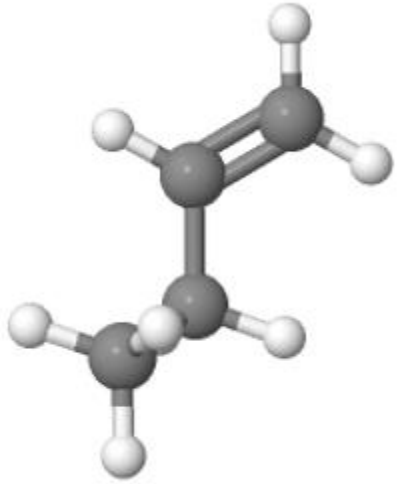
2302263 – Organic Chemistry I – Part III

Lecture 2-3

Alkenes – Reactions 1



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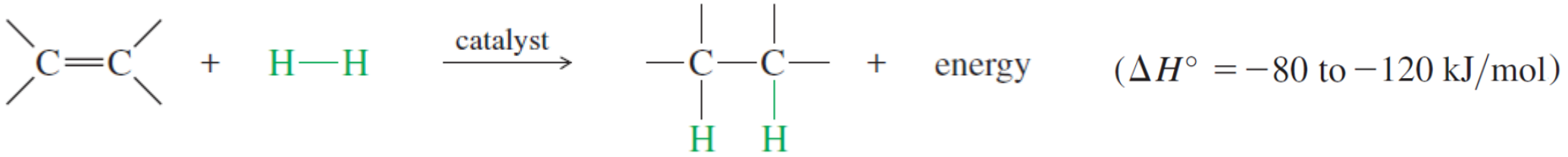
Recommended Textbook:

Chapter 8 in *Organic Chemistry*, 8th Edition, L. G. Wade, Jr., **2010**, Prentice Hall (Pearson Education)

Reactivity of C=C – Addition Reactions

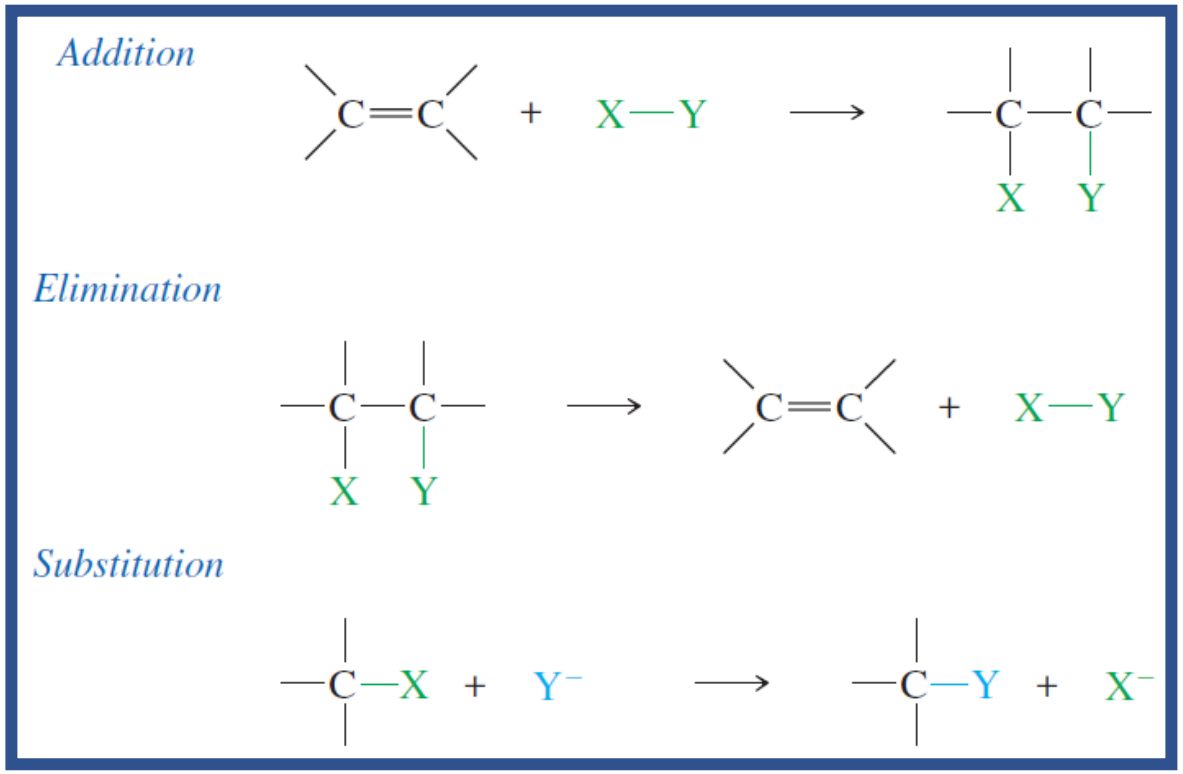
Single bonds (**sigma bonds**) are more stable than **pi bonds**

