CHEM 203

Topics Discussed on Oct. 14

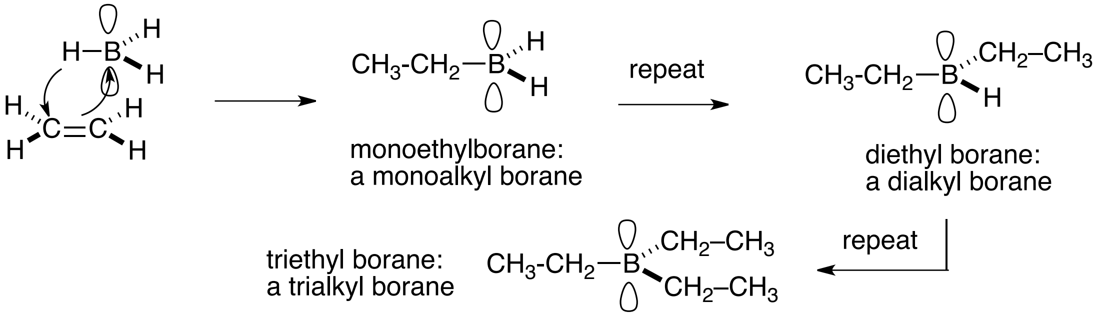
Hydroboration reaction: the addition of a B–H bond across the π system of an alkene

Alkylboranes or organoboranes: compounds containing a C–B bond

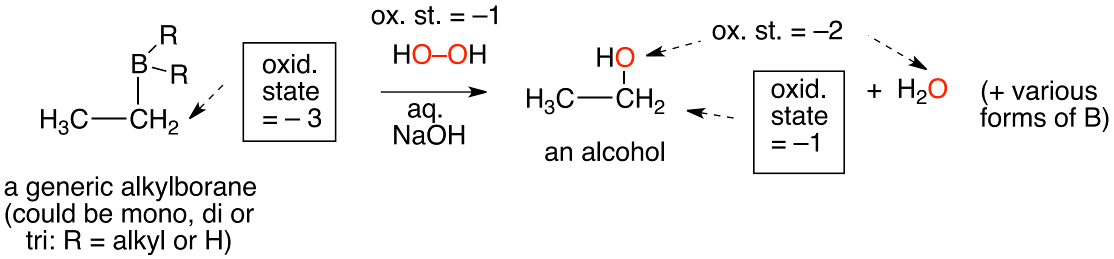
Rich chemistry and technological importance of alkylboranes

Lewis acidic character of the B atom in an alkylborane and possible formation of mono, di-, trialkylboranes through multiple cycles of the above reaction, until all B-H bonds have reacted

E.g., with ethylene:



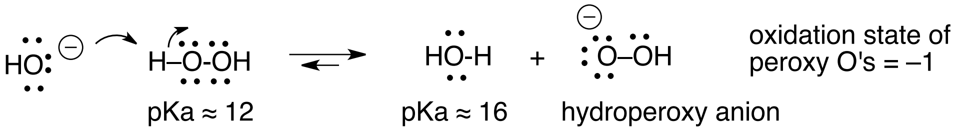
Important reaction of alkylboranes: oxidation of the C–B bond with H_2O_2 / aq. NaOH leading to the formation of alcohols



Description of the overall process shown above as the hydroboration / oxidation of alkenes

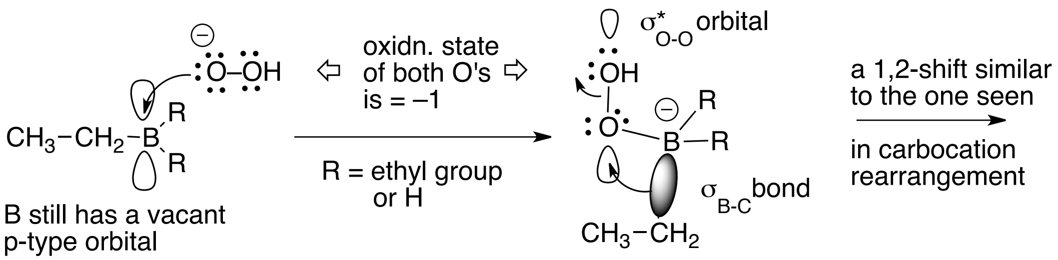
General mechanism of the oxidation of boranes with H_2O_2 / NaOH (aq.)

