OCSP 2020: Lecture 7

alkene C=C

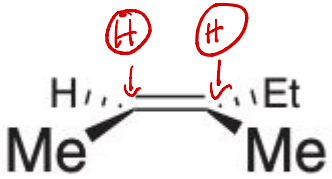
Today's Agenda

- Syn Addition (alkene with H_2 + Pd/C)
- Anti Addition (alkene with Br_2, alkene with Br_2 and H_2O)
- Markovnikov additions (alkene with H-X)
- Anti-Markovnikov additions (alkene with HBr and HOOR)
- Ozonolysis

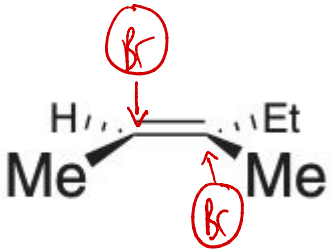
Alkene Additions

- General pattern: the double bond attacks an atom on another molecule, forming an intermediate (often a carbocation)
    - Next, this intermediate is attacked at an electrophilic point,, creating the product

- Syn addition- atoms add to same face of molecule

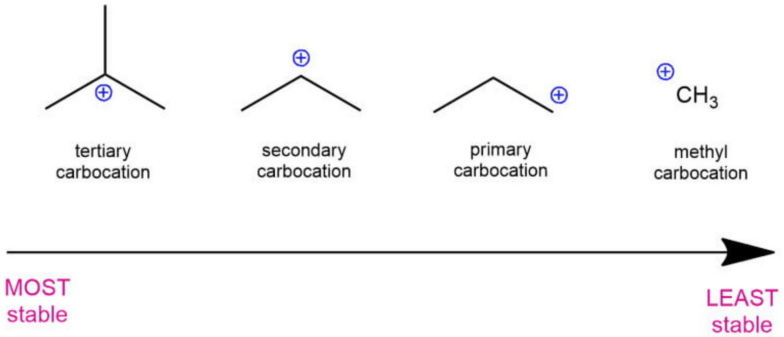


- Anti addition-atoms add to different faces of molecule



Review: stability of carbocations

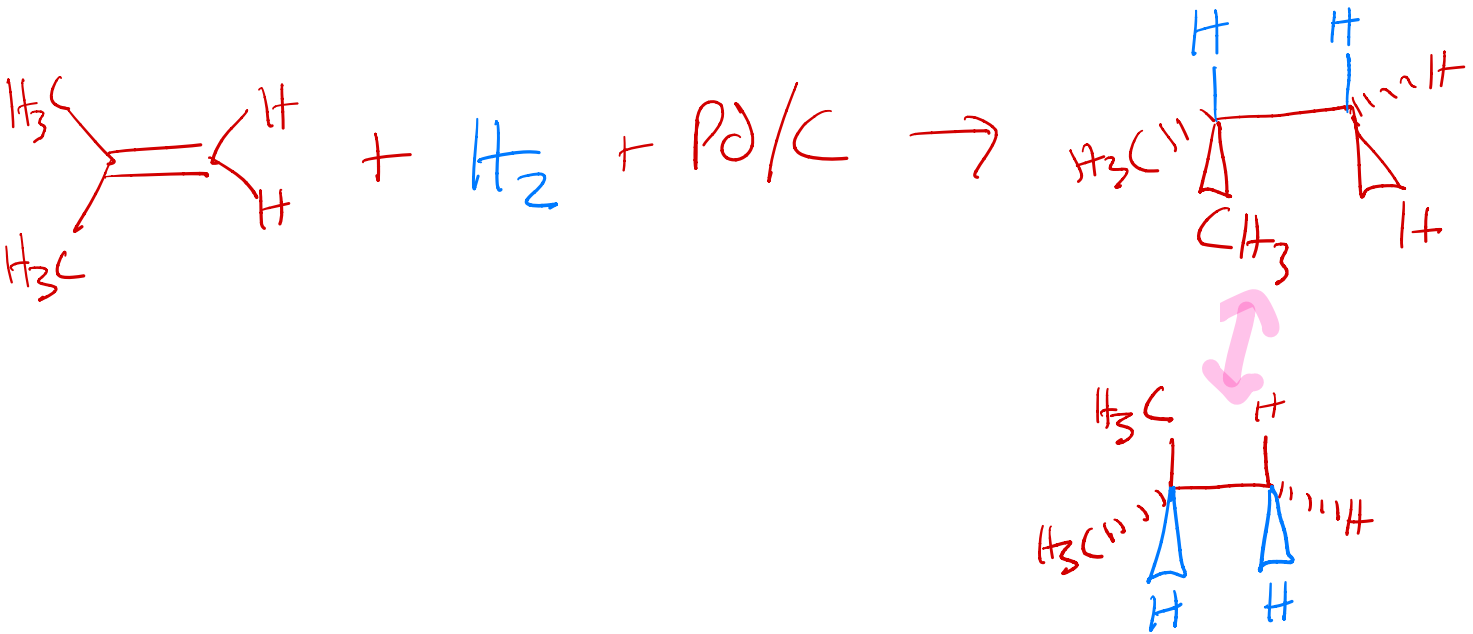
- Tertiary C+ >> secondary C+ >>>> primary C+