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

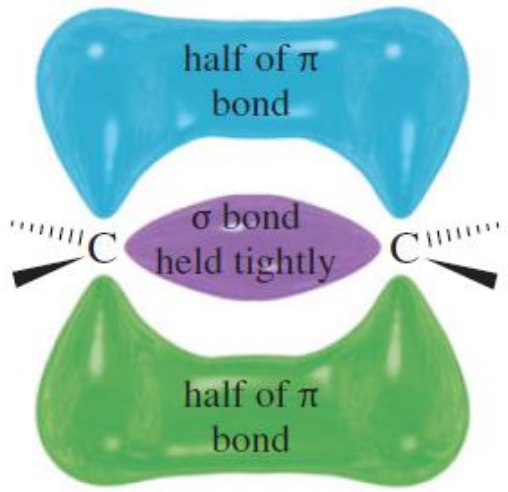


"**Addition**" is one of the three major reaction types we have studied: addition, elimination, and substitution.

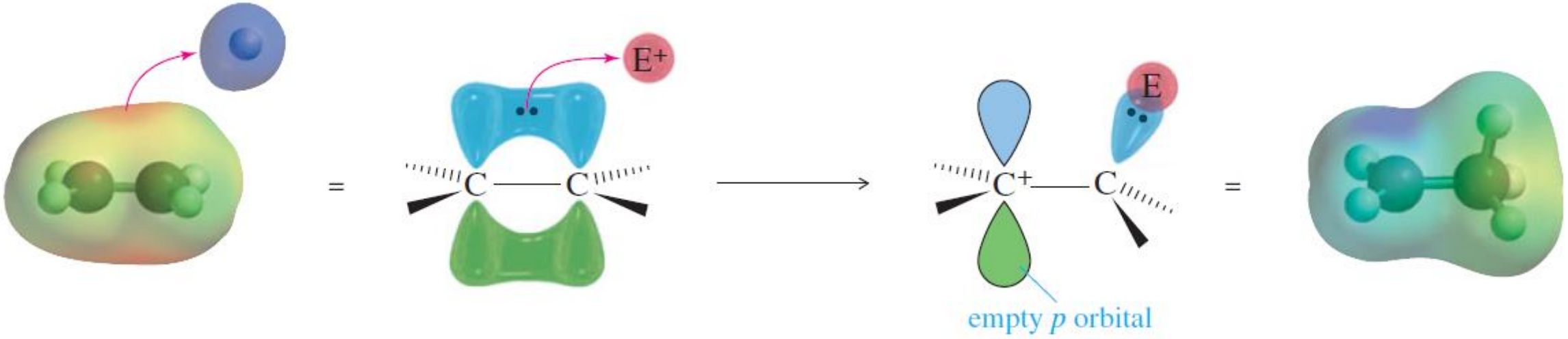
In an addition, **two molecules combine to form one product molecule**. When an alkene undergoes addition, two groups add to the carbon atoms of the double bond and the carbons become saturated.



Electrophilic Addition to Alkenes



The pi-bonding electrons are spread farther from the carbon nuclei, and they are more loosely held. **A strong electrophile** has an affinity for these loosely held electrons. It can pull them away to form a new bond.