- deprotonation of H_2O_2 and formation of the hydroperoxy anion:



Then . . .

- significant nucleophilicity of the hydroperoxy anion and facile addition thereof to the B atom of an organoborane

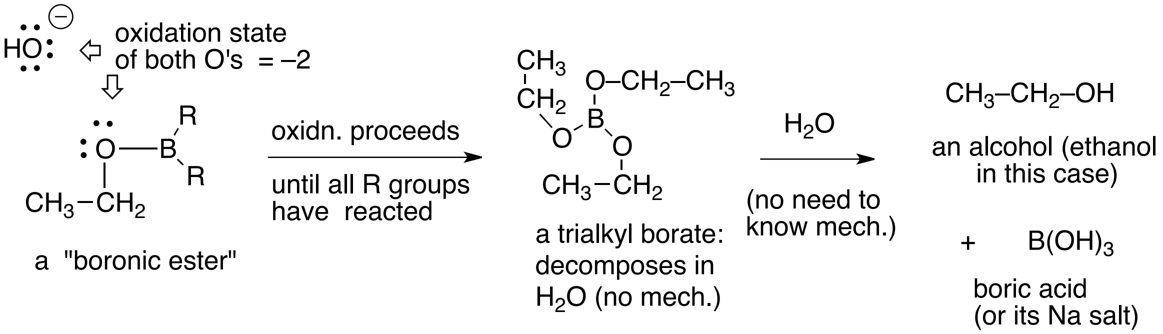


B still has a vacant p-type orbital

The oxygen atoms in the peroxy linkage "want" electrons, because they strive to attain the oxidation state of – 2. Additional electrons can be accommodated into the O–O σ* orbital.

Hyperconjugative interactions between the C–B σ bond and the O–O σ* orbital begin to weaken the O–O σ bond and the terminal OH group begins to depart by taking the pair of electrons connecting it to the internal O atom (i.e., the O–O σ electrons) with it.

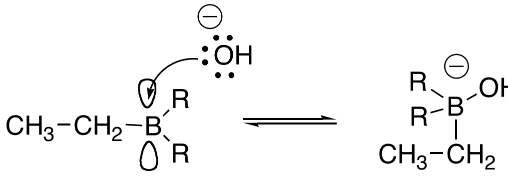
The departure of the OH group as HO^- would leave a highly unfavorable (+) charge on the O atom attached to B. An alkyl group migration occurring in concert with OH departure avoids formation of a highly energetic "O^+". Both O atoms thus reach the more favorable oxidation state of –2.



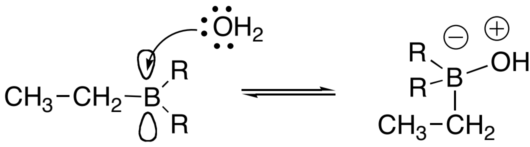
a "boronic ester"

a trialkyl borate: decomposes in H_2O (no mech.)

note: the alkylborane can certainly combine with OH^- or with water, both of which are Lewis basic and nucleophilic:



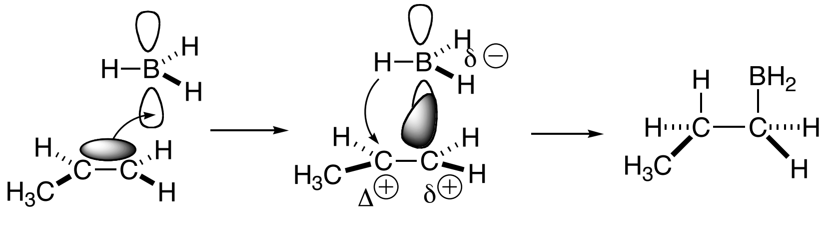
A



B

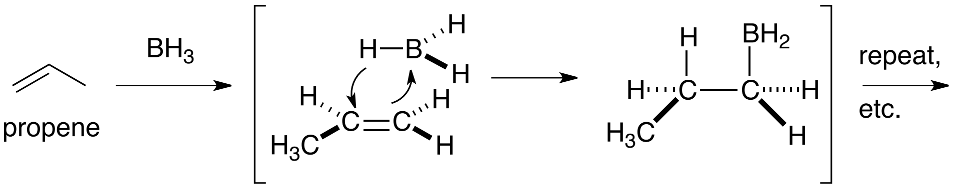
however, such events are non-productive, in the sense that they promote no further reaction. Then, the resulting complexes **A** and **B** will simply equilibrate back with the staring alkylborane. Only when HOO^- connects to the B atom will the complex undergo further chemical change (oxidation to an alcohol, as seen above)