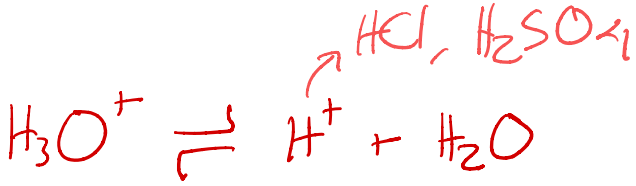
- More stable intermediates and products are preferred and are easier to form

Syn-Addition

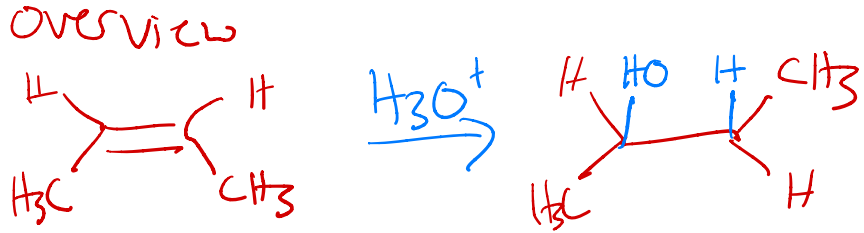
- Example: alkene with H_2 and Pd/C

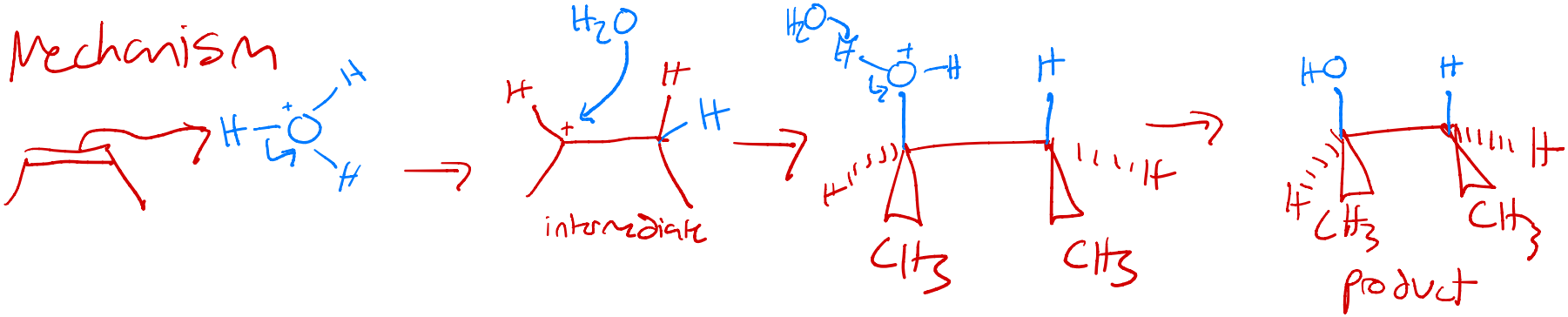


Syn-Addition



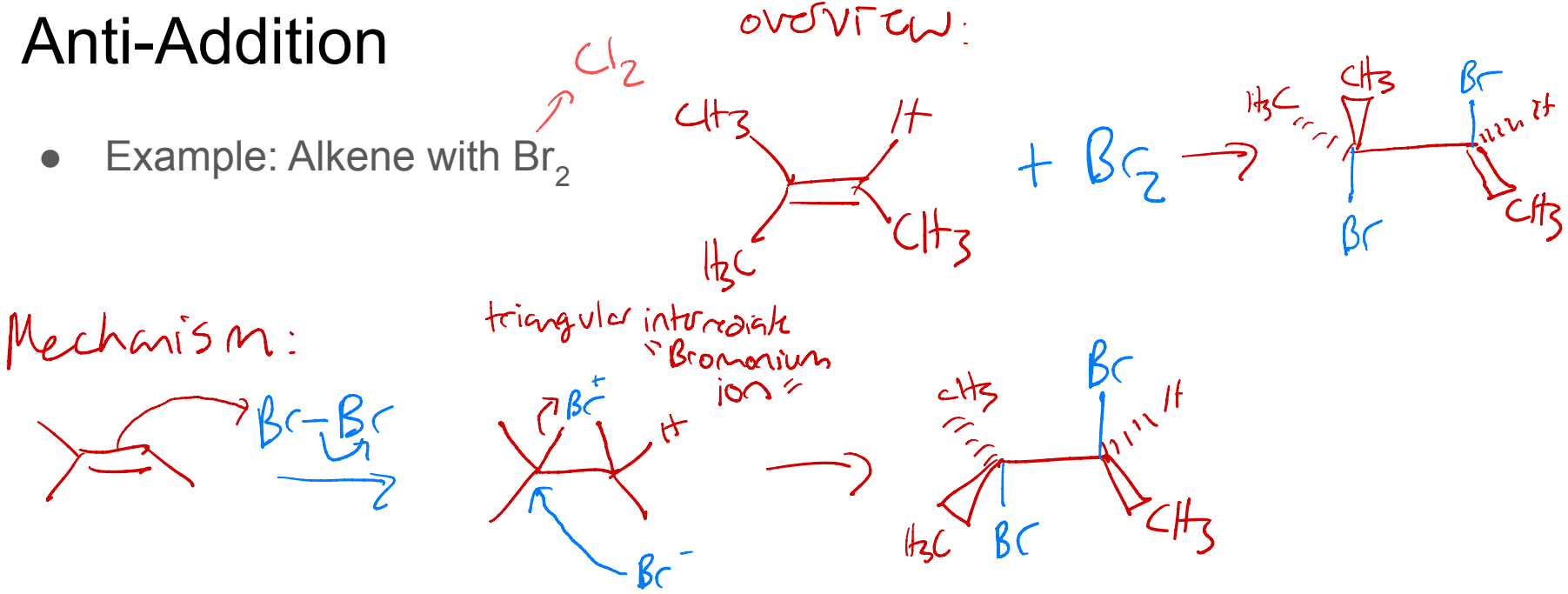
Example: Alkene with H_3O^+ (alternatively: any source of H+ and H_2O)





