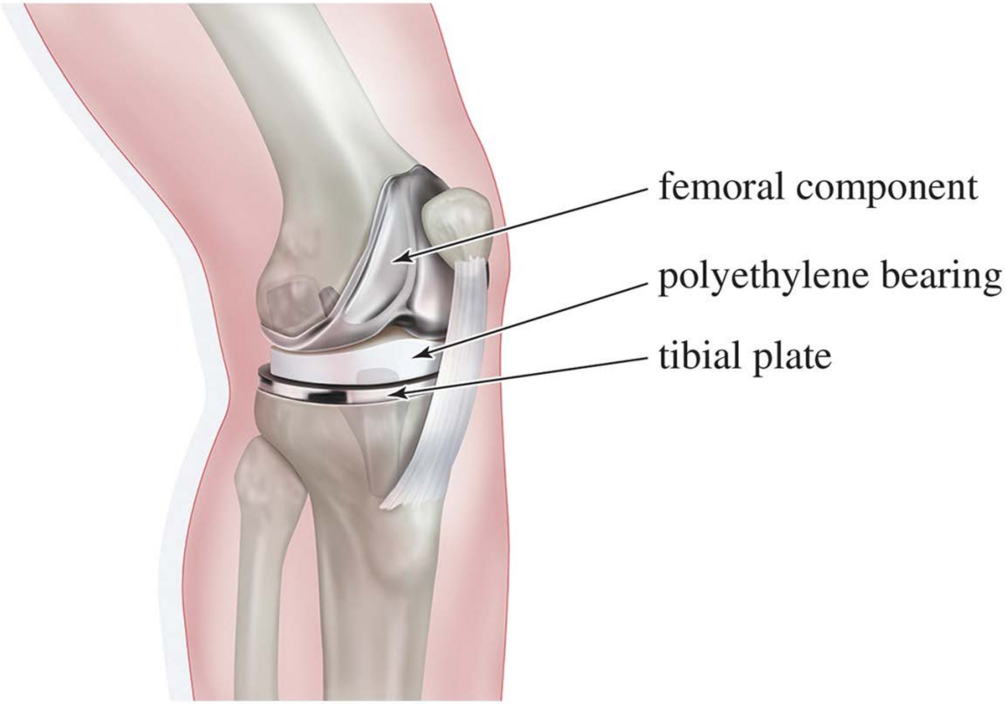
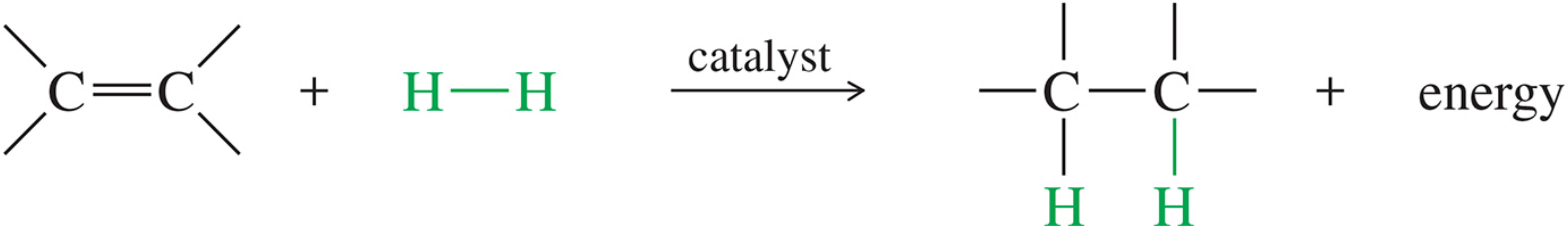


Organic Chemistry,
9th Edition
L. G. Wade, Jr.

Chapter 8
Lecture
Reactions of Alkenes

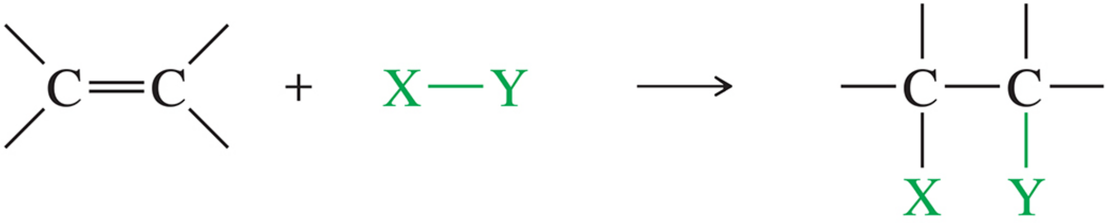
Reactivity of the Carbon–Carbon Double Bond



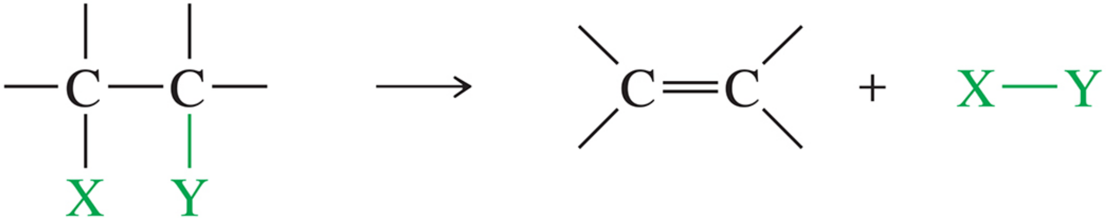
- The most common reactions of double bonds transform the pi bond into a sigma bond.

Types of Alkene Reactions

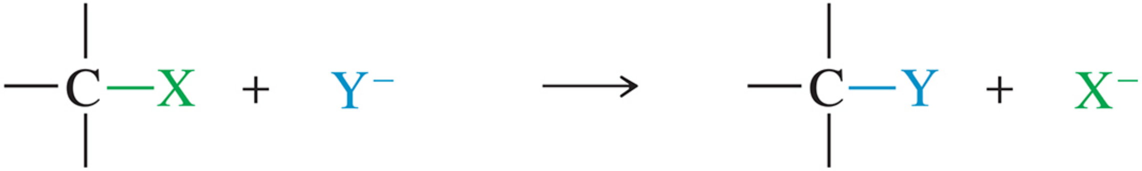
Addition



Elimination

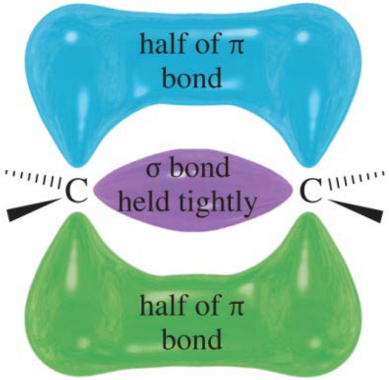


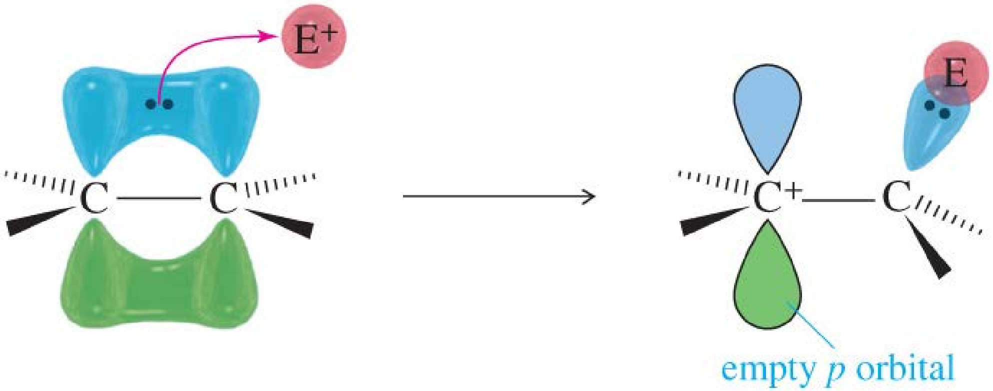
Substitution



Bonding in Alkenes

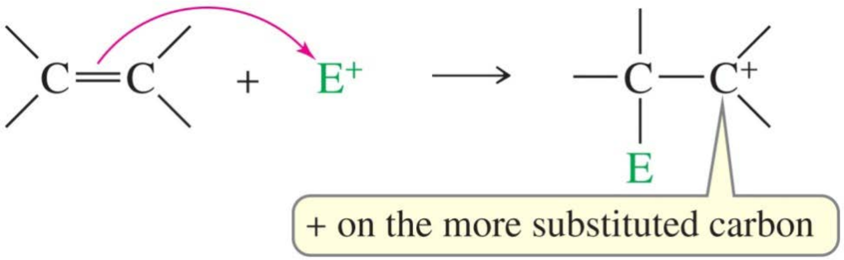
- Electrons in pi bonds are loosely held.
- The double bond acts as a nucleophile attacking electrophilic species.
- Carbocations are intermediates in some of these reactions.
- These reactions are called **electrophilic additions**.



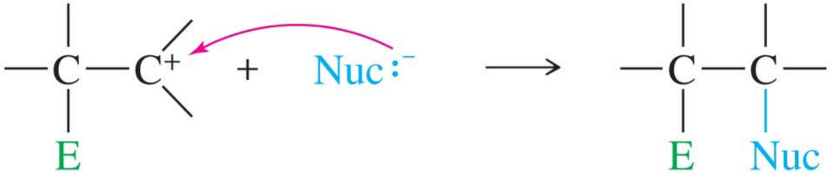


Electrophilic Addition

- Step 1: Pi electrons attack the electrophile.



- Step 2: Nucleophile attacks the carbocation.



