Knochel and co-workers[20] explained the thermal rearrangements of *syn*- and *anti*-tertiary organoboranes, obtained by the hydroboration of tetrasubstituted olefins, to primary organoboranes by a Brown mechanism through a metastable intermediate borane-olefin complex. In recent studies, the *anti*-hydroboration of internal alkynes to give 1,2-disubstituted (*E*)- alkenylboron compounds represents a major challenge. In the proposed catalytic cycle for this *anti*-hydroboration, the *anti* stereochemistry of the reaction comes from the concerted nature of the final elimination step and the B-X interaction (X = N, O, S).[21–23] Under radical conditions, Taniguchi and co-workers achieved the *trans*-hydroboration of internal aryl alkynes[24] and the hydroboration of substituted 1,3-diynes with *N*-heterocyclic carbene boranes to give (*E*)-alkenylboranes.[25] From a mechanistic point of view, it is mandatory to understand the lower energy pathway related to the formation of *anti*-addition products that occur in hydroboration. Recently, we reported the synthesis of *trans*-hydroboration-oxidation products obtained through hydroboration of diosgenin and cholesterol under mild conditions in good yields.[26] The formation of these non-typical products was explained by a retrohydroboration mechanism. This has motivated us to understand the details of olefins hydroboration better and, in particular, its rearrangements.

How to explain the different products obtained by Wood and Rickborn? In this work, we revisited the hydroboration of **A**.[12] We have elucidated the pathways for all experimentally synthesized products by quantum chemical computations. Hydroboration/oxidation of olefin **A** yields eight products (from **1**-**8,** see Figure 2). Four of them are *anti* (**4**, **5**, **7**, and **8** marked in red boxes), and two are primary alcohols (**2** and **6**). Our computations indicate that the products are not formed by a single mechanism but by a cascade of diverse mechanisms.

Computational Details

The elucidation of the mechanisms was carried out at the MP2[27]/def2-TZVP[28] level, considering the effects of the solvent (THF) via the SMD[29] solvation model. Gibbs free energies were obtained at the SMD-DLPNO-CCSD(T)[30–32]/def2-TZVPP[28] level, taking into account entropic contributions and thermal corrections computed at the SMD-MP2/def2-TZVP level at 373.15 K (the reaction temperature). The harmonic vibrational frequencies determined the nature of each stationary point. The intrinsic reaction coordinate (IRC)[33] approach ensures that each TS correctly connects the corresponding reactants and products. All computations were done in Gaussian 16[34] and Orca 4.1.2.[35] The temperature effects over hydroboration and rearrangement reactions are analyzed using the Eyringpy program.[36,37] With Eyringpy, the thermochemical properties are calculated from the partition functions at different temperatures.

Results

Let us focus our analysis on the hydroboration mechanism since it is supposed that the alcohol formed retains its configuration in the oxidation step; so, we label the alkylborane as **1′** to that which produces **1** after oxidation. The formation of **1'** is exergonic (7.6 kcal mol^{-1} with respect to the reactants, see Figure 4) and involves a 4MR-TS (**TS1**$_{\mathbf{A\text{-}1'}}$) with a barrier of 7.6 kcal mol^{-1}.

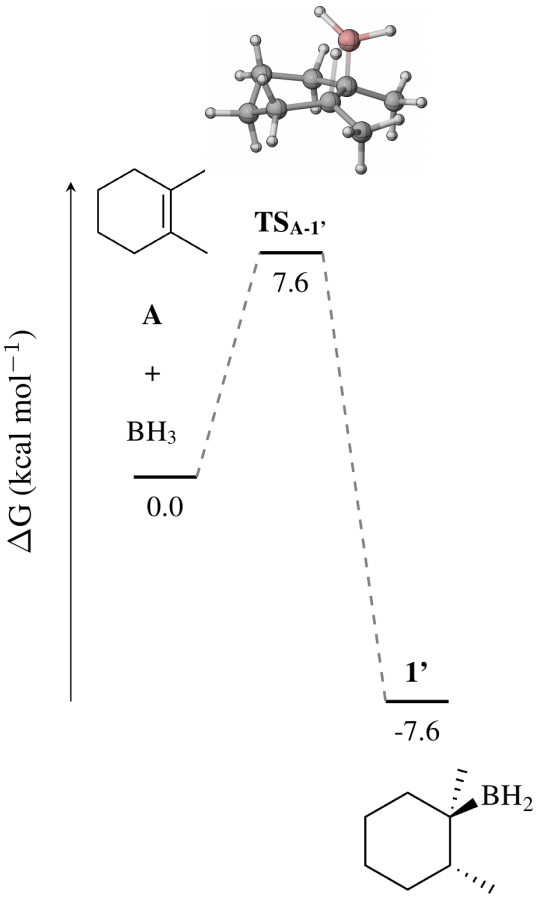

Figure 4. Free energy profile for the hydroboration of **1**. Gibbs free energies in kcal mol^{-1}. C, B, and H atoms are denoted by gray, pink, and white colors, respectively.

Converting the tertiary alkylborane **1'** to **2'** could take place through any of the three mechanisms discussed above (BR, WR, and ES). We must consider that the six-membered ring is flexible, and its dynamics could favor certain trajectories. In fact, the BR and WR mechanisms require a chair-to-chair conformational isomerization from **1'** to **1a'** (see Figure S1). Briefly, the first step of this conformational change is the rate-limiting step with a barrier of 11.8 kcal mol^{-1} (**TS1**$_{1'\text{-}1a'}$), and after three steps with barriers lower than 6.3 kcal mol^{-1}, the intermediate **1a'** is obtained. Figure 5a shows the tertiary-primary rearrangement from **1a'** to **2'** (green line) following the WR pathway. **1a'**, which is 2.0 kcal mol^{-1} less stable than **1'**, undergoes retrohydroboration via **TS1**$_{1a'\text{-}2'}$ ($\Delta G^{\ddagger}$=15.4 kcal mol^{-1}), producing the π-complex