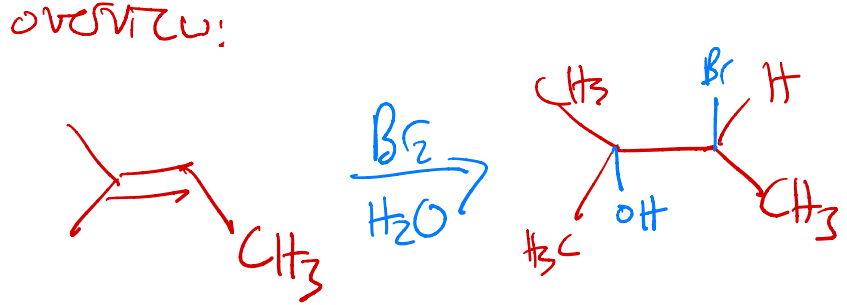
Anti-Addition

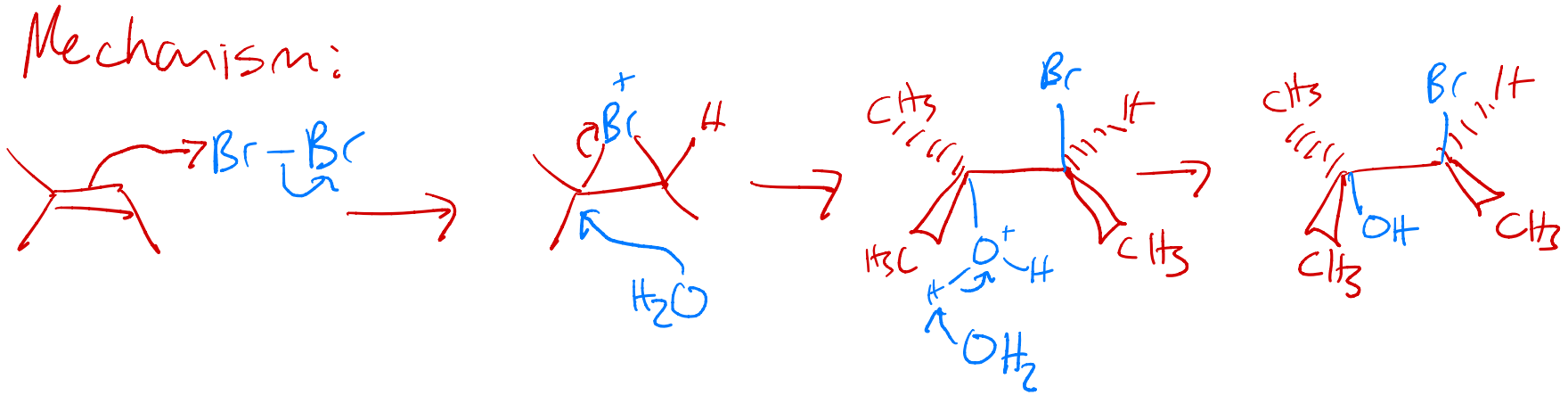
- Example: Alkene with Br_2



Anti-Addition

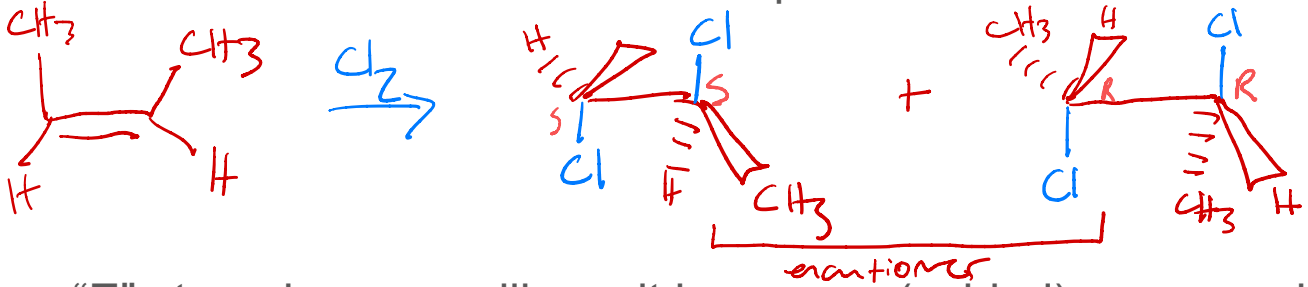
-Example: alkene with Br_2 and H_2O



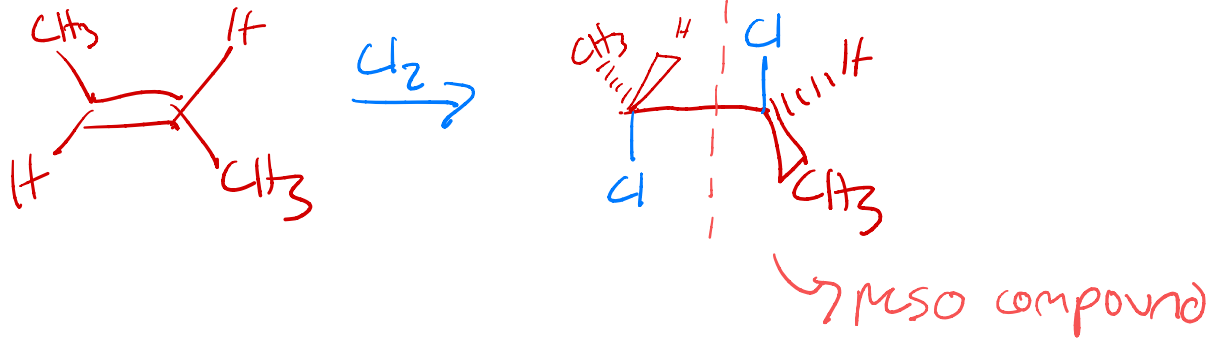


Stereochem and Anti-Addition