Types of Additions

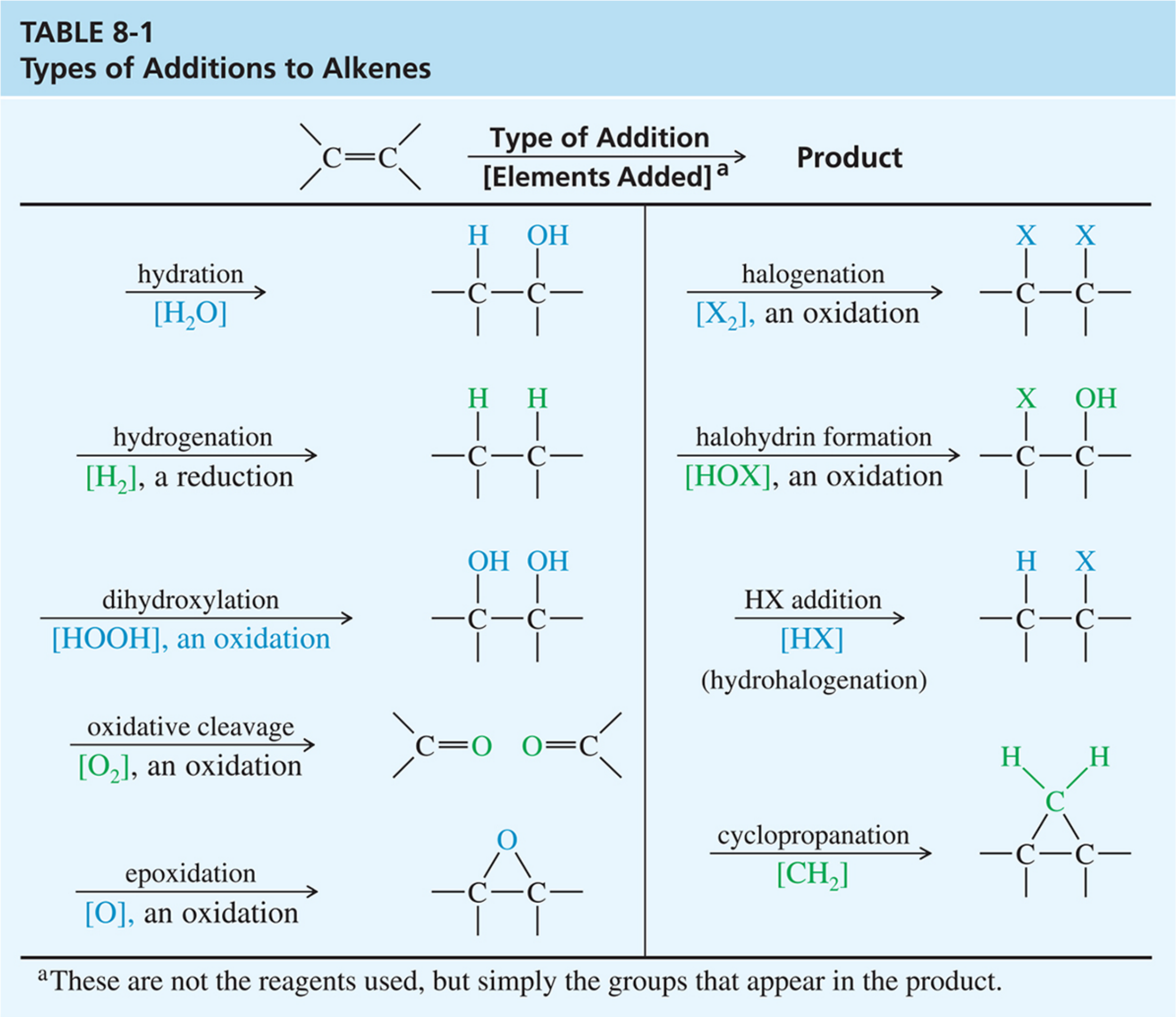


TABLE 8-1
Types of Additions to Alkenes

Type of Addition	[Elements Added][a]
hydration	[H_2O]
hydrogenation	[H_2], a reduction
dihydroxylation	[HOOH], an oxidation
oxidative cleavage	[O_2], an oxidation
epoxidation	[O], an oxidation
halogenation	[X_2], an oxidation
halohydrin formation	[HOX], an oxidation
HX addition (hydrohalogenation)	[HX]
cyclopropanation	[CH_2]

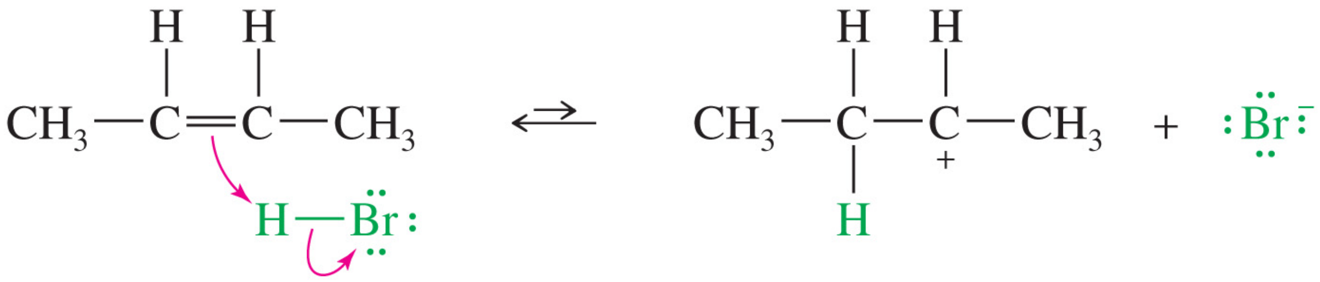
[a] These are not the reagents used, but simply the groups that appear in the product.

Addition of HX to Alkenes

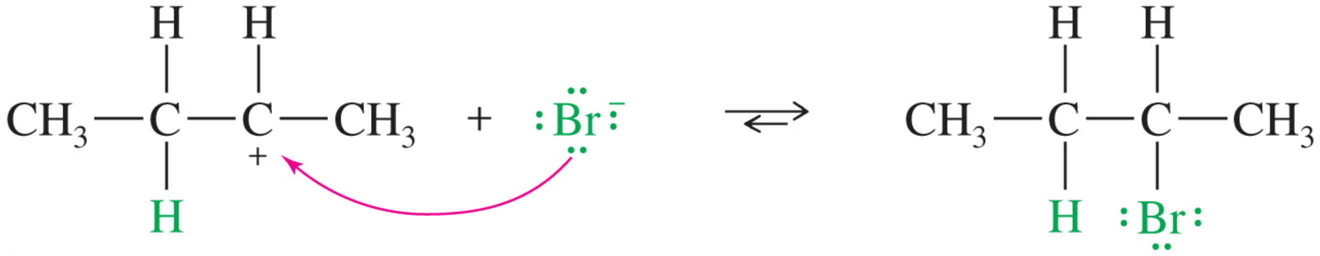
- Step 1 is the protonation of the double bond.
- The protonation step forms the most stable carbocation possible.
- In step 2, the nucleophile attacks the carbocation, forming an alkyl halide.
- HBr, HCl, and HI can be added through this reaction.

Mechanism of Addition of HX

Step 1: Protonation of the double bond



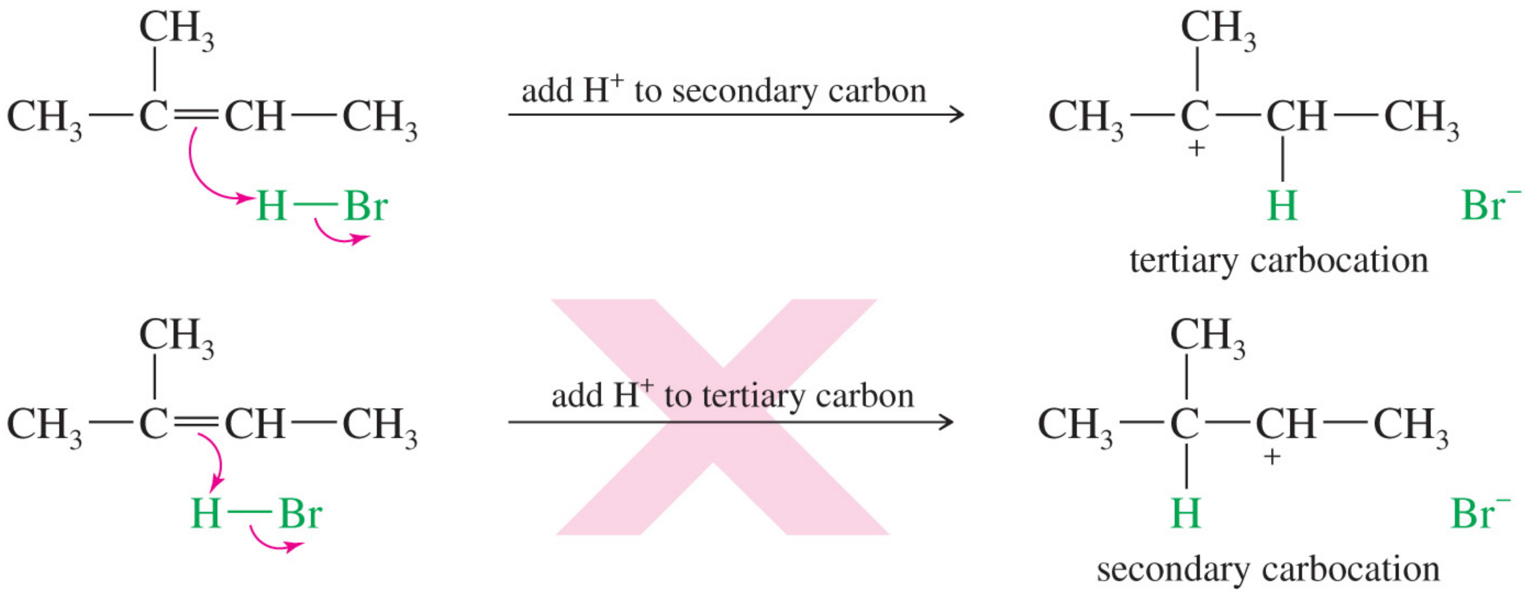
Step 2: Nucleophilic attack of the halide on the carbocation