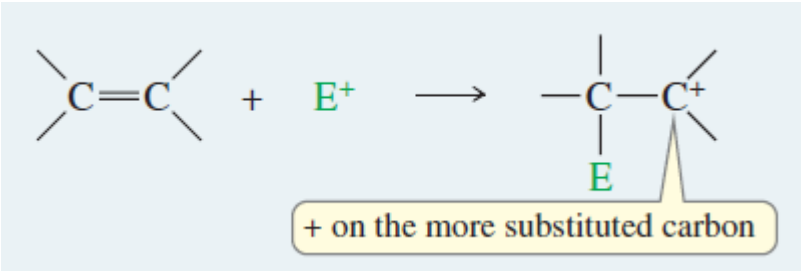


Electrophilic Addition to Alkenes

Mechanism

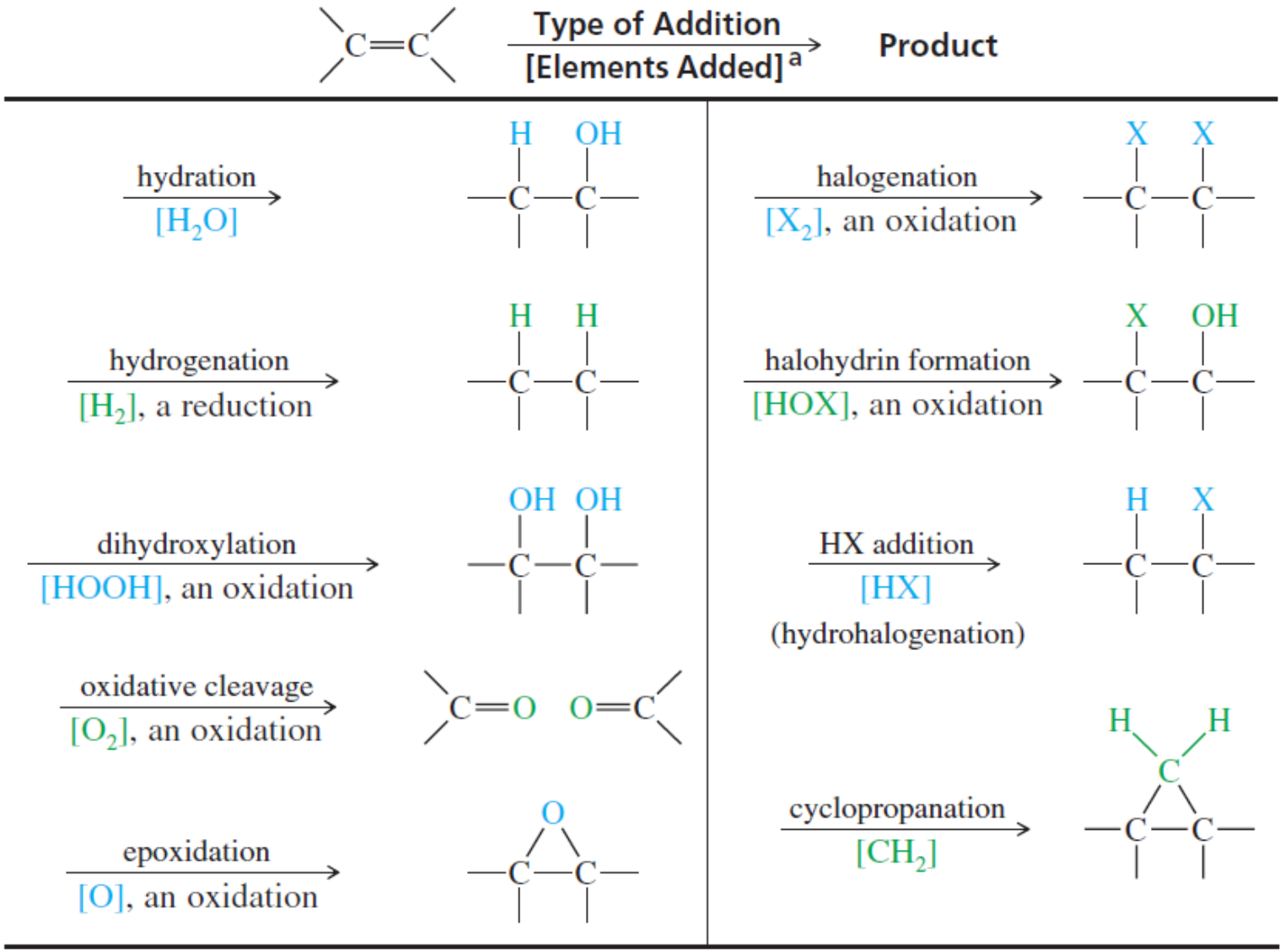
Step 1: Attack of the pi bond on the electrophile forms a carbocation.

Step 2: Attack by a nucleophile gives the addition product.