- "Z" stereoisomers *can* result in a product and its enantiomer

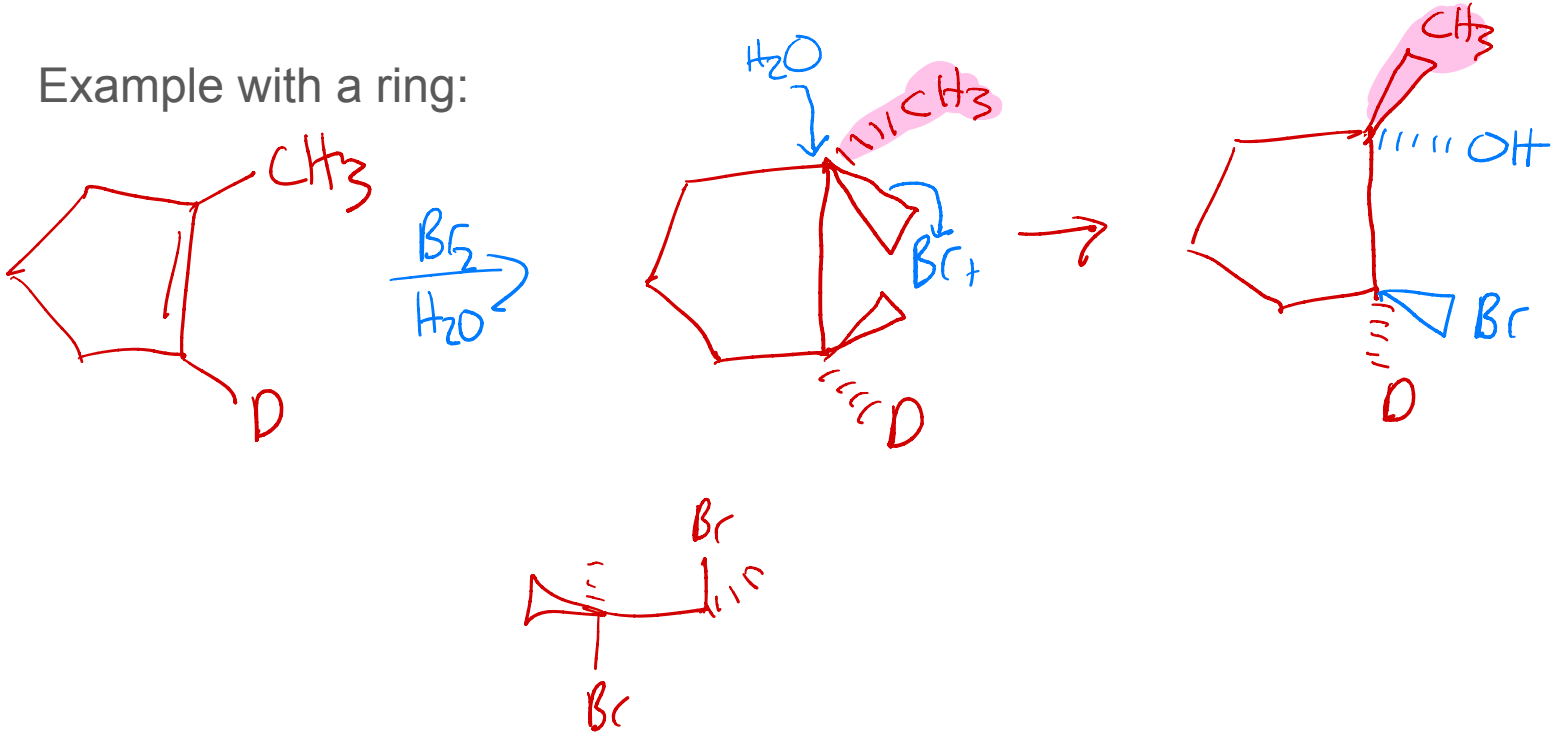


- "E" stereoisomers will result in a meso (achiral) compound



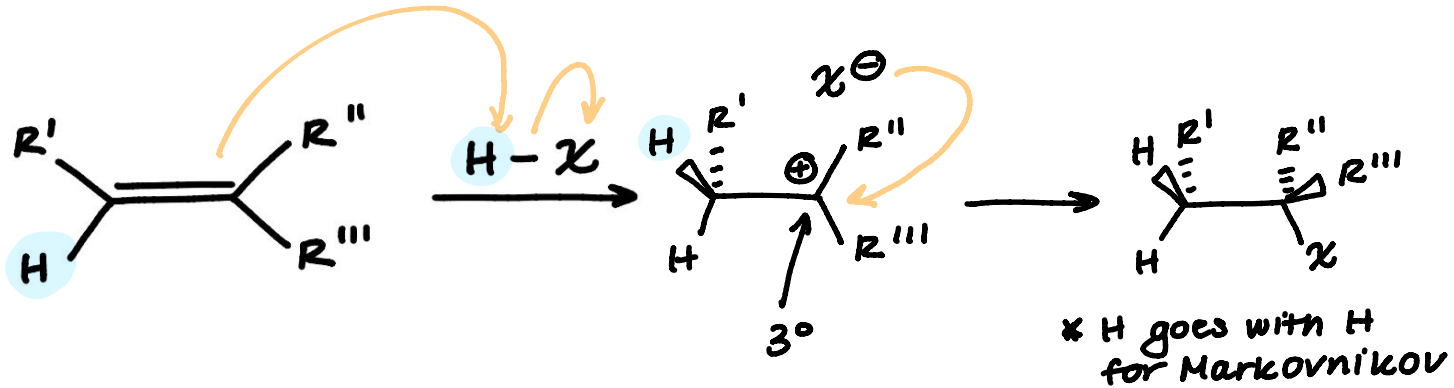
Stereochem of Anti-Addition

- Example with a ring:



Markovnikov Rule

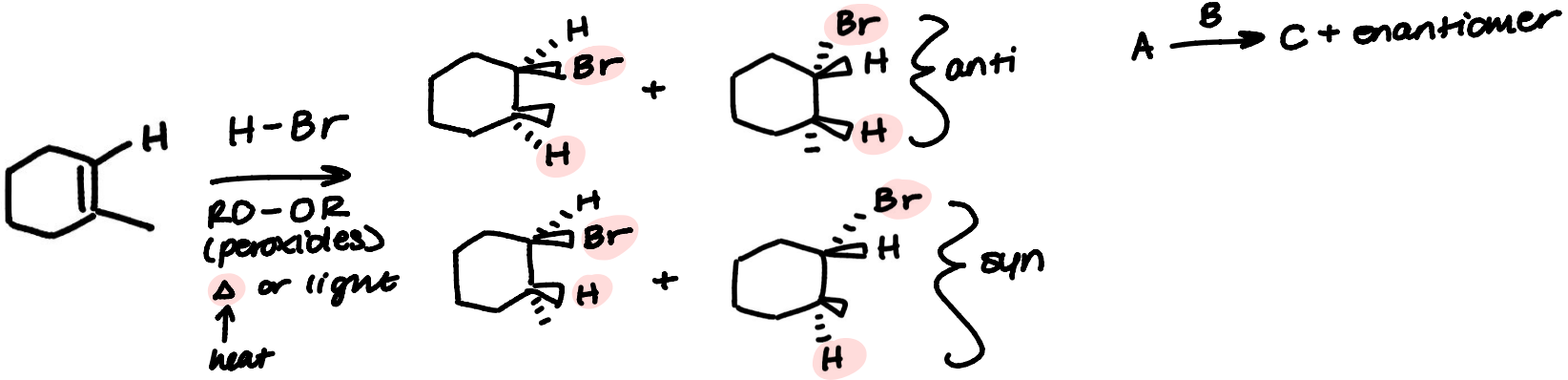
- Alkene addition; product with the **most stable C+ intermediate** is *preferable* (MAJOR)
  - X (halogen: Cl, Br, I) adds to more substituted C (→ most other carbons attached)
  - H prefers C with more H's
- This intermediate will be the most stable
- Example: Alkene & H-X (e.g. HBr) (HX → hydrogen halide)