Regioselectivity

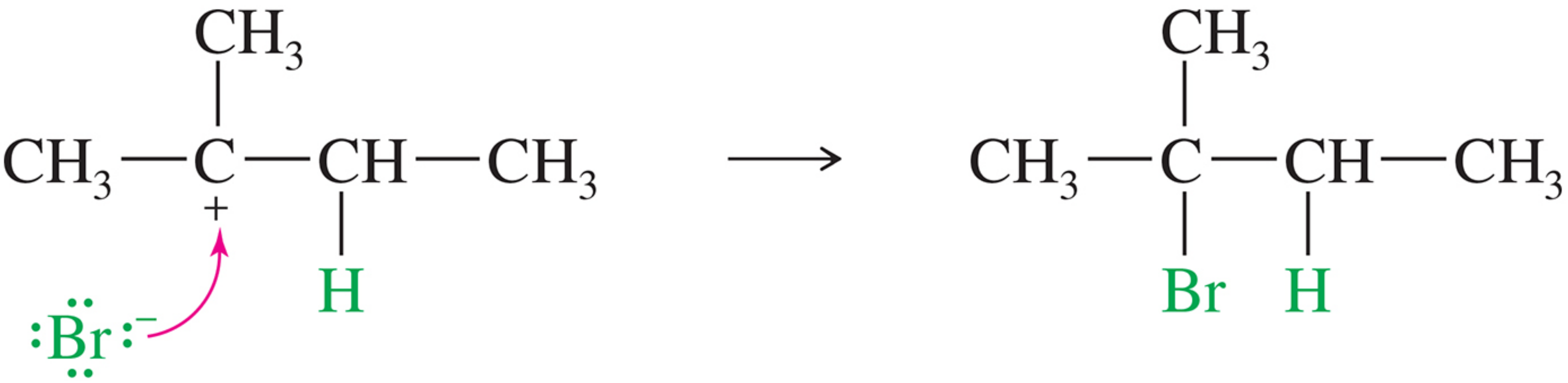
- **Markovnikov’s rule**: The addition of a proton to the double bond of an alkene results in a product with the acidic proton bonded to the carbon atom that already holds the greater number of hydrogens.
- **Markovnikov’s rule (extended)**: In an electrophilic addition to the alkene, the electrophile adds in such a way that it generates the most stable intermediate.

Markovnikov's Rule



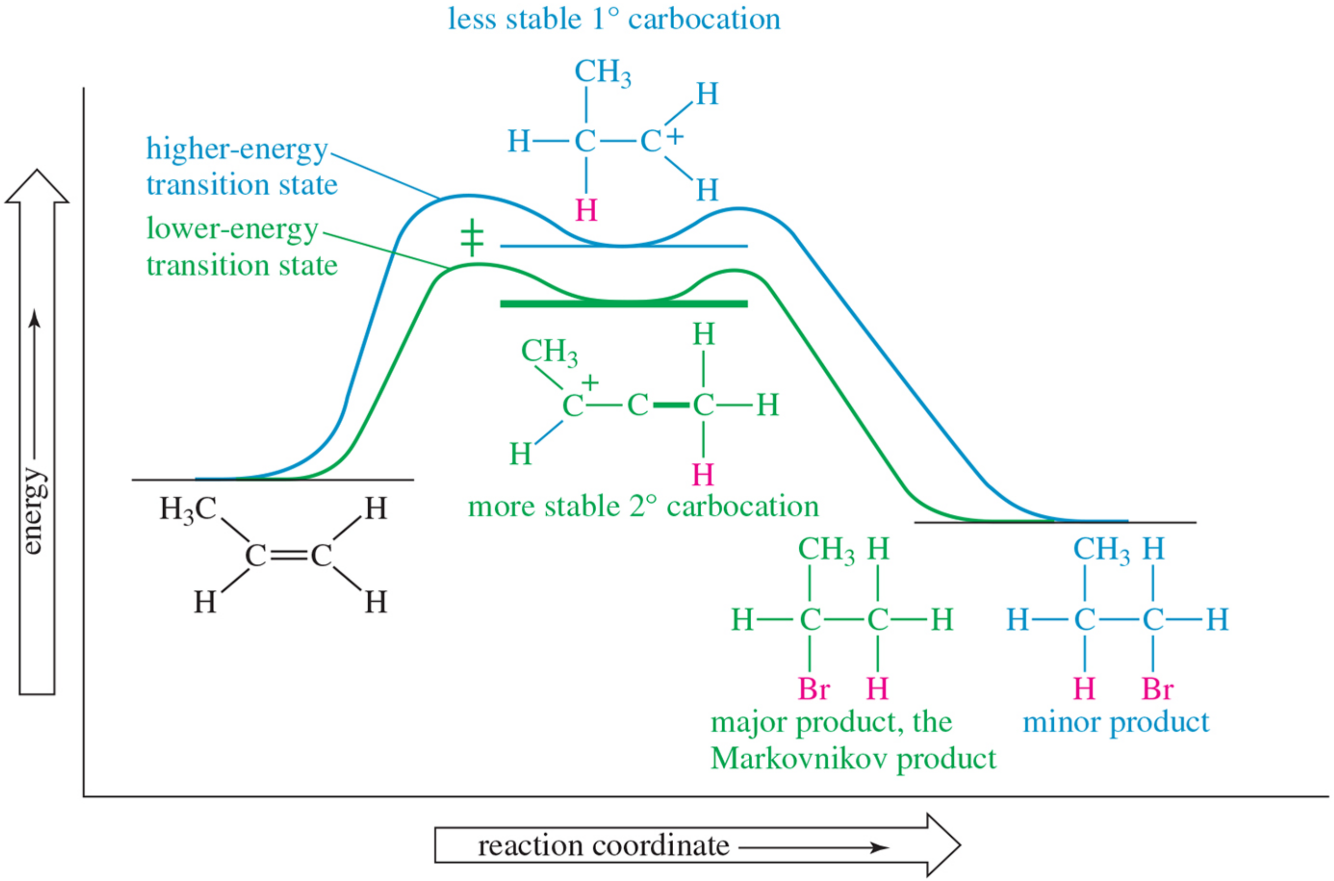
The acid proton will bond to carbon 3 in order to produce the most stable carbocation possible.

Markovnikov’s Rule (Continued)



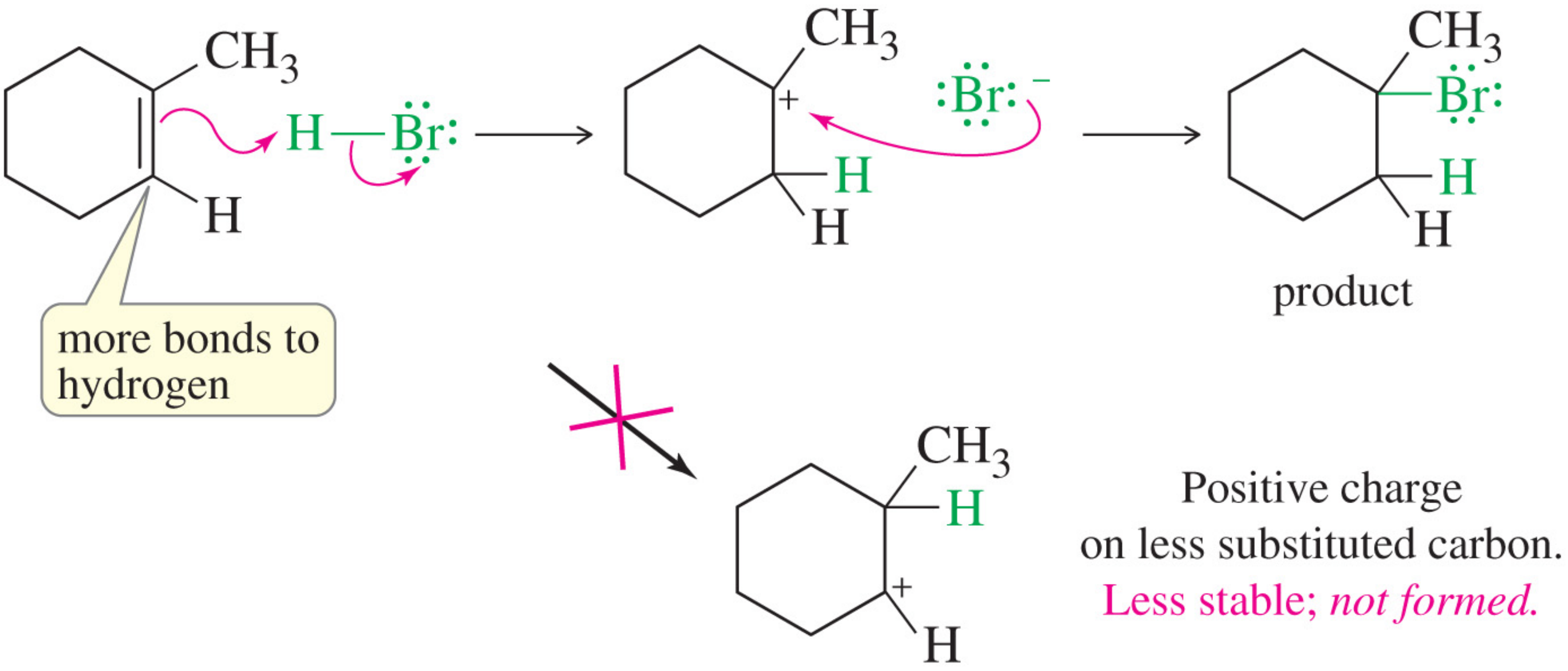
- The bromide anion then adds to the carbocation.