Example

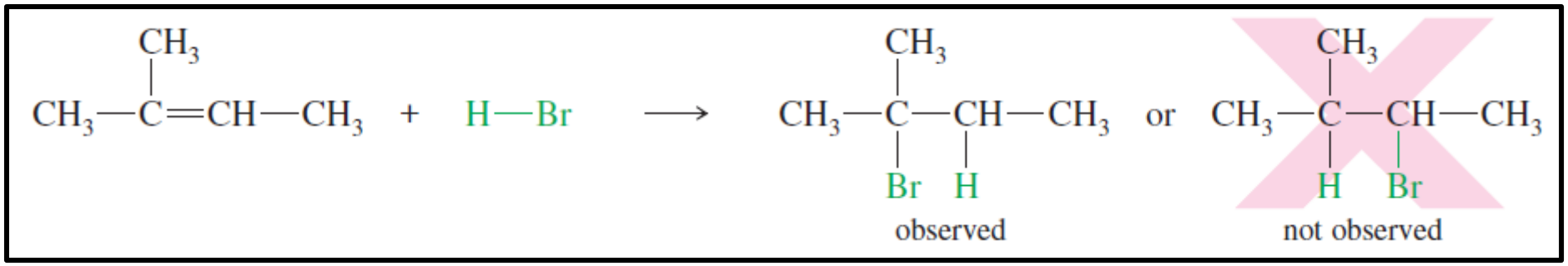
Types of Additions to Alkenes

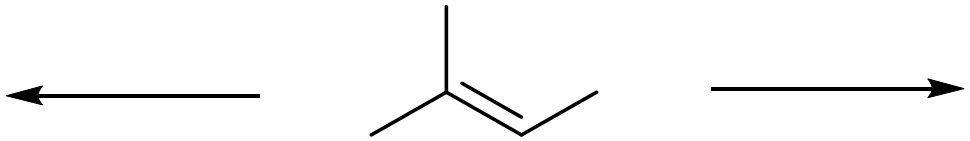


[a]These are not the reagents used but simply the groups that appear in the product.

1) Addition of Hydrogen Halides

- **Orientation of Addition: Markovnikov's Rule**





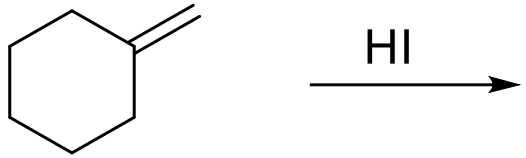
***Regioselectivity**

The proton adds to the end of the double bond that is less substituted to give the **more substituted carbocation**

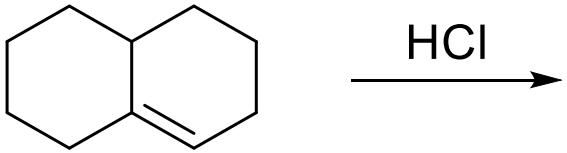
1) Addition of Hydrogen Halides

Example 1 Predict the major products of the following reactions and propose mechanisms to support your predictions.

(a)

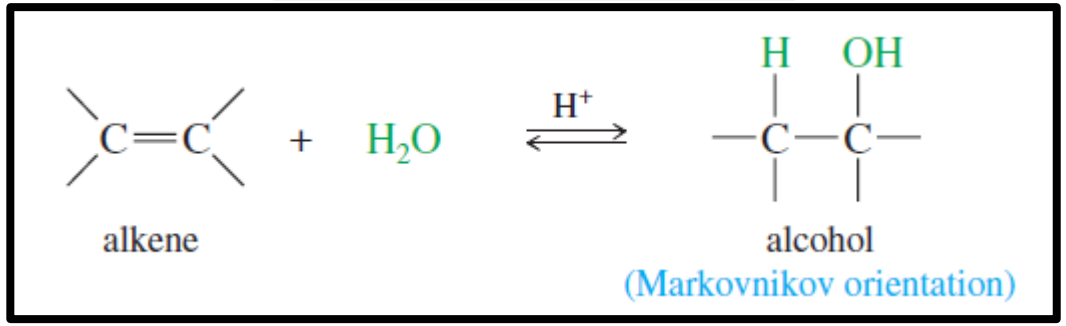


(b)