Anti-Markovnikov Additions

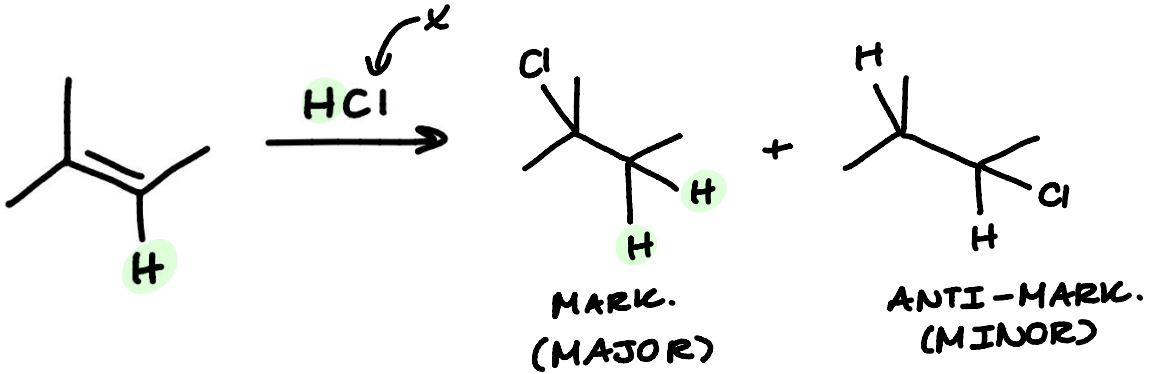
X added to C with most H's

- **OPPOSITE HAPPENS!** (H added to more substituted C)
- Example: alkene + HBr with peroxide (RO-OR) HOOR → free radicals ·O-R



- Mechanism involves radicals - do not worry about memorizing
- We will cover more anti-markovnikov additions later this week!

Quick Check | What are the product(s) of this rxn?



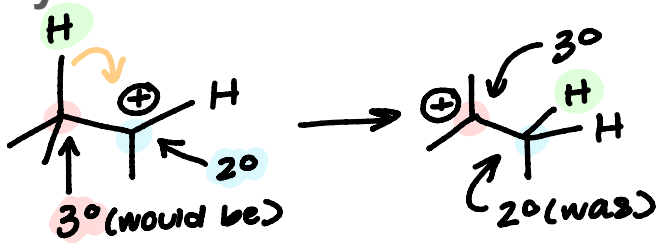
H-R

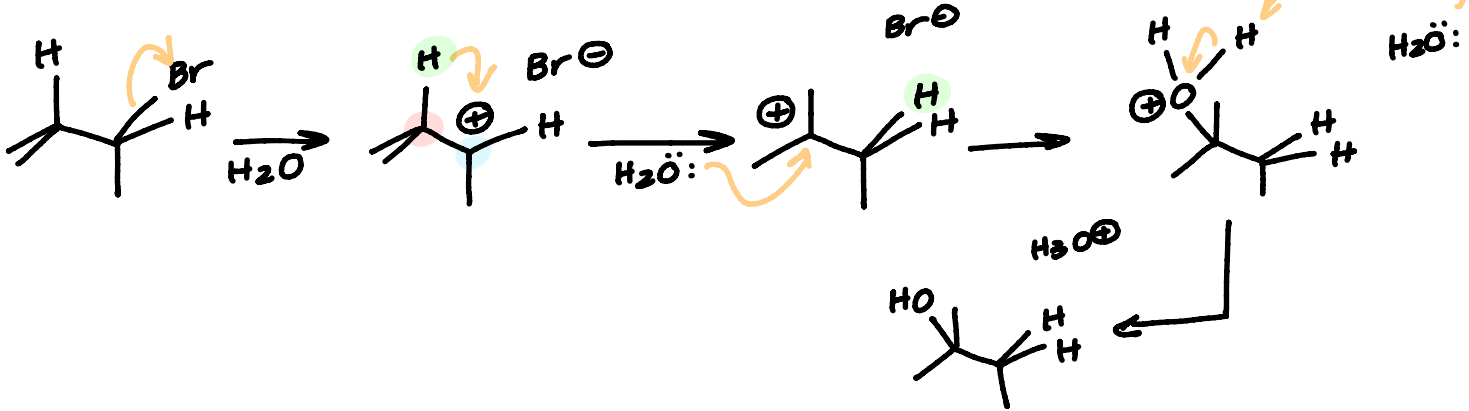
Watch out for hydride shifts!