The Reaction-Energy Diagram



The first step is rate-determining in the electrophilic addition to an alkene.

Example



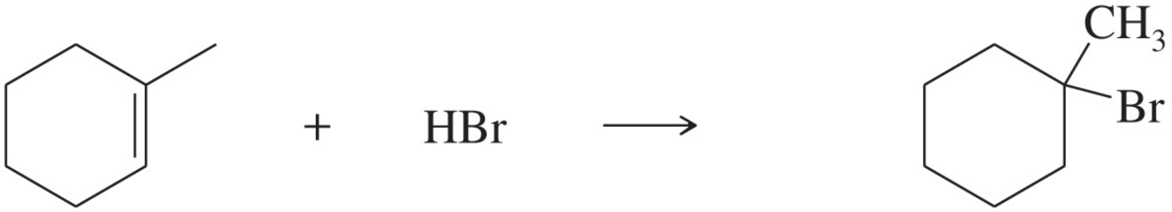
Positive charge
on less substituted carbon.
Less stable; *not formed.*

Solved Problem 1

Show how you would accomplish the following synthetic conversions.
(a) Convert 1-methylcyclohexene to 1-bromo-1-methylcyclohexane.

Solution

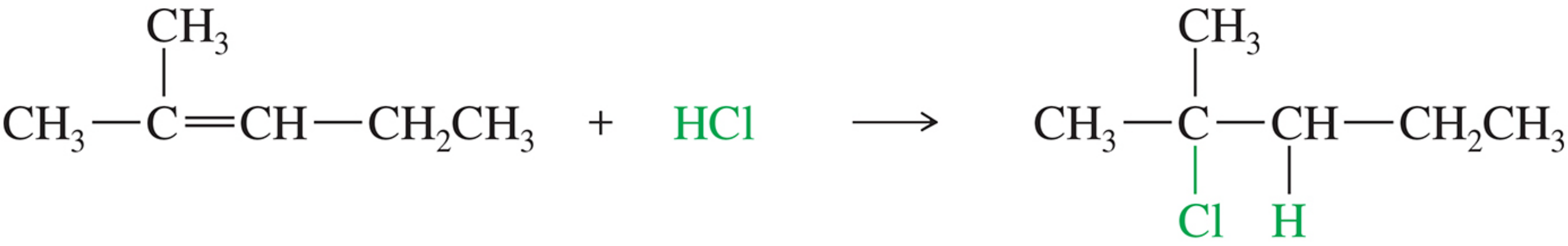
This synthesis requires the addition of HBr to an alkene with Markovnikov orientation. Ionic addition of HBr gives the correct product.



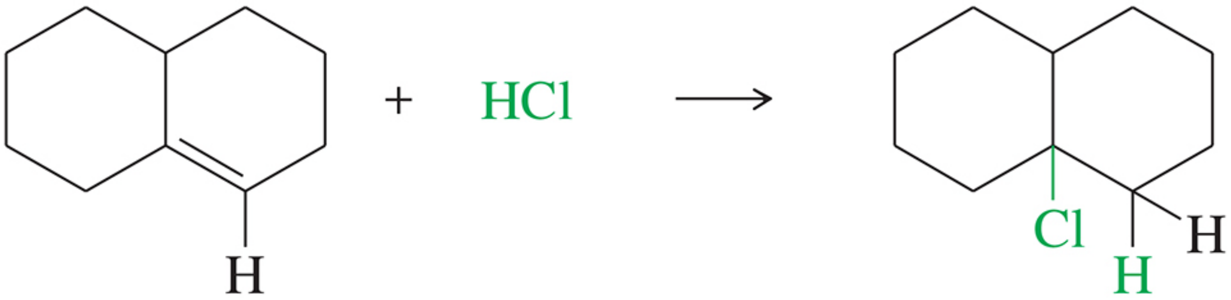
1-methylcyclohexene

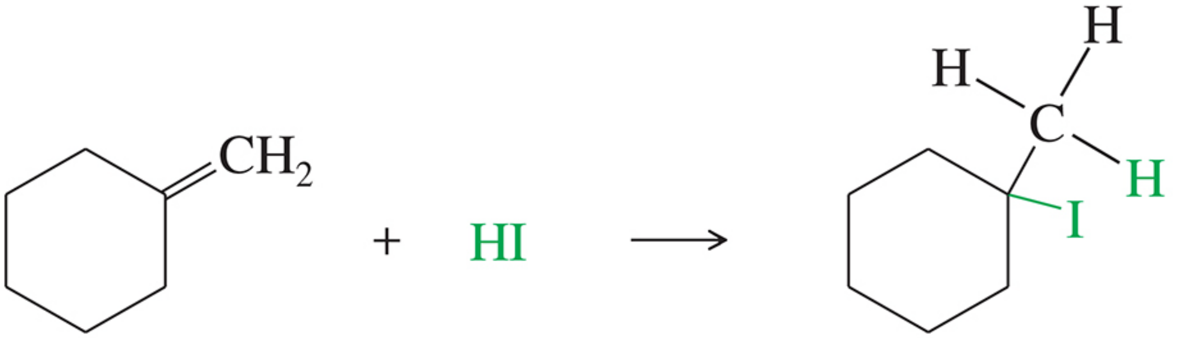
1-bromo-1-methylcyclohexane

More Examples



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH-CH_2CH_3 + HCl \longrightarrow CH_3-\underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\underset{\underset{\displaystyle H}{|}}{CH}-CH_2CH_3$$





Free-Radical Addition of HBr

- In the presence of peroxides, HBr adds to an alkene to form the “anti-Markovnikov” product.
- Peroxides produce free radicals.
- *Only* HBr has just the right reactivity for each step of the free-radical chain reaction to take place.
- The **peroxide effect** is not seen with HCl or HI because the reaction of an alkyl radical with HCl or HI is strongly endothermic.

Free-Radical Initiation

- The peroxide bond breaks homolytically to form the first radical: (Not Responsible for this mechanism on my exam)

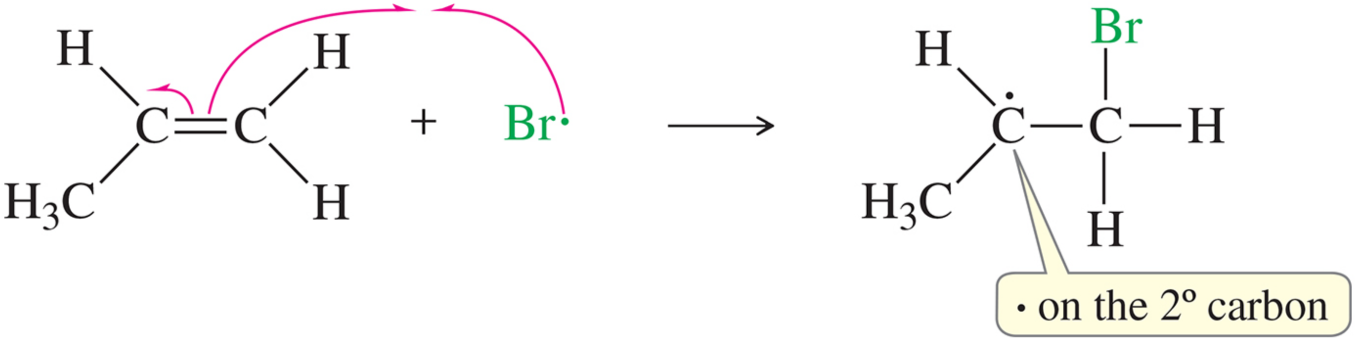
$$R-\ddot{\underset{..}{O}}-\ddot{\underset{..}{O}}-R \xrightarrow{\text{heat}} R-\ddot{\underset{..}{O}}\cdot + \cdot\ddot{\underset{..}{O}}-R \qquad \Delta H^\circ = +150\text{ kJ } (+36\text{ kcal})$$

- Hydrogen is abstracted from HBr.

Propagation Steps

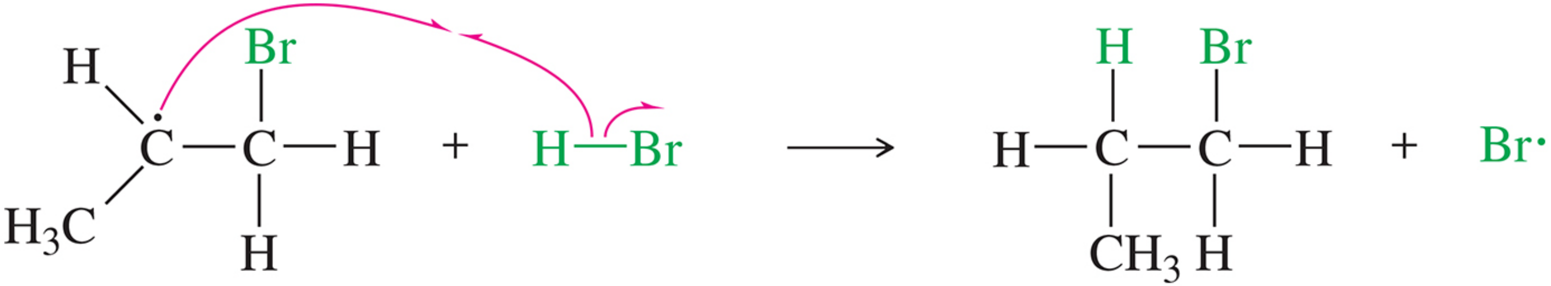
Not responsible for this mechanism on my exam.