intermediate **Int1**$_{\mathbf{1a'\text{-}2'}}$. This complex can dissociate to **B** (blue line) and borane since these reactants are only 0.1 kcal mol^{-1} energetically less stable than **Int1**$_{\mathbf{1a'\text{-}2'}}$. So, the BR mechanism is also energetically favorable at 100 °C. From **Int1**$_{\mathbf{1a'\text{-}2'}}$, the primary organoborane **Int2**$_{\mathbf{1a'\text{-}2}}$ is obtained with a small barrier of 1.5 kcal mol^{-1} through **TS2**$_{\mathbf{1a'\text{-}2'}}$. Finally, a conformational rearrangement across a low barrier (**TS3**$_{\mathbf{1a'\text{-}2'}}$, $\Delta G^{\ddagger}$ = 0.9 kcal mol^{-1}) leads to **2'**. Note that the formation of **2'** is 2.1 kcal mol^{-1}, more exergonic than that of **1'**.

In contrast, the first step in the ES mechanism (**TS1**$_{\mathbf{1'\text{-}2'}}$) involves the migration of the BH_2 unit from C1 of **1'** to the vicinal methyl group, requiring 17.1 kcal mol^{-1} to overcome the barrier (Figure 5b, red line). This step, which is 1.7 kcal mol^{-1} higher than the rate-determining barrier (**TS1**$_{\mathbf{1a'\text{-}2'}}$) of the WR pathway, turns out to be the rate-determining step of the tertiary-primary intramolecular rearrangement of **1'**. The imaginary frequency indicates that boron accepts a hydrogen atom from the methyl group to form BH_3, and concomitantly a rotation of the BH_3 unit occurs, forming the C1-H bond and linking the BH_2 moiety to the methyl group to give **Int1**$_{\mathbf{1'\text{-}2'}}$. The next four steps comprise a chair-to-chair conformational change (purple line, Figure S2) of **Int1**$_{\mathbf{1'\text{-}2'}}$. This process through the half-chair and boat conformations yields **2'** with a barrier of 10.2 kcal mol^{-1}.

Thus, the **1'** to **2'** transformation prefers the WR pathway over the BR or ES mechanisms and, according to our computations, the **1'** to **1a'** conformational arrangement facilitates the conversion from tertiary to primary alkylborane by the WR pathway at the reaction temperature.

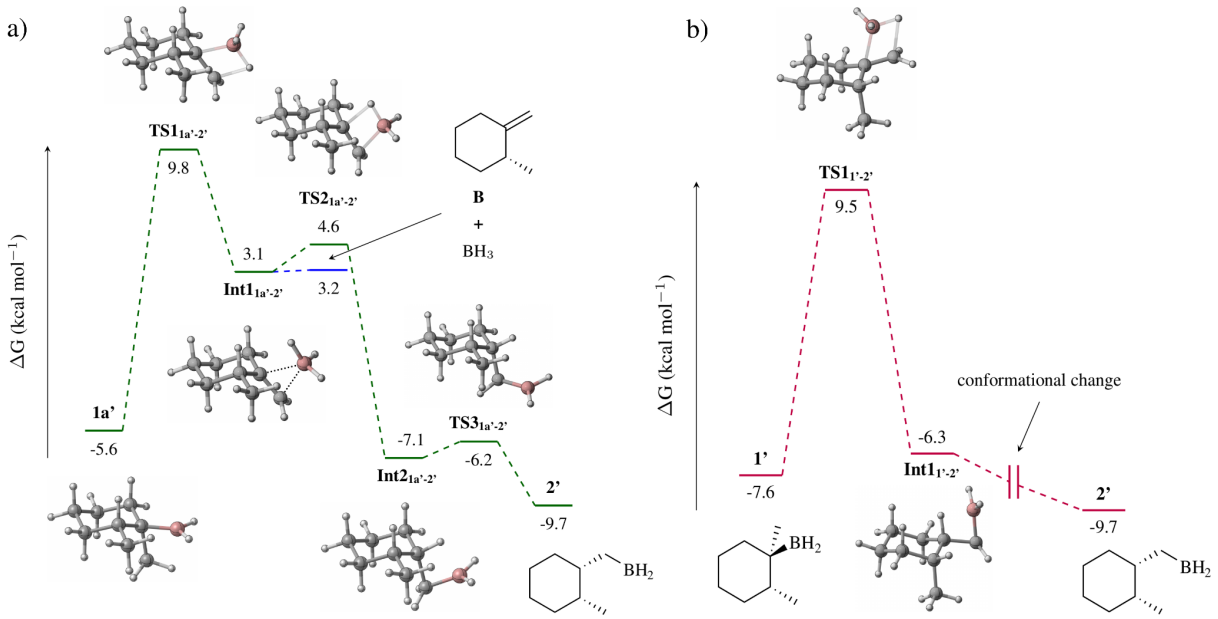

Figure 5. Free energy profiles for the rearrangement a) from **1a'** to **2'** via the WR mechanism, and b) from **1'** to **2'** via the ES mechanism followed by a conformational arrangement depicted in Figure S2. Gibbs free energies in kcal mol^{-1}.

1' also gives rise to **3**' (see Figure 6). The first process ($\mathbf{TS1_{1'\text{-}C}}$, $\Delta G^{\ddagger} = 8.9$ kcal mol^{-1}) involves a chair-to-boat conformational change. Next, the intermediate $\mathbf{Int_{1'\text{-}C}}$ is retrohydroborated through $\mathbf{TS2_{1'\text{-}C}}$, forming olefin **C** and borane. The formation of $\mathbf{Int_{1'\text{-}C}}$ reduces the retrohydroboration barrier of $\mathbf{TS2_{1'\text{-}C}}$ (10.7 kcal mol^{-1}), which is similar to that computed for $\mathbf{TS1_{1'\text{-}C}}$. The expected π-complex does not form due to its thermal instability with respect to **C** and borane. This implies that the rearrangement prefers the BR alternative over the WR mechanism at reaction temperature. Hydroboration of olefin **C** could produce **3'** but involves crossing two small barriers of 7.1 and 1.0 kcal mol-1 via $\mathbf{TS1_{C\text{-}3'}}$, and $\mathbf{TS2_{C\text{-}3'}}$, respectively. Note that **3'** is slightly more stable than **1'**. Therefore, the conversion of **1'** to **3'** is a tertiary-secondary rearrangement involving the BR mechanism.