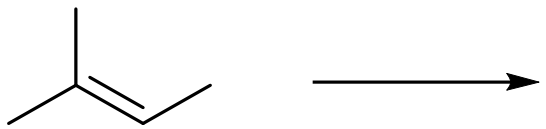
2) Addition of Water: Hydration

Hydration of an alkene



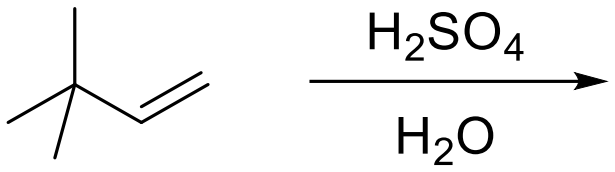
Dehydration of an alcohol

Mechanism



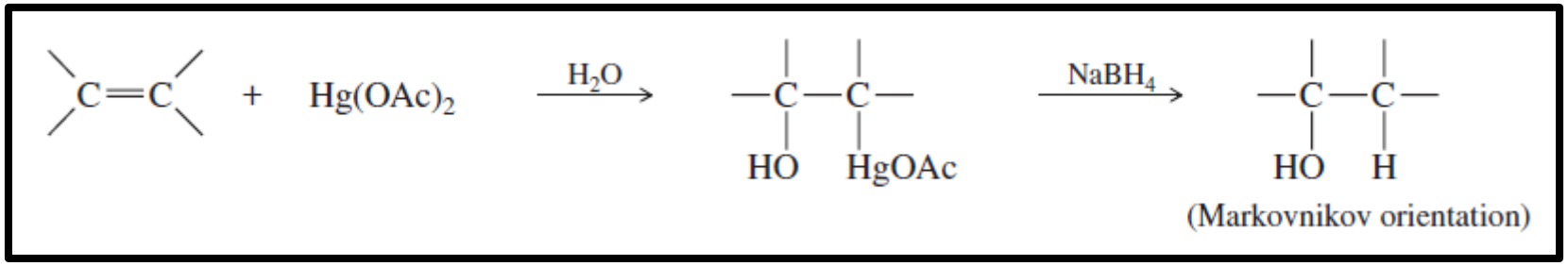
2) Addition of Water: Hydration

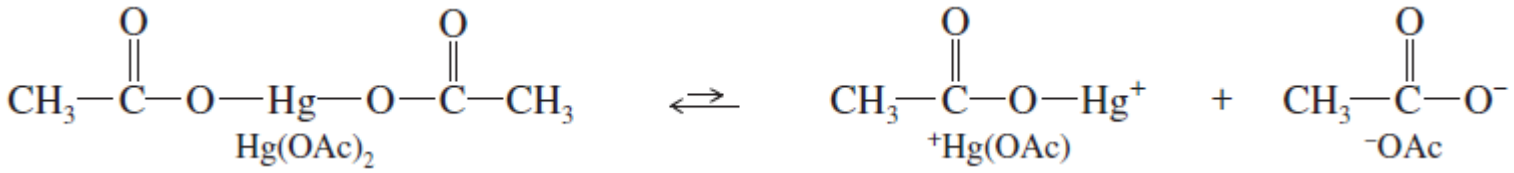
Example 2 Predict the major products of the following reactions and propose mechanisms to support your predictions.

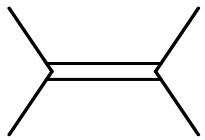


3) Hydration by Oxymercuration–Demercuration

- Works with many alkenes that do not easily undergo direct hydration.
- Takes place under milder conditions.
- No free carbocation is formed, so there is no opportunity for rearrangements or polymerization.







mercurinium ion

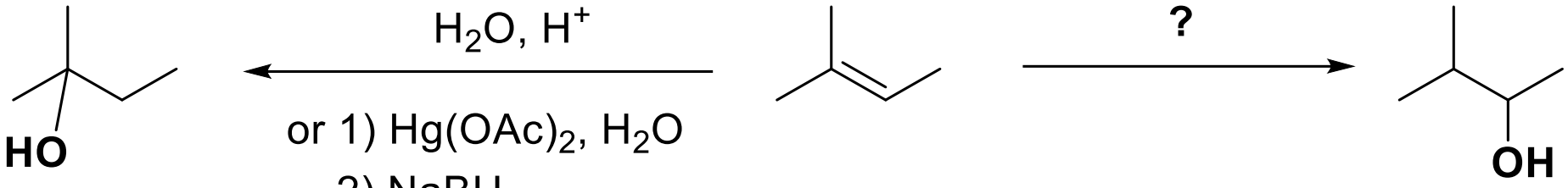
3) Hydration by Oxymercuration–Demercuration