- Bromine adds to the double bond, forming the most stable radical possible:

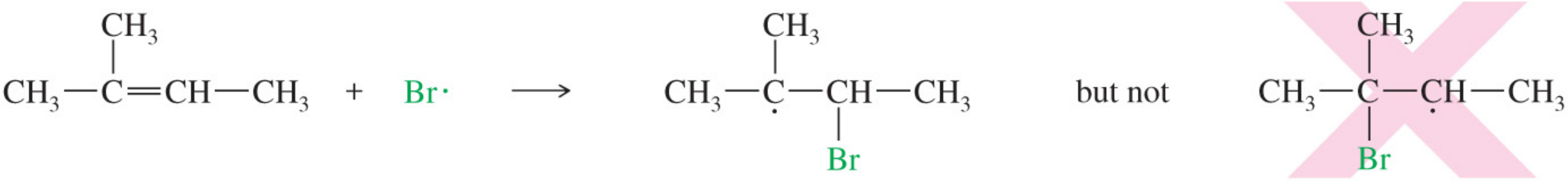


· on the 2° carbon

- Hydrogen is abstracted from HBr:



Anti-Markovnikov Stereochemistry



$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CH_3 + Br\cdot \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{\dot{C}}-\underset{\underset{Br}{|}}{CH}-CH_3 \quad \text{but not} \quad CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}-\dot{C}H-CH_3$$

tertiary radical (more stable)

secondary radical (less stable)

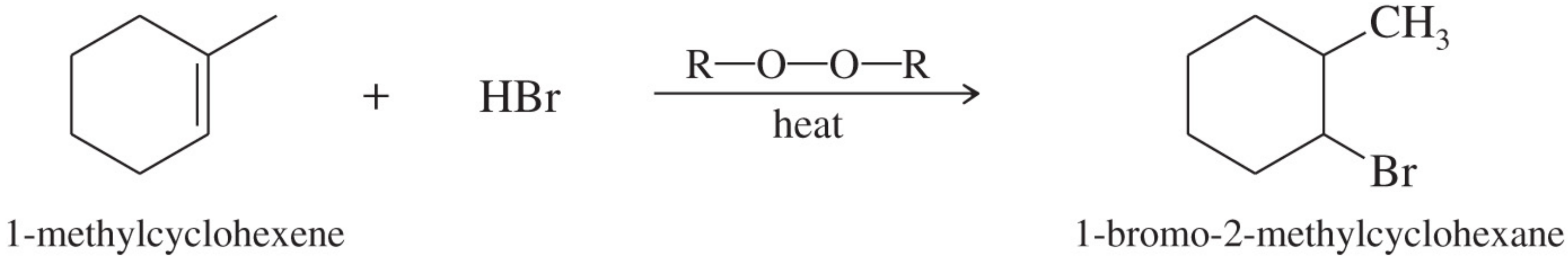
- The intermediate tertiary radical forms faster because it is more stable.

Solved Problem 2

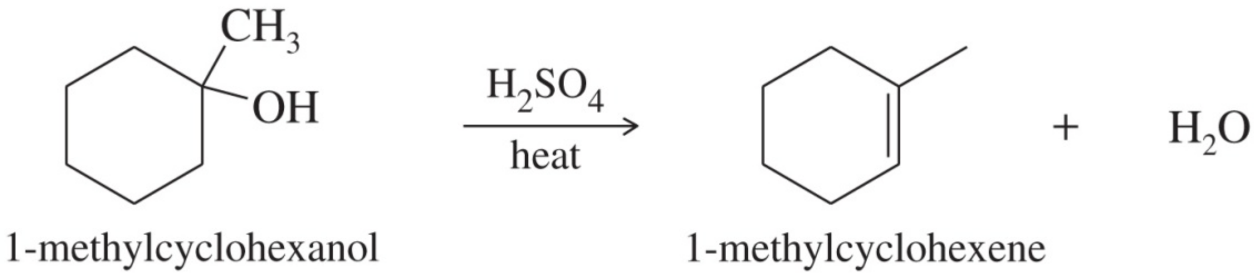
Convert 1-methylcyclohexanol to 1-bromo-2-methylcyclohexane.

Solution

This synthesis requires the conversion of an alcohol to an alkyl bromide with the bromine atom at the neighboring carbon atom. This is the anti-Markovnikov product, which could be formed by the radical-catalyzed addition of HBr to 1-methylcyclohexene.



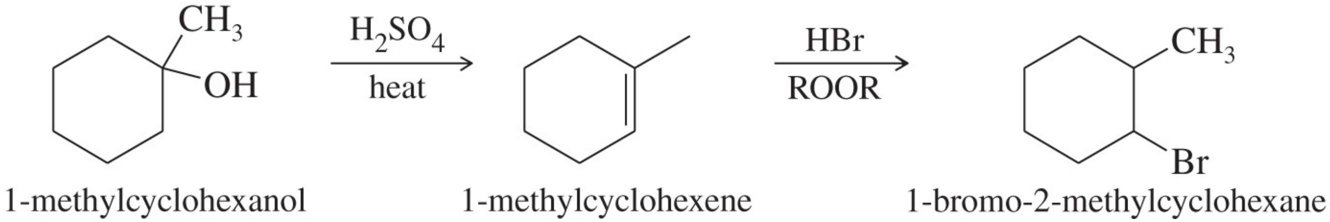
1-Methylcyclohexene is easily synthesized by the dehydration of 1-methylcyclohexanol. The most substituted alkene is the desired product.



Solved Problem 2 (Continued)

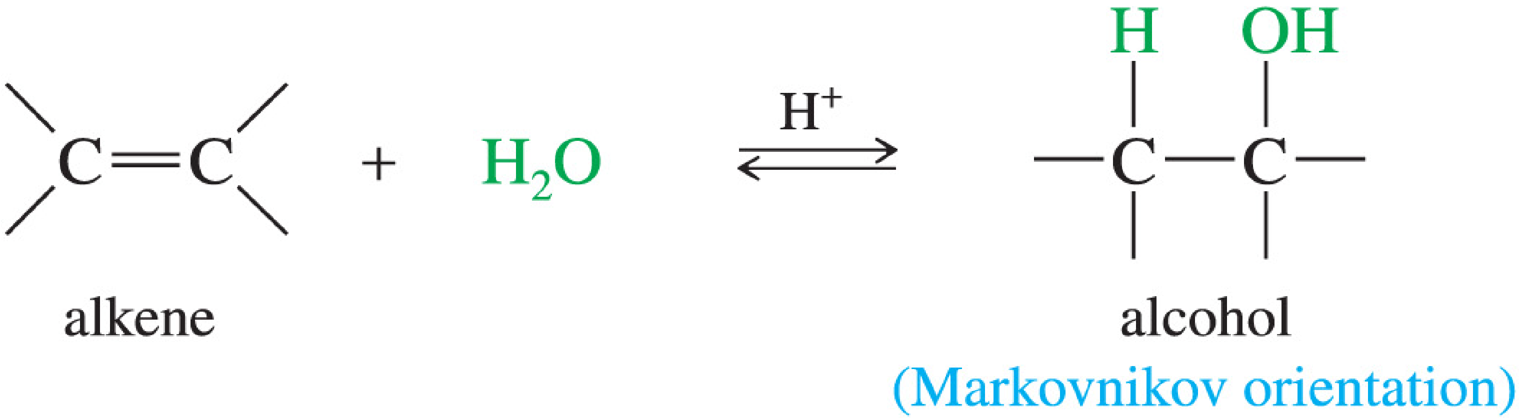
Solution (Continued)

The two-step synthesis is summarized as follows:



Hydration of Alkenes

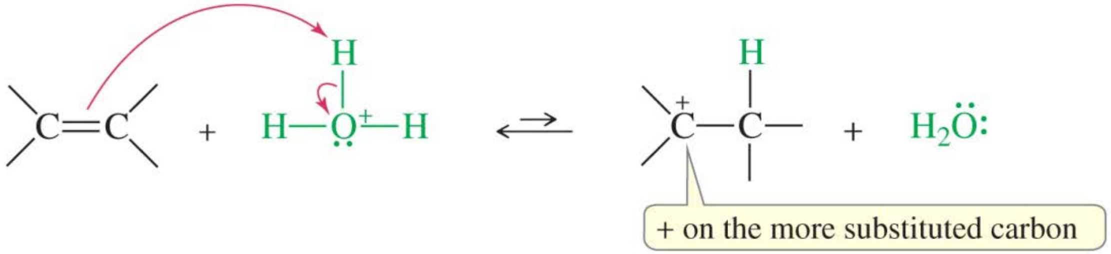
3 ways to add water to alkene (1st method here, Markovnikov with possibility of rearrangement)



- Addition of water to the double bond forms an alcohol.
- The addition follows Markovnikov’s rule.
- This is the reverse of the dehydration of alcohol.
- It uses dilute solutions of H_2SO_4 or H_3PO_4 to drive equilibrium toward hydration.

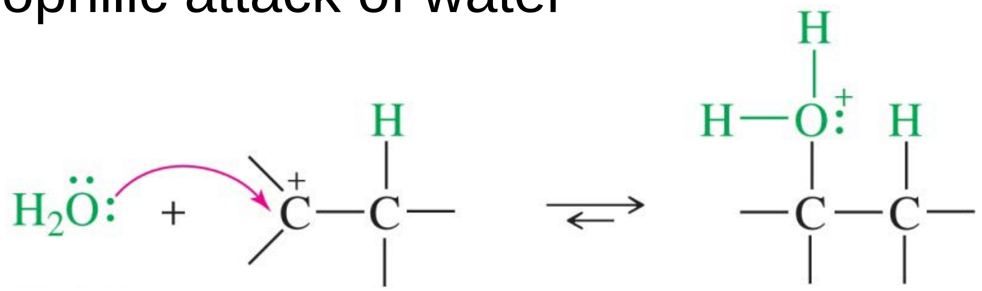
Mechanism for Hydration

Step 1: Protonation of the double bond forms a carbocation.