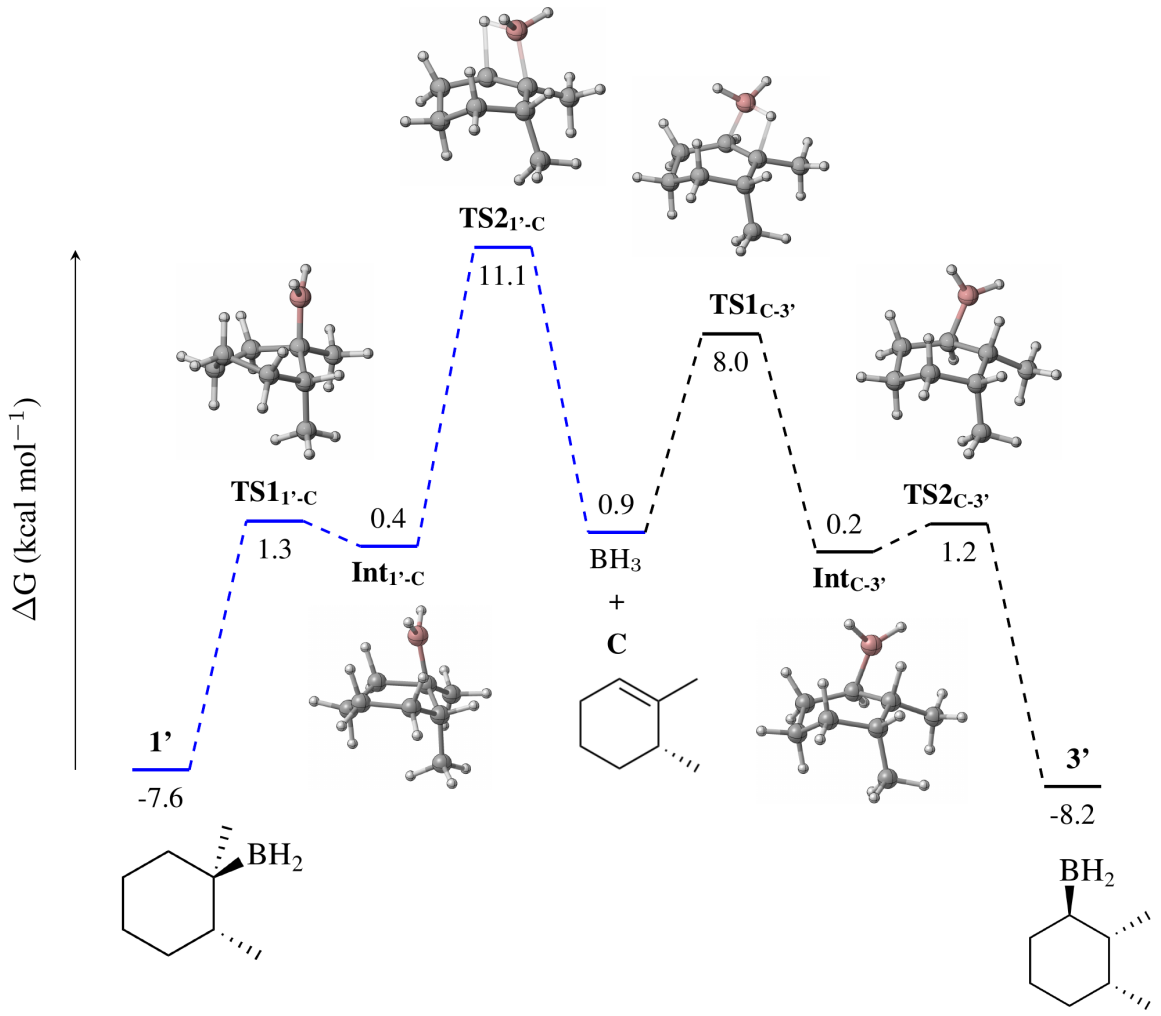

Figure 6. Free energy profile for the tertiary-secondary rearrangement of **1'** to give **3'** involving retrohydroboration. Gibbs free energies in kcal mol^{-1}.

The formation of **C** via the BR mechanism is crucial to explain the presence of the other products. When **C** is hydroborated from its other face in both Markovnikov (cyan line, Figure 7) and anti-Markovnikov (black line, Figure 7) *syn*-additions, the *anti*-addition products **4'** and **5'** are obtained. The difference between $\mathbf{TS1}_{\mathbf{C\text{-}4'}}$ and $\mathbf{TS1}_{\mathbf{C\text{-}5'}}$ ($\Delta\Delta G^{\ddagger}$ = 2.6 kcal mol^{-1}) favors the anti-Markovnikov product (**4'**), a secondary alkylborane. $\mathbf{Int}_{\mathbf{C\text{-}4'}}$ is then transformed directly to the product **4'** via an almost barrier-free conformational arrangement ($\mathbf{TS2}_{\mathbf{C\text{-}4'}}$, $\Delta G^{\ddagger}$ = 0.2 kcal mol^{-1}). In contrast, the tertiary alkylborane **5'** is obtained via two

steps ($\mathbf{TS2}_{\mathbf{C\text{-}5'}}$ and $\mathbf{TS3}_{\mathbf{C\text{-}5'}}$), involving conformational changes with low activation energies (1.4 and 6.2 kcal mol^{-1}).