Mechanism

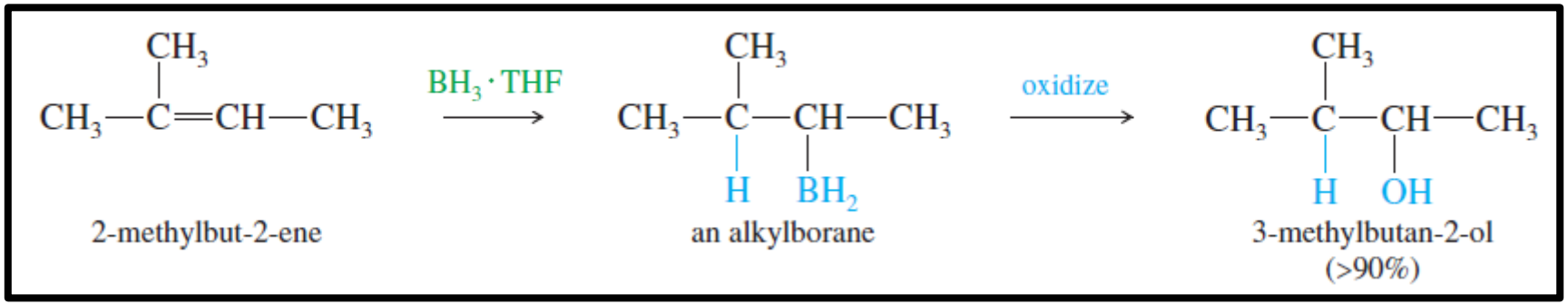
3) Hydration by Oxymercuration–Demercuration

Example 3 Predict the major products of the following reactions and propose mechanisms to support your predictions.

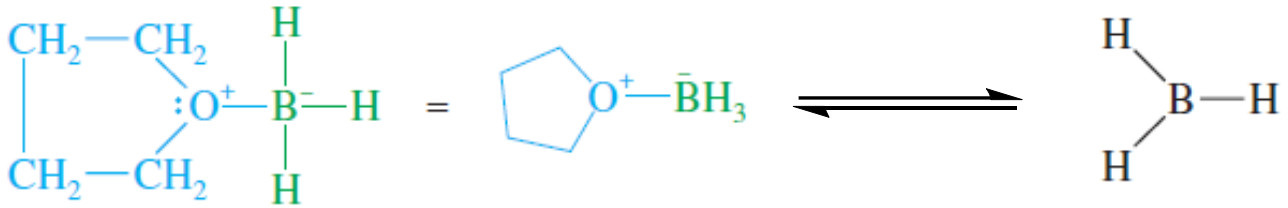
4) Hydroboration



Markovnikov ***anti-Markovnikov***



2-methylbut-2-ene — an alkylborane — 3-methylbutan-2-ol (>90%)



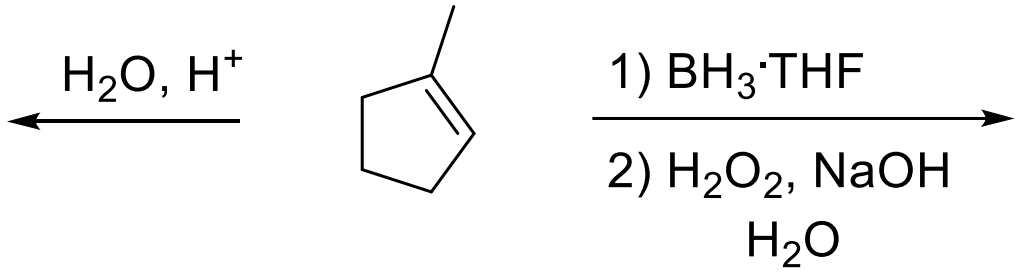
borane–THF complex = $BH_3 \cdot THF$ borane