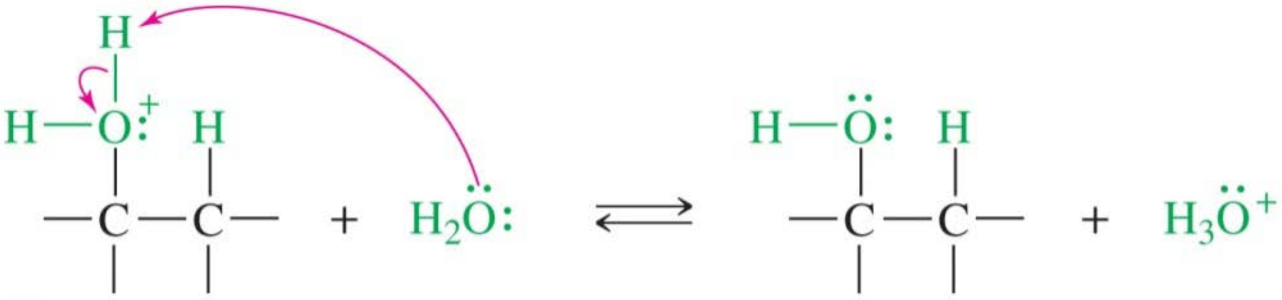


+ on the more substituted carbon

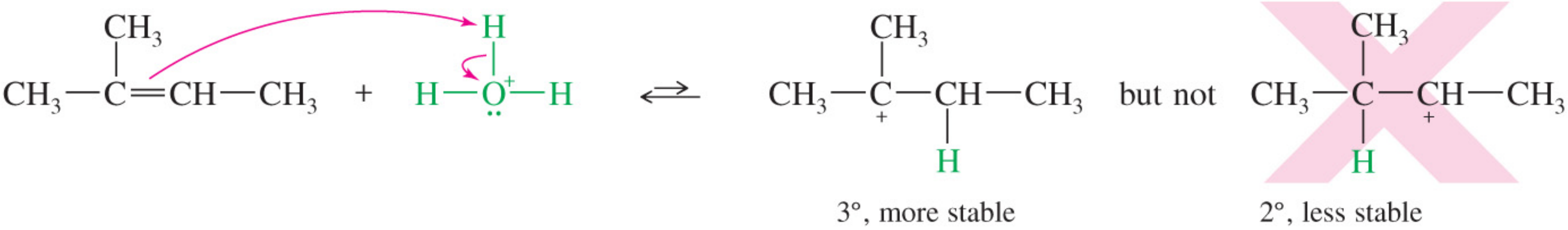
Step 2: Nucleophilic attack of water



Step 3: Deprotonation of the alcohol

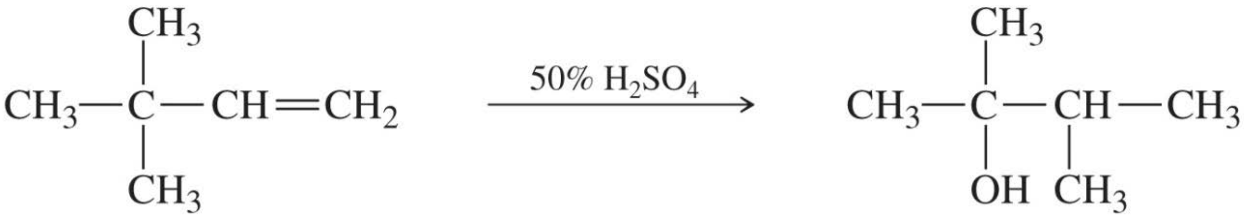


Orientation of Hydration



The protonation follows Markovnikov's rule: The proton adds to the less substituted end of the double bond, so the positive charge appears at the more substituted end (most stable carbocation).

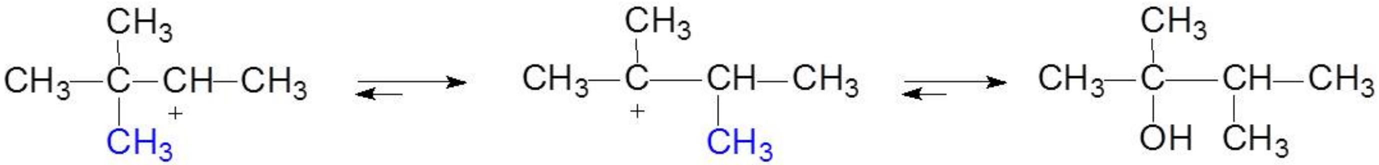
Rearrangements Are Possible



3,3-dimethylbut-1-ene

2,3-dimethylbutan-2-ol
(major product)

Methyl Shift:



2°, less stable

3°, more stable

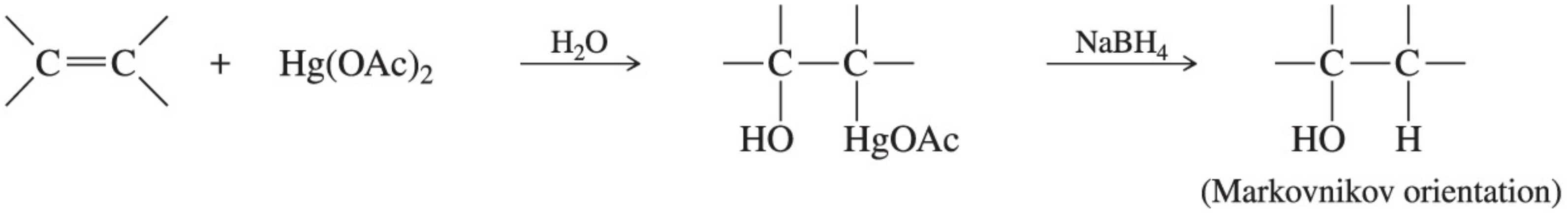
2,3-dimethyl-2-butanol
(major product)

- A methyl shift after protonation will produce the more stable tertiary carbocation.

Oxymercuration–Demercuration Reaction

3 ways to add water to alkene (2nd method here, Markovnikov without possibility of rearrangement)

Oxymercuration–Demercuration



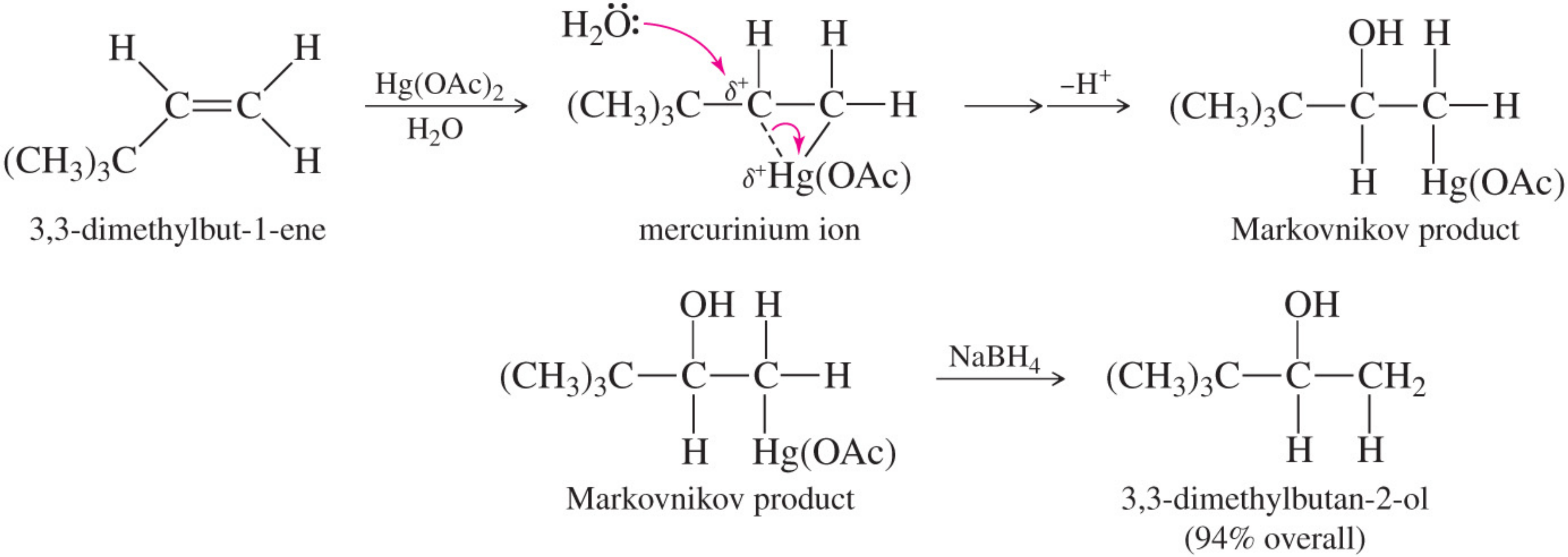
(Markovnikov orientation)

- Markovnikov addition of water to the double bond
- Milder conditions than direct hydration
- No rearrangements or polymerization

Oxymercuration Reaction

- The reagent is mercury(II) acetate, which dissociates slightly to form $^{+}Hg(OAc)$.
- $^{+}Hg(OAc)$ is the electrophile that adds to the pi bond.
- The intermediate is a three-membered ring called the **mercurinium ion**.
- Overall, the addition of water follows Markovnikov’s rule.