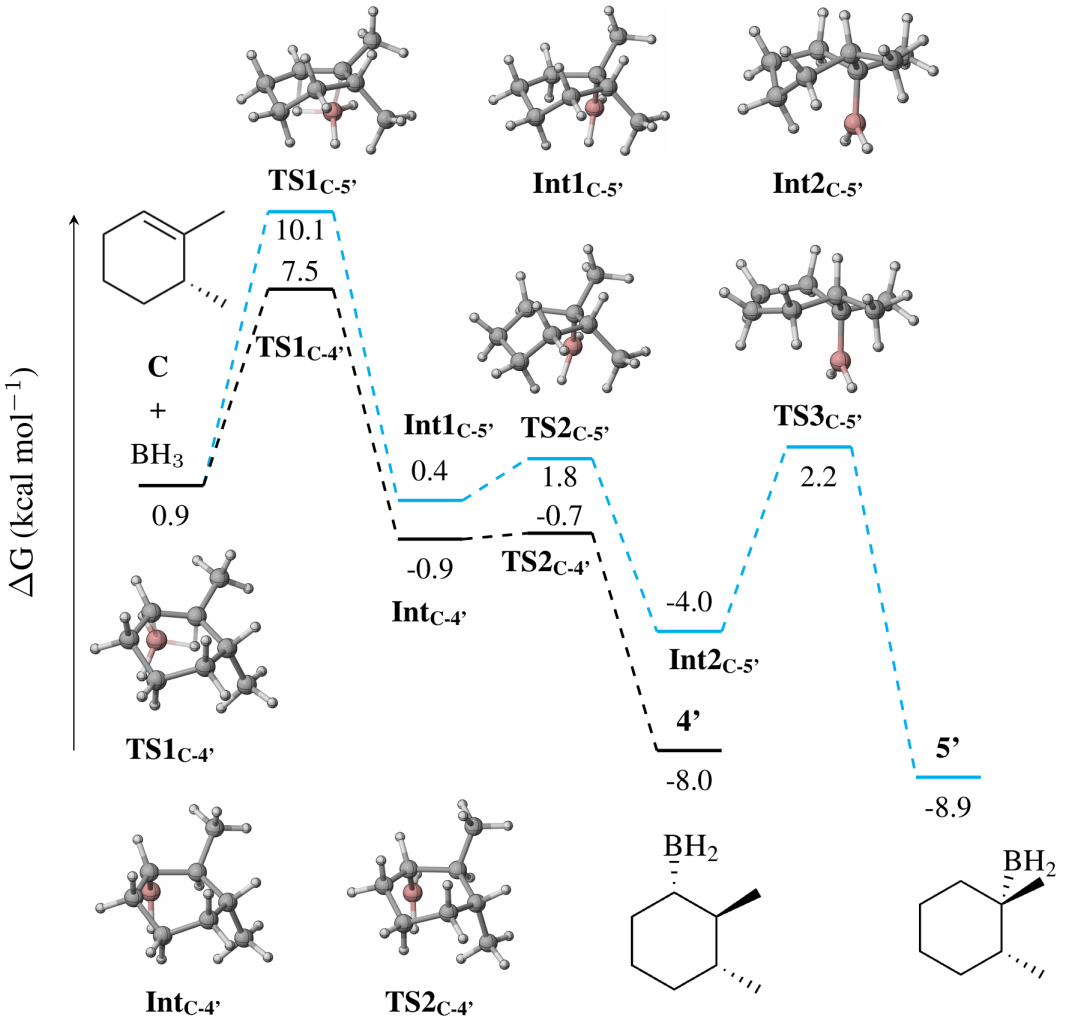

Figure 7. Free energy profile for the hydroboration of **C** by opposite face to yield **4'** and **5',** the anti-Markovnikov and Markovnikov products, respectively. Gibbs free energies in kcal mol^{-1}.

Subsequently, **5'** becomes **6'** through an ES mechanism that follows a tertiary-primary rearrangement process. First, **5'** undergoes a chair-to-chair conformational arrangement leading to **5a'** (Figure S3). Similar to the **1'-1a'** rearrangement, **5'** to **5a'** interconversion requires a stepwise mechanism involving a chair, half-chair, twist boat, and boat conformations. In this process, the rate-limiting step is $\mathbf{TS1}_{\mathbf{5'\text{-}5a'}}$ ($\Delta G^{\ddagger}$ = 11.1 kcal mol^{-1}) and

involves a half-chair conformation. In **5a'**, both methyl groups are axial and BH_2 is equatorial. In the second step, intramolecular migration rearranges **5a'** to **6'** (Figure 8a). The BH_2 unit migrates to the -CH_3 group via $\mathbf{TS1}_{\mathbf{5a'\text{-}6'}}$, with a rate-determining barrier of 15.6 kcal mol^{-1}. This TS follows the same reaction path as the ES mechanism, similar to that of $\mathbf{TS1}_{\mathbf{1'\text{-}2'}}$ (Figure 5b), leading directly to the primary alkylborane $\mathbf{Int1}_{\mathbf{5a'\text{-}6'}}$, without forming a π-complex. Eventually, $\mathbf{Int1}_{\mathbf{5a'\text{-}6'}}$, is conformationally arranged to **6'** (see Figure S4). The chair conformation of this primary alkylborane (**6'**) has both substituents in equatorial positions; therefore, it favors the interaction between the boron atom and a hydrogen atom of the methyl group. Consequently, the formation of **6'** becomes more exergonic (ΔG_{rxn} = 11.6 kcal mol^{-1}) than **2'** (ΔG_{rxn} = 9.7 kcal mol^{-1}).