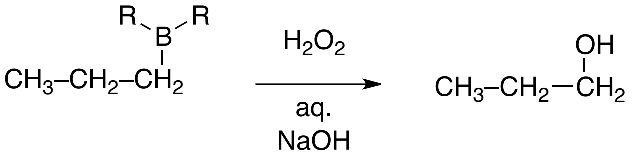
Regiochemical course of the hydroboration reaction of unsymmetrical olefins: the H atom of the H–B bond connects to the more highly substituted C atom of the alkene; the B atom, to the less highly substituted C:



as the interaction between the B atom and the π system becomes stronger, the more highly substituted C atom acquires a greater fraction of positive charge (better hyperconjugative stabilization). Consequently, it is the more highly substituted, more positive C atom that captures the (formal) hydride from BH_3.

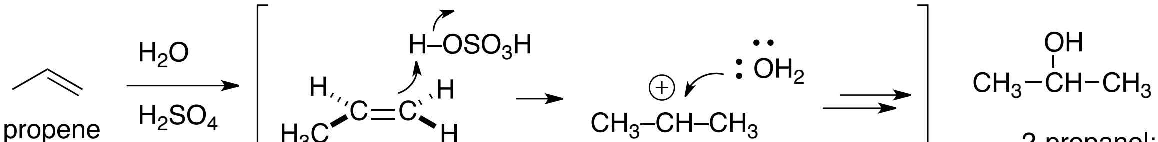
Interesting consequence of the hydroboration / oxidation of unsymmetrical olefins: formation of "anti-Markownikov" alcohols. E.g.:





1-propanol: an
"anti-Markownikov"
alcohol

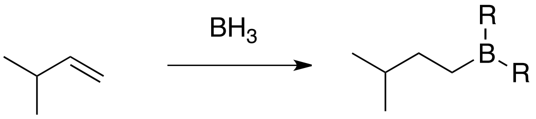
WHEREAS



2-propanol:
"Markownikov" alcohol

The hydroboration – oxidation process as a net "anti-Markownikov" addition of water to an alkene (i.e. the regioselectivity is opposite that of an acid-catalyzed hydration reaction)

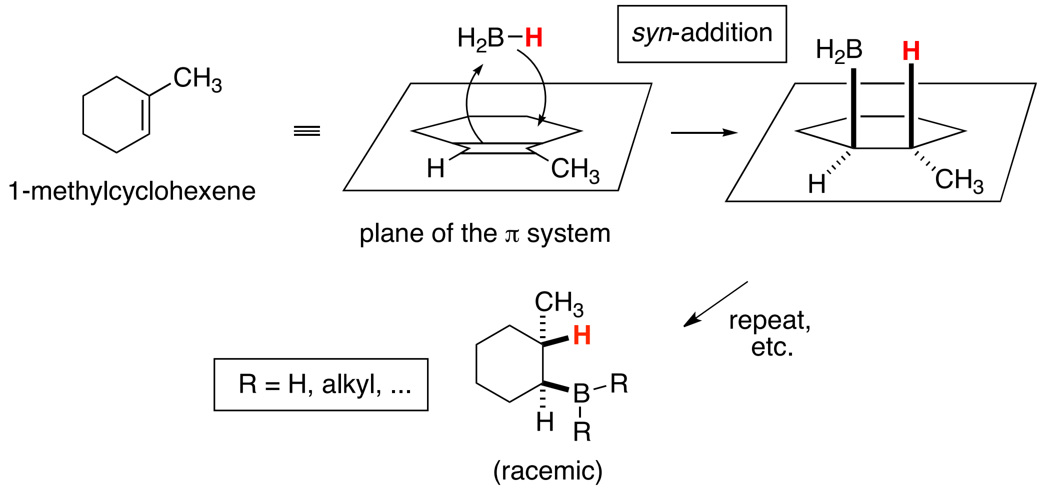
Absence of rearrangements in the hydroboration reaction (no carbocation intermediates are formed); e.g.:



(mono, di or trialkyl
borane: R = alkyl or H)

Stereochemical aspects of the hydroboration/oxidation reaction: the question of *syn* vs. *anti* addition of BH_3 to an alkene

e.g., with a more complex olefins such as 1-methylcyclohexene:



The hydroboration reaction as a strictly *syn* addition: B and H atoms must necessarily add from the same face of the π system.