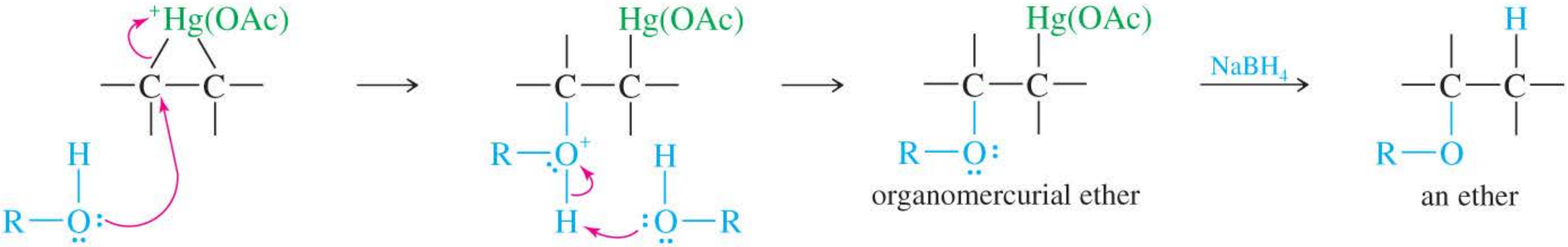
Oxymercuration–Demercuration of 3,3,-Dimethylbut-1-ene



The reaction does not suffer from rearrangements because there is no carbocation intermediate.

Alkoxymercuration–Demercuration

If the nucleophile is an alcohol (ROH), instead of water, an ether is produced.

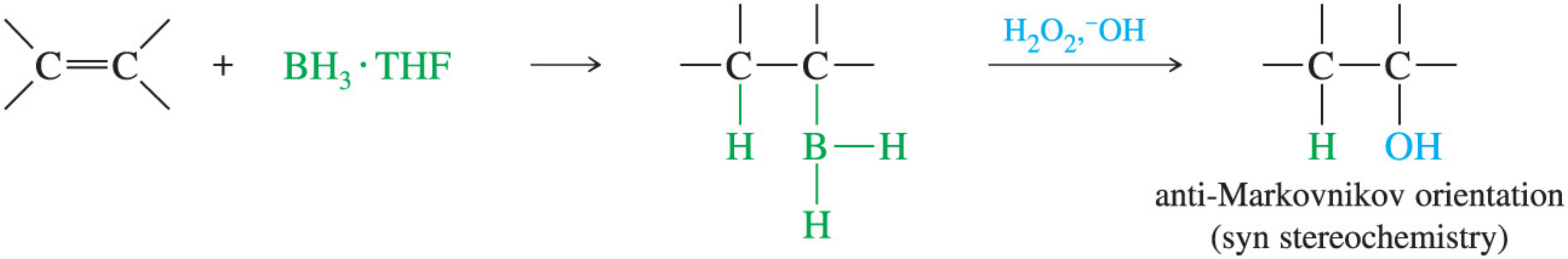


Hydroboration of Alkenes

3 ways to add water to alkene

(3rd method here, anti-Markovnikov)

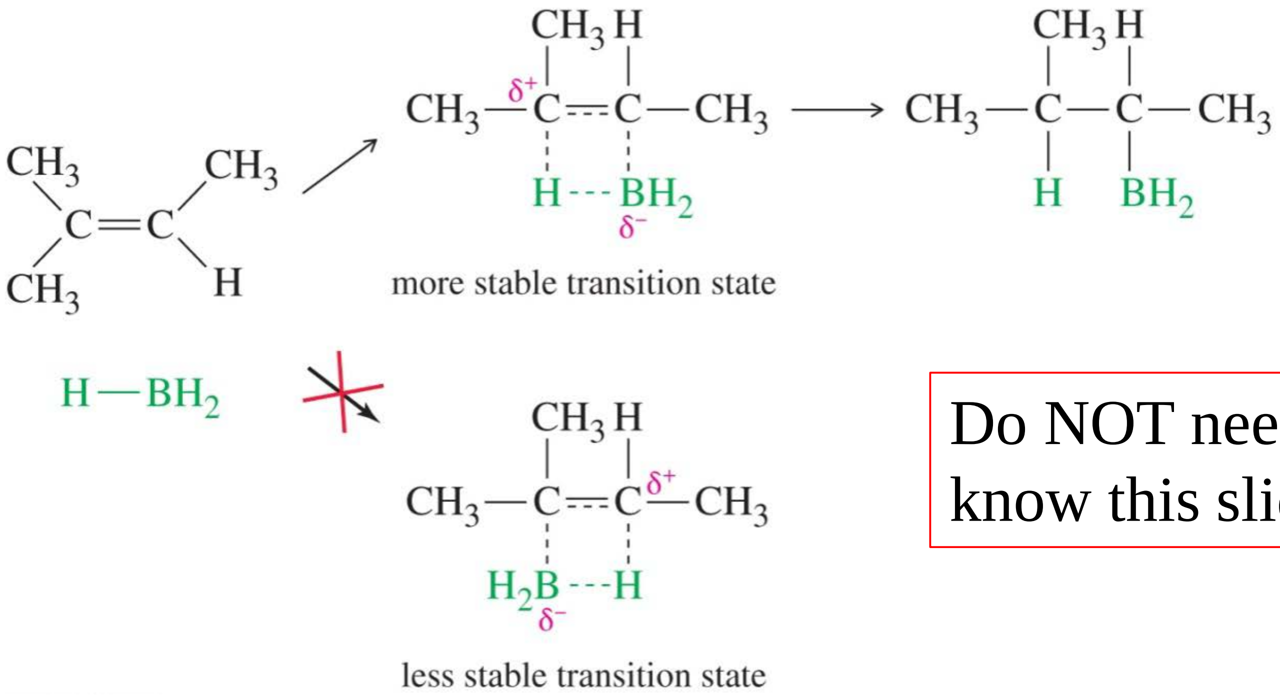
Hydroboration–oxidation:



anti-Markovnikov orientation
(syn stereochemistry)

- H. C. Brown of Purdue University discovered that diborane (B_2H_6) adds to alkenes with anti-Markovnikov orientation to form alkylboranes, which, after oxidation, give anti-Markovnikov alcohols.
- Brown received the Nobel Prize in Chemistry in 1979 for his work in the field of borane chemistry.

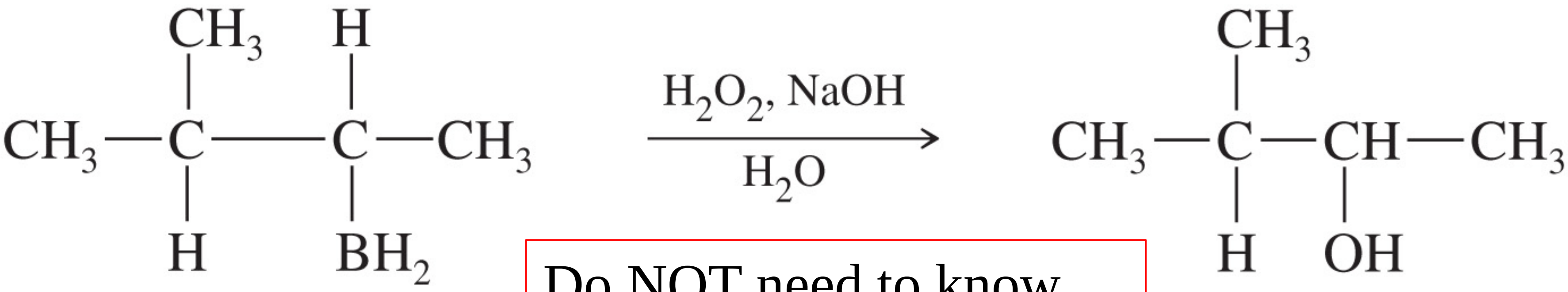
Mechanism of Hydroboration



Do NOT need to know this slide

- Borane adds to the double bond in a single step, with boron adding to the less substituted carbon and hydrogen adding to the more highly substituted carbon.
- This orientation places the partial positive charge in the transition state on the more highly substituted carbon atom.

Oxidation to Alcohol

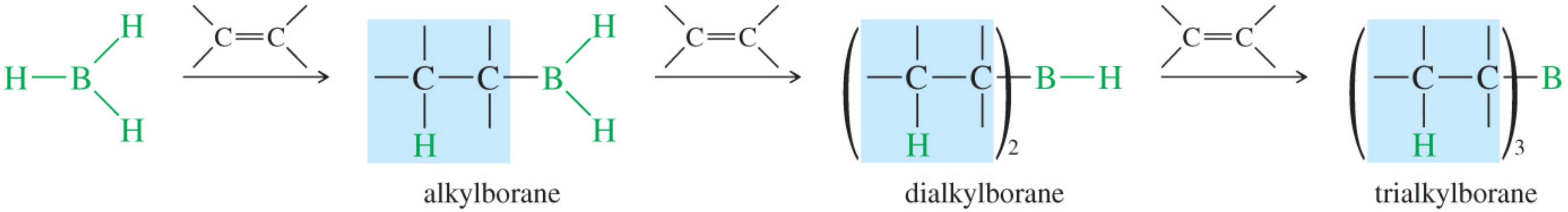


$$CH_3-\underset{H}{\overset{CH_3}{C}}-\underset{BH_2}{\overset{H}{C}}-CH_3 \xrightarrow[H_2O]{H_2O_2,\ NaOH} CH_3-\underset{H}{\overset{CH_3}{C}}-\underset{OH}{CH}-CH_3$$

Do NOT need to know this slide

- Oxidation of the alkyl borane with basic hydrogen peroxide produces the alcohol.
- Orientation is anti-Markovnikov.

Stoichiometry of Hydroboration



- Three moles of alkene can react with each mole of BH_3.