But the **5'** to **6'** rearrangement can also occur directly through the same ES mechanism (Figure 8b). The first barrier of 18.7 kcal mol^{-1} ($\mathbf{TS1}_{\mathbf{5'\text{-}6'}}$) associated with the displacement of the BH_2 unit from C1 of **5'** to the vicinal carbon atom of the methyl group is the rate-limiting step. Depending on the reaction path, this migration involves the formation, rotation, and dissociation of the BH_3 fragment, giving $\mathbf{Int1}_{\mathbf{5'\text{-}6'}}$. The determining barrier of this pathway is 3.1 kcal mol^{-1} higher in energy than that of the previous via $\mathbf{TS1}_{\mathbf{5a'\text{-}6'}}$, (Figure 8a). The most stable conformation of **6'** is reached in the last step ($\mathbf{TS2}_{\mathbf{5'\text{-}6'}}$, $\Delta G^{\ddagger}$ = 0.5 kcal mol^{-1}). Note that the primary alkylborane **6'** comes from **5'**, a nontypical Markovnikov addition product of **C** (Figure 7). Then, **C** is a product of the retrohydroboration of **1'** (Figure 6). These energetically less favorable reactions to produce **6'** explain its poor yield and selectivity compared to **2'**. Nevertheless, the formation of **6'** is favored by the exergonicity and thermal and structural stability.

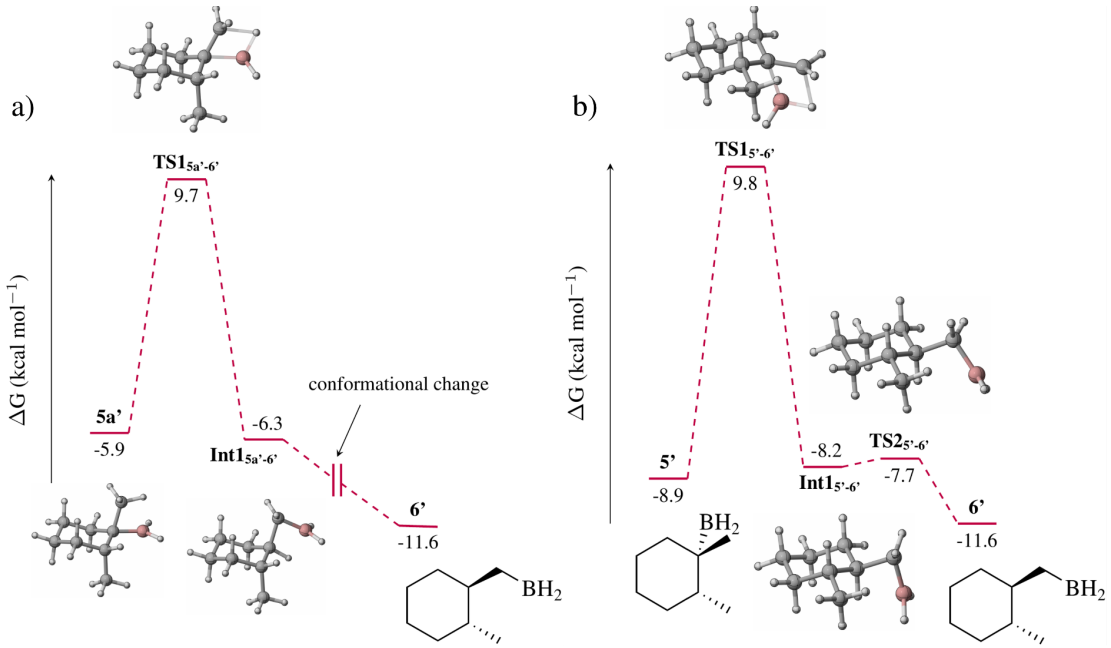

Figure 8. Free energy profile for the intermolecular rearrangement from **5a'** (a) and **5'** (b) to **6'** via the ES mechanism followed by a conformational arrangement depicted in Figure S4. Gibbs free energies in kcal mol^{-1}.

To obtain **7**, **3'** must undergo a secondary-secondary rearrangement via the BR mechanism, which involves an elimination to form olefin **D** followed by successive Markovnikov (cyan line) and anti-Markovnikov (black line) additions on the opposite face of **D** (Figure 9). **3'** is retrohydroborated first (**TS$_{3'-D}$**) and yields the free olefin **D** and borane. Unlike the two-step retrohydroboration of **1'** (see Figure 6), this mechanism is concerted and has a higher but still reasonable barrier ($\Delta G^{\ddagger}$ = 18.2 kcal mol^{-1}). Then, borane attacks **D** on the other face in both Markovnikov and anti-Markovnikov manner, producing 2,3-dimethylcyclohexylborane (**7'**) and an unreported product 3,4-dimethylcyclohexylborane (**9'**), respectively. The $\Delta\Delta G^{\ddagger}$ for the transition states (**TS$_{D-7'}$** and **TS$_{D-9'}$**) leading to the two products is relatively low (0.9 kcal mol^{-1}), and their formations are almost degenerate in energy ($\Delta\Delta G_{rxn}$ = 0.2 kcal mol^{-1}).