Stereochemical aspects of the oxidation of alkylboranes to alcohols with H_2O_2 / aq. NaOH

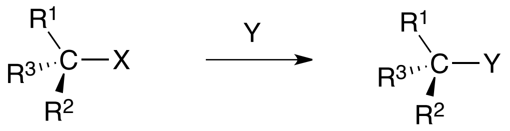
The oxidation of boranes is a substitution reaction

General pattern of a substitution reaction (no mechanism implied):

$$C—X \; + \; Y \; \longrightarrow \; C—Y \; + \; X$$

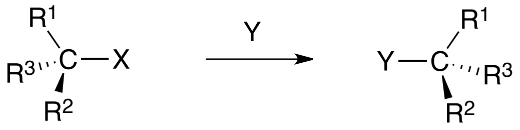
Possible stereochemical outcomes of a generic substitution reaction:

retention of configuration: the substituting group, Y, enters with the *same* orientation as the departing group, X:



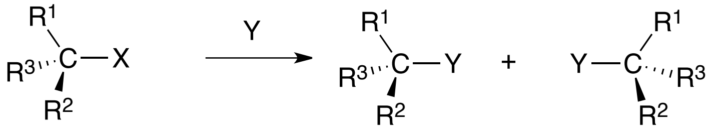
product resulting through **retention of configuration**

inversion of configuration: the substituting group, Y, enters with the *opposite* orientation relative to the departing group, X:



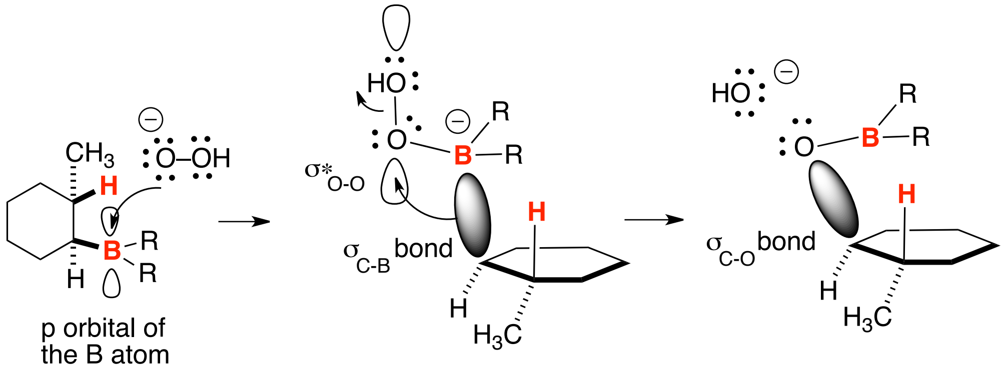
product resulting through **inversion of configuration**

loss of configuration: the substituting group, Y, enters partly with the same orientation and partly with the opposite orientation relative to the departing group, X

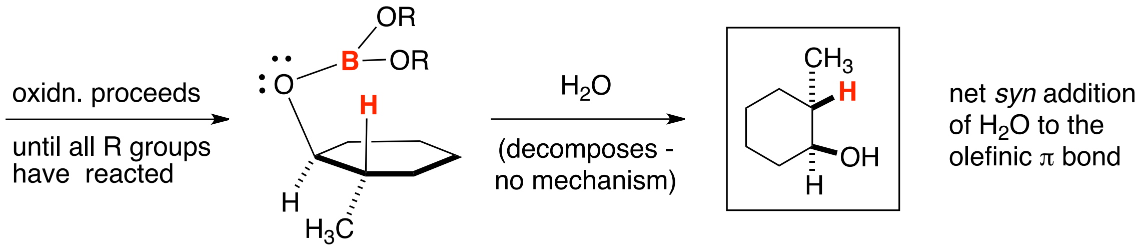


products resulting through **loss of configuration**

Strict **retention of configuration** observed during the oxidation of boranes, as a result of mechanistic constraints:



then



net *syn* addition of H_2O to the olefinic π bond

The hydroboration – oxidation process as a net "anti-Markownikov" *syn* addition of water to an alkene (i.e. the regioselectivity is opposite that of an acid-catalyzed hydration reaction)