4) Hydroboration

Mechanism

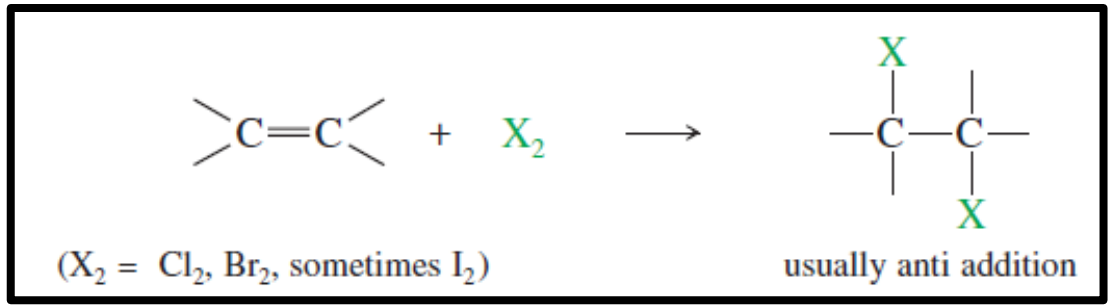
4) Hydroboration

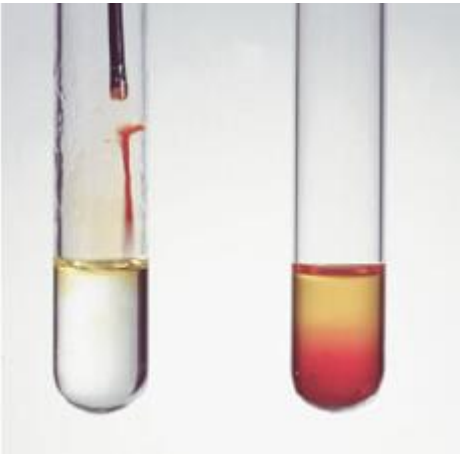
Example 4 Predict the major products of the following reactions and propose mechanisms (of the addition step) to support your predictions.



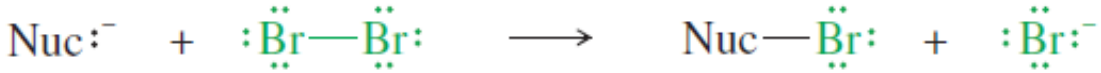
5) Halogenation

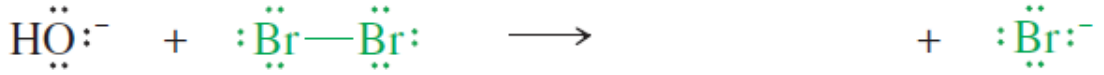
Halogens add to alkenes to form **vicinal dihalides**.

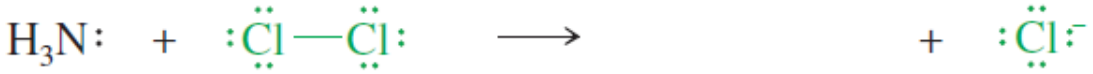


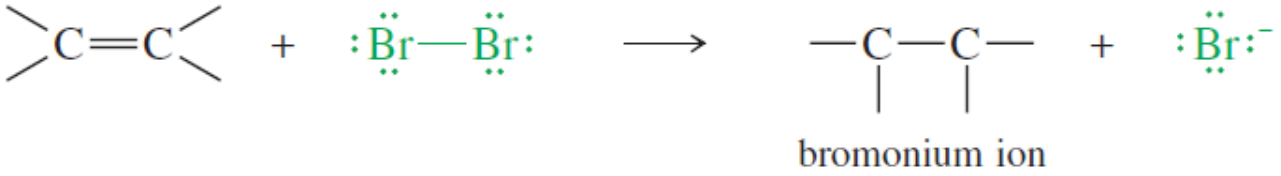


A halogen molecule (**Cl_2**, **Br_2**, **I_2**) is **electrophilic**; a nucleophile can react with a halogen, displacing a halide ion:

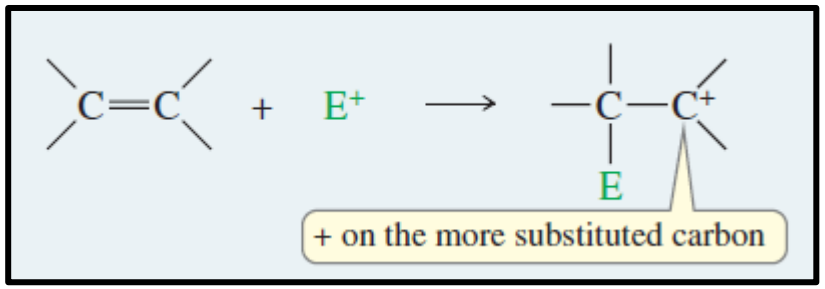




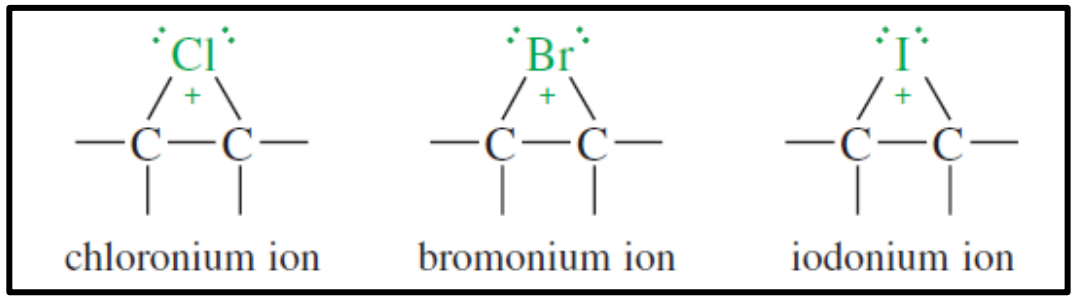




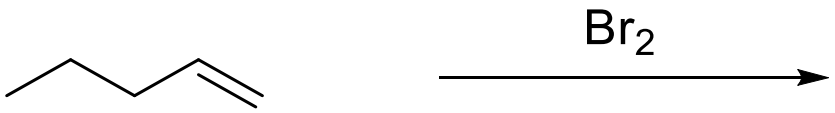
5) Halogenation



vs.

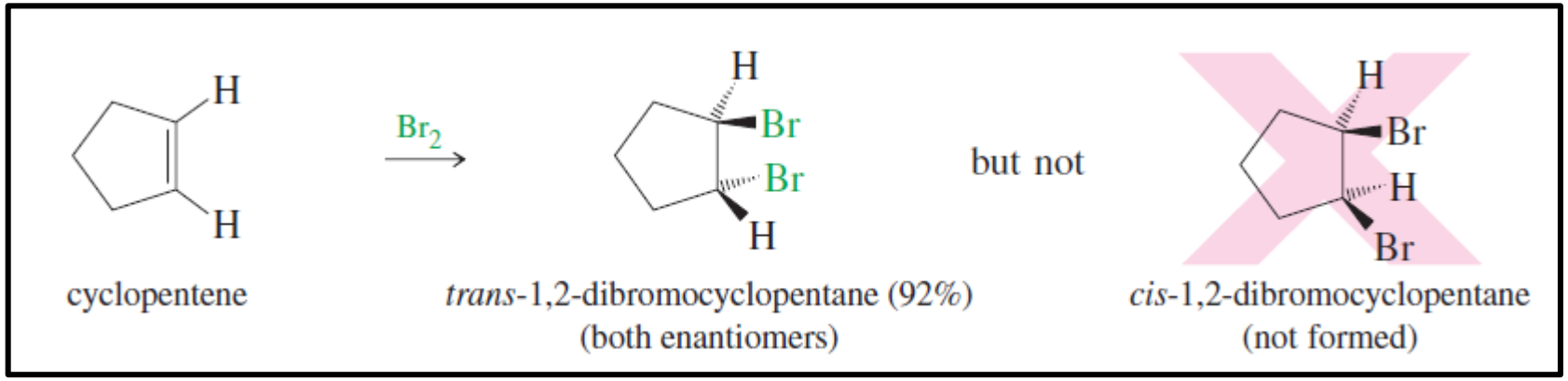


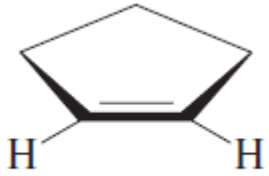
Mechanism



5) Halogenation

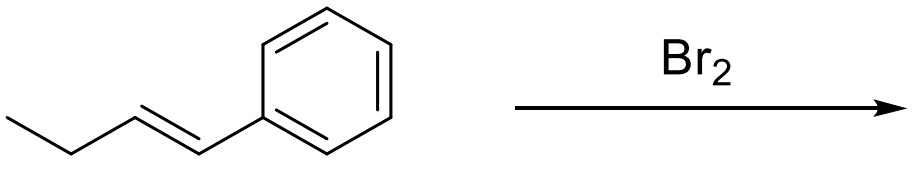
Stereochemistry of Halogen Addition





5) Halogenation

Example 5 Propose mechanisms and predict the major products of the following reactions. Include stereochemistry where appropriate.



Example 6 Propose mechanisms and predict the major products of the following reactions. Include stereochemistry where appropriate.