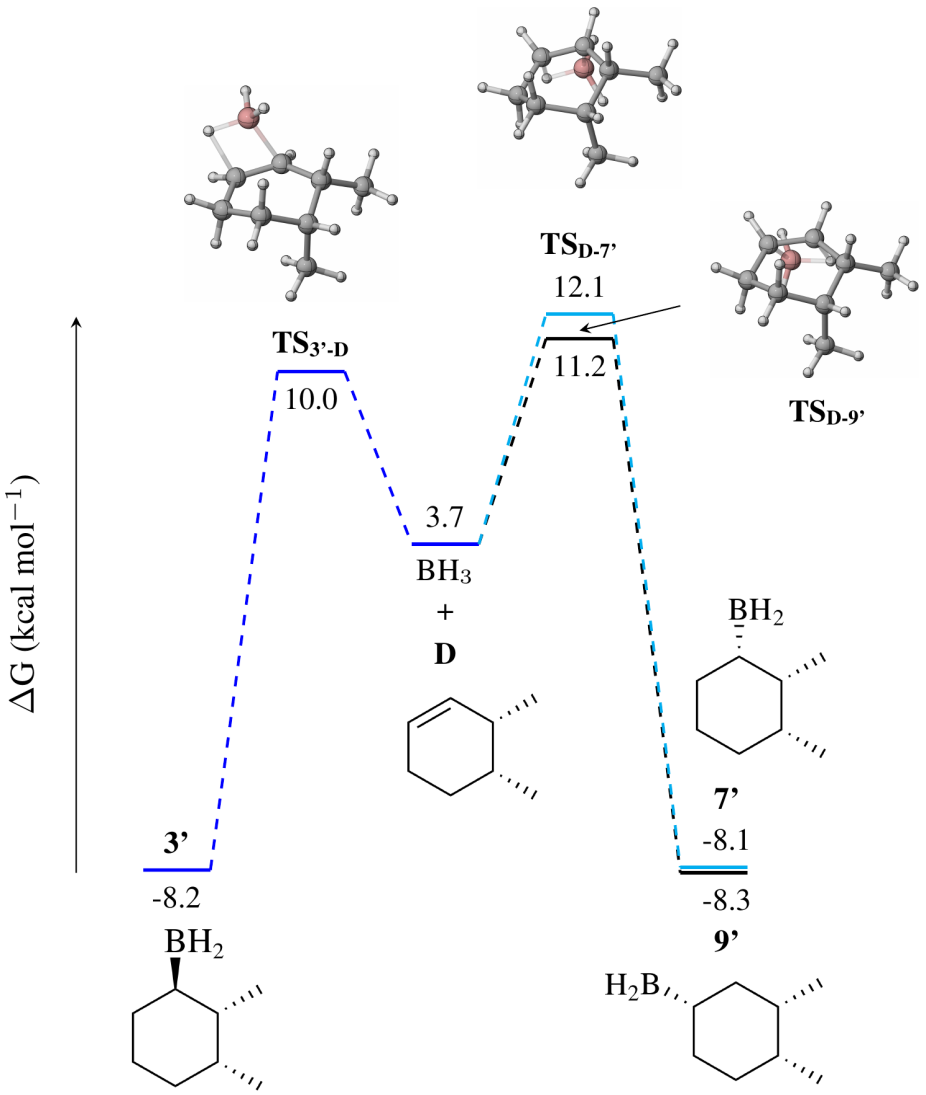

Figure 9. Free energy profile for the intermolecular rearrangement from **3'** to **7'** and **9'** via the BR mechanism. Gibbs free energies in kcal mol^{-1}.

Finally, **4'** rearranges into the secondary alkylborane **8'**, following the BR mechanism (Figure 10). As in the previous case, the conversion of **4'** to **8'** proceeds by retrohydroboration, and a subsequent rehydroboration from the opposite face of the olefin **E**. **4'** directly generates olefin **E** and BH_3 via a 4MR-TS ($\mathbf{TS_{4'\text{-}E}}$). The retrohydroboration barrier ($\mathbf{TS_{4'\text{-}E}}$) is 1.9 kcal mol^{-1} higher than the **3'** to **7'** rearrangement ($\mathbf{TS_{3'\text{-}D}}$). The olefin **E** is attacked by borane on the other face of its double bond. Thus, **E** then undergoes Markovnikov (cyan line) and anti-Markovnikov (black line) hydroboration through barriers ($\mathbf{TS1_{E\text{-}8'}}$ and

TS1$_{E-10'}$) that are degenerate in energy via 4MR-TSs. Before obtaining the final products (**8'** and **10'**, the latter being an unreported product), the intermediates **Int$_{E-8'}$** and **Int$_{E-10'}$** are ordered via **TS2$_{E-8'}$** ($\Delta G^{\ddagger}$ = 1.2 kcal mol^{-1}) and **TS2$_{E-10'}$** (barrierless), respectively. The formation of **8'** and **10'** is degenerate (ΔG_{rxn} = 7.9 kcal mol^{-1}).