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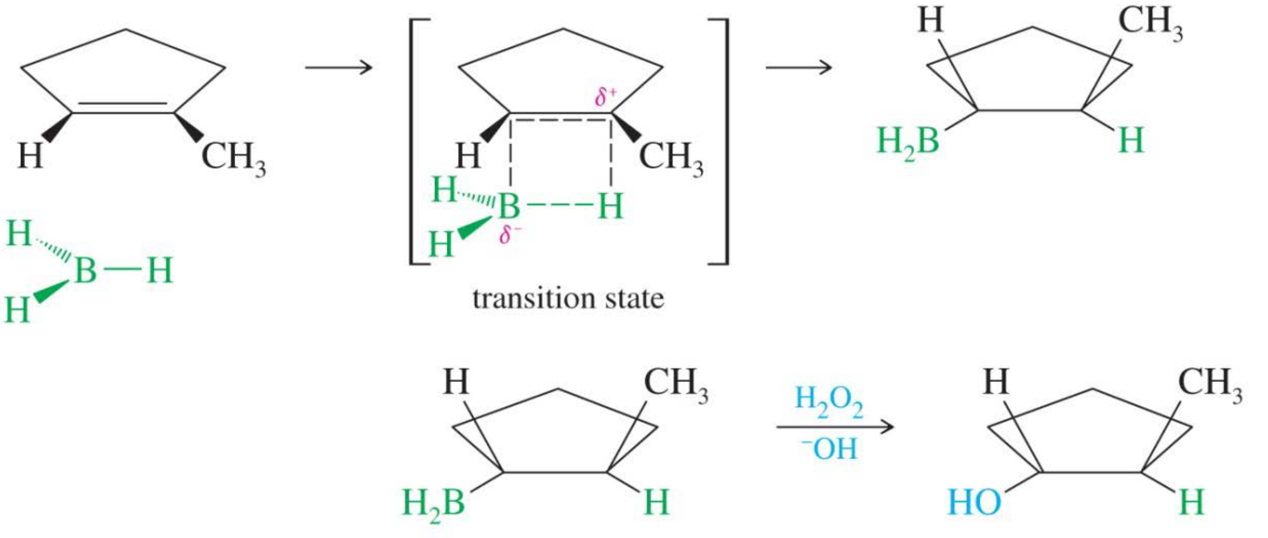
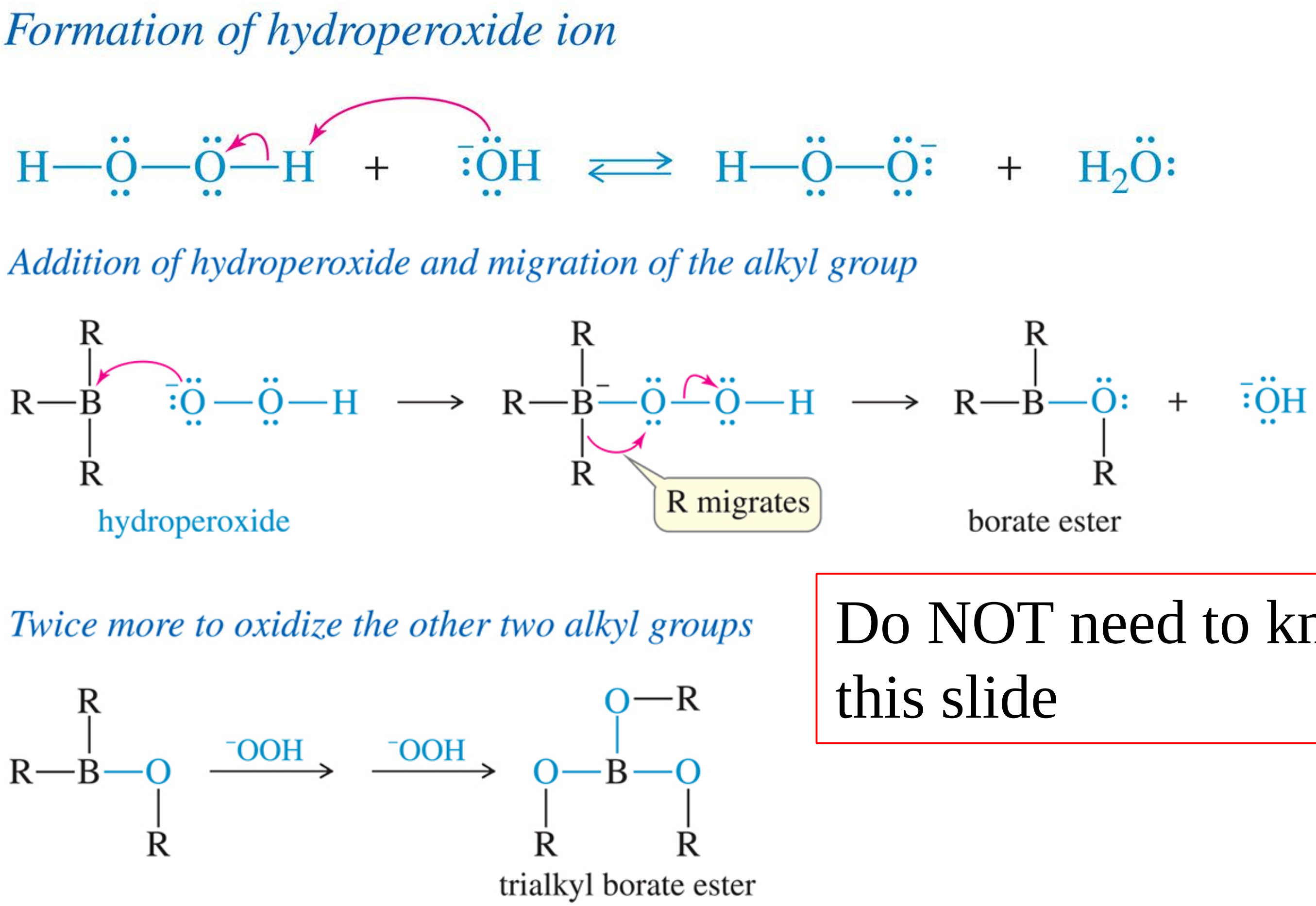
Stereochemistry of Hydroboration



trans-2-methylcyclopentanol
(85% overall)
(racemic mixture of enantiomers)

- The hydroboration step adds the hydrogen and the boron to the same side of the double bond (**syn addition**).
- When the boron is oxidized, the OH will keep the same stereochemical orientation.

The Role of the Hydroperoxide Ion



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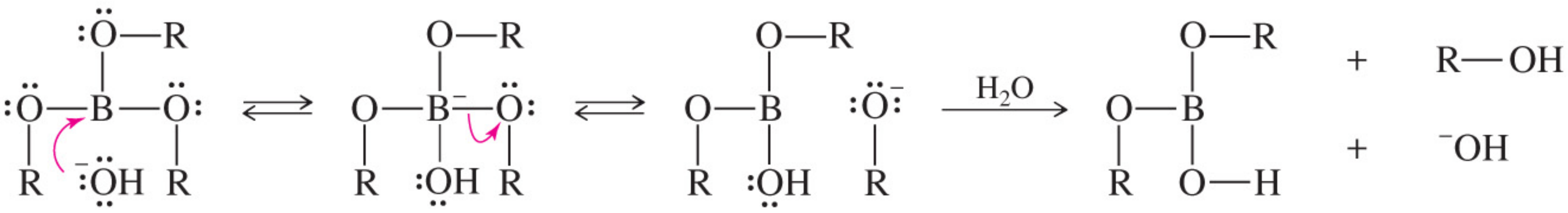
Oxidation of a Trialkylborane

Hydrolysis of the borate ester



(The other two OR groups hydrolyze similarly.)

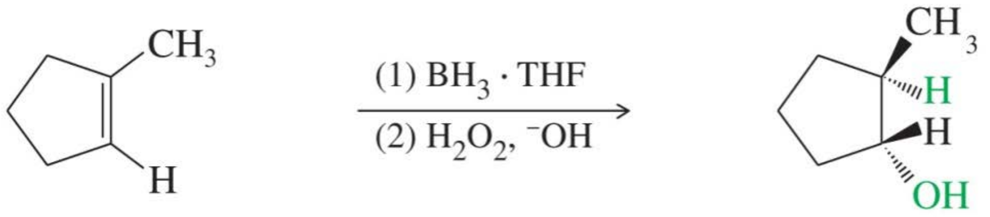
Do NOT need to know this slide

Solved Problem 3

Show how you would convert 1-methylcyclopentanol to 2-methylcyclopentanol.

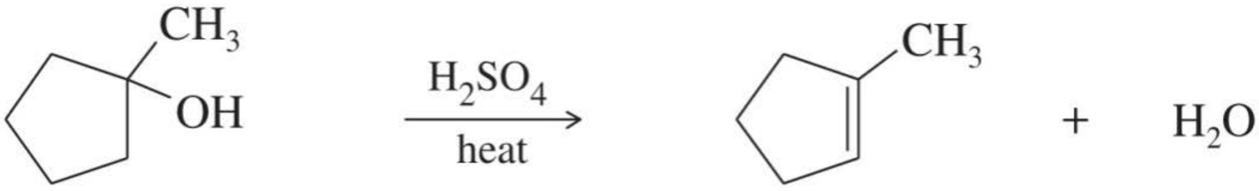
Solution

Working backward, use hydroboration–oxidation to form 2-methylcyclopentanol from 1-methylcyclopentene. The use of (1) and (2) above and below the reaction arrow indicates individual steps in a two-step sequence.



1-methylcyclopentene → *trans*-2-methylcyclopentanol

The 2-methylcyclopentanol that results from this synthesis is the pure trans isomer. This stereochemical result is discussed in Section 8-7C. 1-Methylcyclopentene is the most substituted alkene that results from dehydration of 1-methylcyclopentanol. Dehydration of the alcohol would give the correct alkene.



1-methylcyclopentanol → 1-methylcyclopentene

End 10/19/16 class