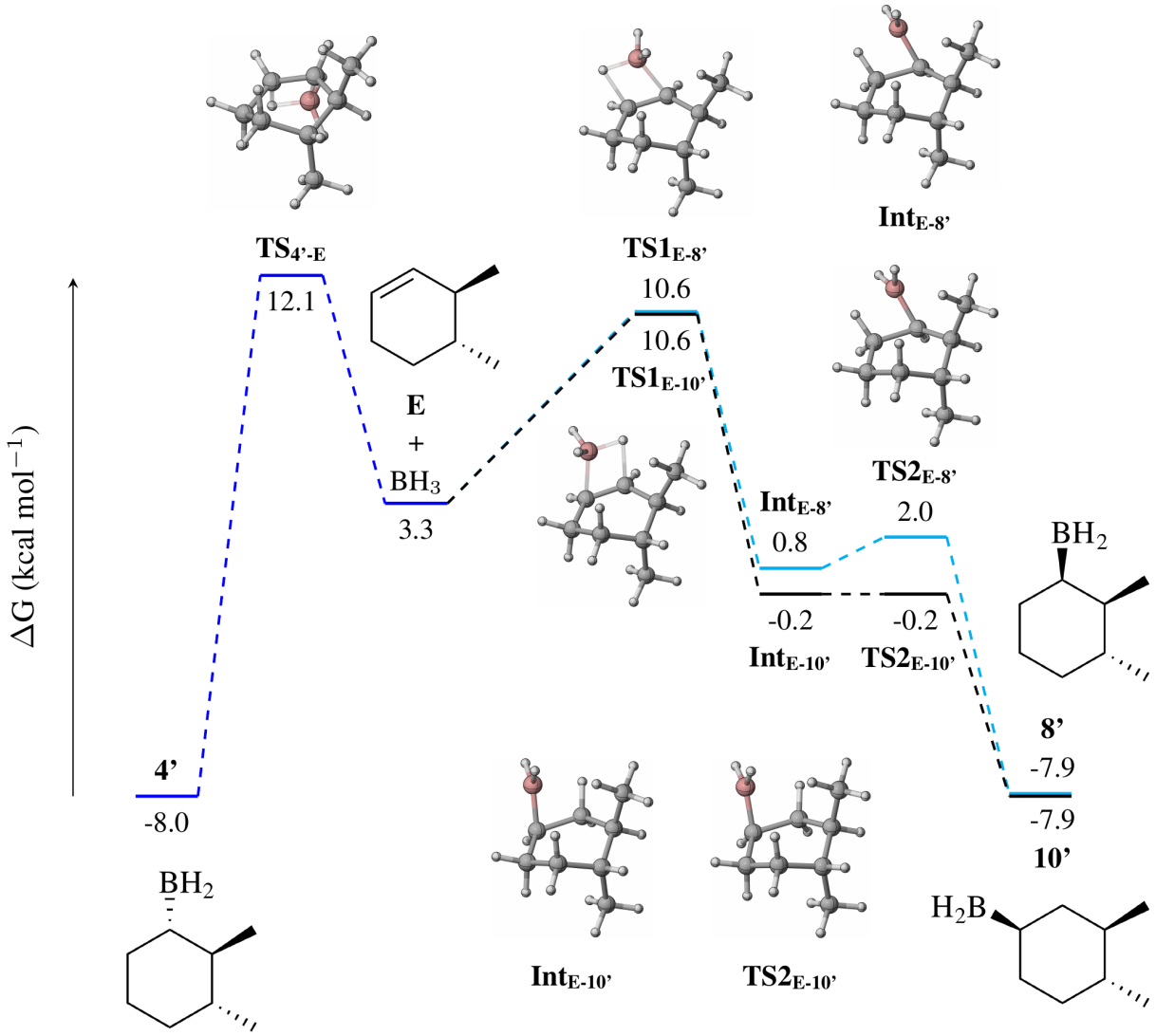

Figure 10. Free energy profile for the intermolecular rearrangement from **4'** to **8'** and **10'** via BR mechanism. Gibbs free energies in kcal mol^{-1}.

The proposed mechanisms explain the products reported by Wood and Rickborn in their original paper, except for two of them (**5** and **6**, Figure S5). Only the formation of **5** and **6** can occur from **A**, but Wood and Rickborn report the corresponding enantiomers.

Interestingly, the authors reported that hydroboration of olefin **C** yields the same products as **A**, although they do not specify the stereochemistry of **C**. It should be noted that the experimental analysis is based solely on retention times and shows no evidence of ^{1}H NMR. Suppose we carry out the retrohydroboration of **1'**. In that case, we return to the original olefin **A**. Although the formation of the π-complex takes place on the opposite side, it is not possible to form the enantiomer of **5**. In the case of **6**, which comes from **5**, it is also impossible to form its enantiomer from **A**. Another detail is that we find **9** and **10**, two products that have not been reported but whose barriers indicate that they could be formed.

Since rearrangement reactions occur upon heating, we analyzed the effect of temperature on the reaction mechanisms. Figures S6-16 show all energy profiles already discussed but computed at room temperature (298.15 K). In general, all reactions become more exergonic at room temperature. Consequently, the hydroboration and retrohydroboration barriers are also affected, although not significantly. Note that the formation of the π-complexes $\mathbf{Int1}_{\mathbf{A\text{-}1'}}$, $\mathbf{Int2}_{\mathbf{1'\text{-}3'}}$, $\mathbf{Int}_{\mathbf{3'\text{-}D}}$, and $\mathbf{Int1}_{\mathbf{E\text{-}8'}}$ (Figures S6, S10, S15, and S16, respectively) is energetically viable at 298.15 K, but not at the reaction temperature (373.15 K), implying that the hydroboration reaction is unimolecular at room temperature but bimolecular at higher temperatures. In other words, these rearrangements proceed by the WR mechanism at room temperature, while at higher temperatures, the BR mechanism is prevalent.

Summary and Outlooks

Typical hydroboration of olefin **A** followed by a series of retrohydroborations and new hydroborations in *syn* manner give rise to all synthesized products, as summarized in Figure 11, including *anti*-addition products. In summary,

1. **1'** is produced by the classical hydroboration of olefin **A**.

2. **2'** is obtained from **1'**, which must first be conformationally arranged to **1a'** and then undergoes a tertiary-primary rearrangement via the WR mechanism.
3. **3'** is formed by a tertiary-secondary rearrangement of **1'** via the BR mechanism.
4. **4'** and **5'** results from **1'** via the BR mechanism. The retrohydroboration of **1'** yields a free olefin intermediate **C** followed by rehydroboration from its opposite face, giving anti-Markovnikov **4'** and Markovnikov **5'** products.
5. **6'** comes from **5'** through the ES mechanism. A conformational arrangement first converts the Markovnikov product **5'** to **5a'**, facilitating its tertiary-primary transformation toward **6'**.
6. **7'** and **8'** are obtained from **3'** and **4'**, respectively, via the BR mechanism in which, in each case, retrohydroboration forms free olefin intermediates (**D** and **E**) followed by readdition from their opposite faces.

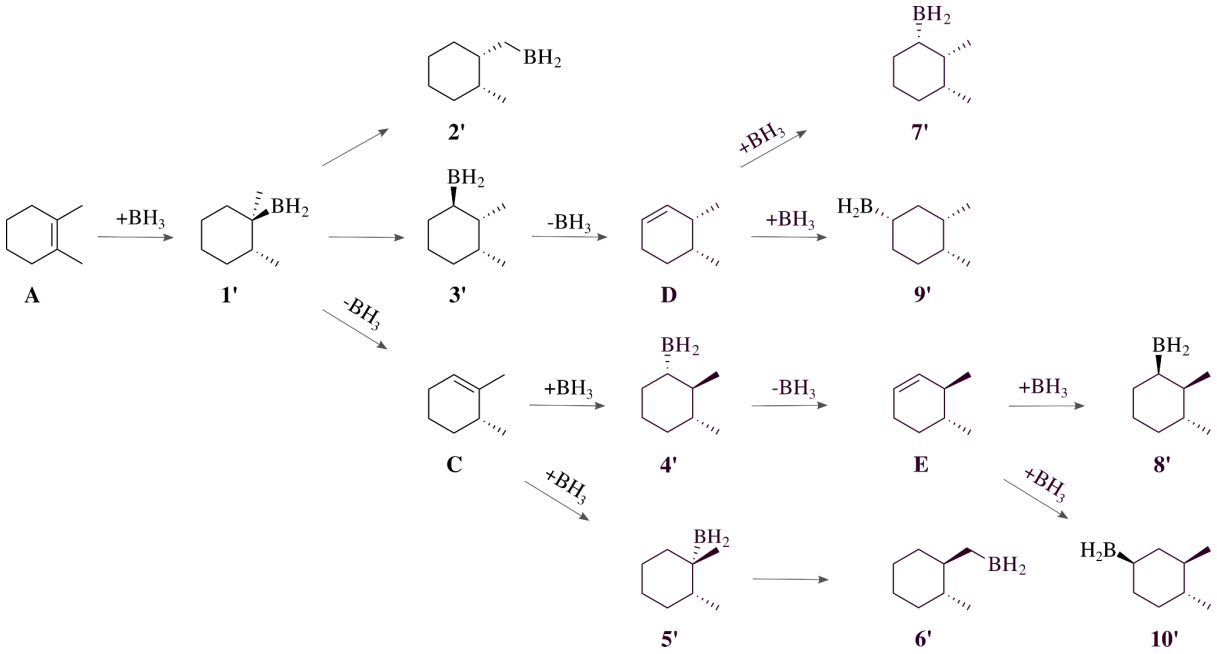

Figure 11. Reaction sequence in the formation of products from hydroboration of olefin **A**.

Thus, the typical hydroboration of olefin **A**, followed by a series of retrohydroborations and further hydroborations in *syn* manner, give rise to all the reported

products, including the *anti*-addition ones. In general, the tertiary-primary rearrangements occur by an intramolecular migration of the BH_2 fragment from a tertiary carbon to a methyl group to form a primary alkylborane, forming a π-complex intermediate. The tertiary-secondary and secondary-secondary rearrangements proceed via a retrohydroboration mechanism involving a 4MR-TS to give a π-complex, which can be dissociated into a new "free" olefin and borane. This dissociation leads to an intermolecular attack of borane on the opposite face of the newly formed olefin, producing *anti*-addition products due to a retrohydroboration mechanism. If dissociation of the π-complex does not occur, the olefin is then rehydroborated, adding the BH_2 unit to the vicinal methylene group. The repetition of this retrohydroboration-rehydroboration sequence allows the BH_2 moiety to migrate intramolecularly towards the cyclohexane ring, with the π-complex as intermediate. Note that the conformational arrangements on the ring can define the type of mechanism by which the reaction takes place. However, these processes are affected by the thermal stability of the π-complex, which becomes endergonic at high temperatures and thus influences the hydroboration and retrohydroboration barriers. As expected, hydroboration exhibits an anti-Markovnikov selectivity and, together with retrohydroboration, can take place in a concerted or two-step manner. When it occurs in two steps, the retrohydroboration pathway is facilitated by forming an intermediate, which lowers the free energy barriers. Thus, retrohydroboration is a competitive mechanism for alkylborane rearrangements.

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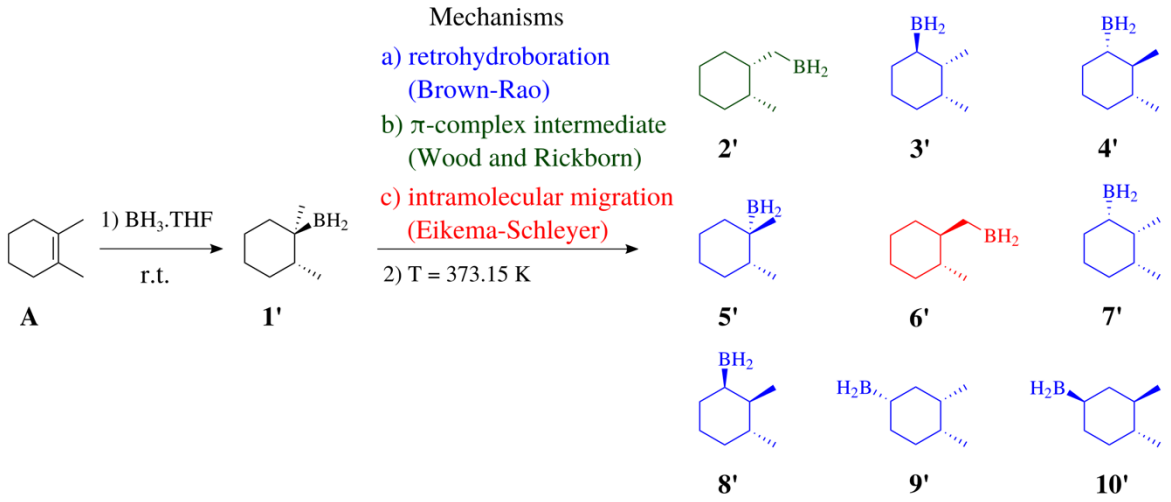
TOC


Mechanisms
a) retrohydroboration
(Brown-Rao)
b) π-complex intermediate
(Wood and Rickborn)
c) intramolecular migration
(Eikema-Schleyer)
1) BH3.THF
r.t.
2) T = 373.15 K
BH2
A
1'
2'
3'
4'
5'
6'
7'
8'
9'
10'
H2B