tertiary carbocation
3° > 2° > 1°

- **Hydride shifts** can occur if… 3° next to 2°, 3° next to 1°, or 2° next to 1°

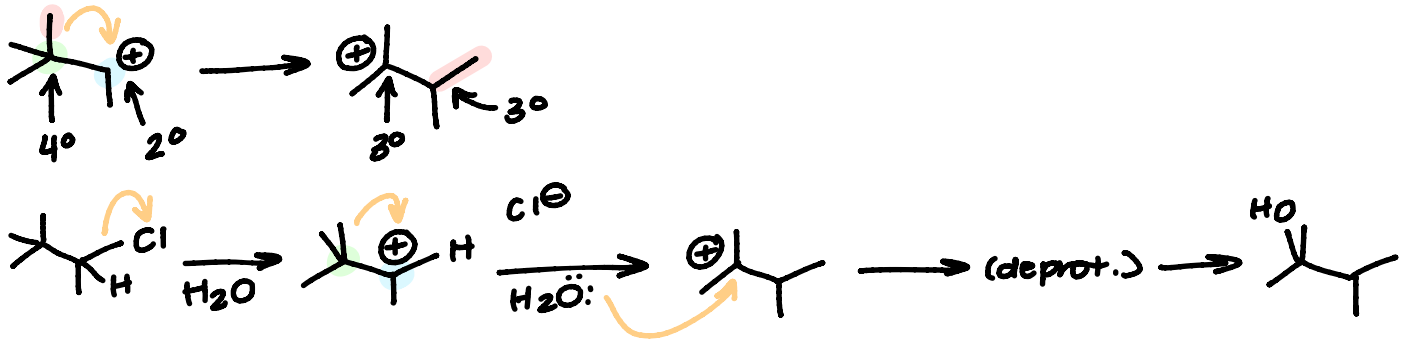
secondary C⊕





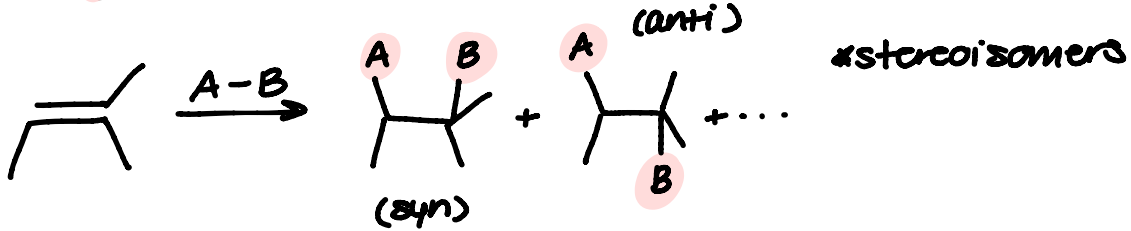
Watch out for methyl shifts!

- **Methyl** (or alkyl) **shifts** can occur if... 4° next to 2°, 4° next to 1°
  - Don't occur as readily as H shifts because they are larger (think steric hindrance)

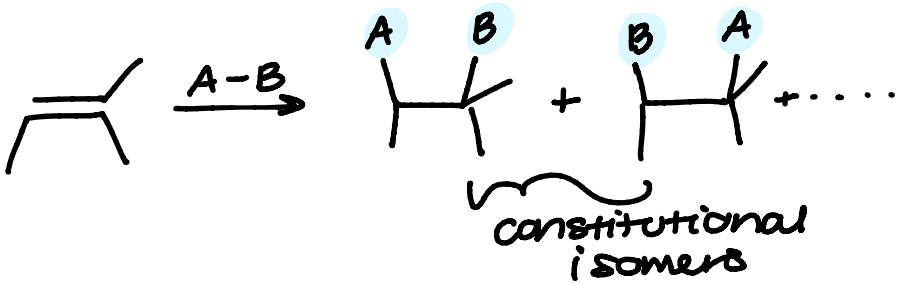


Regiochemistry vs. Stereochemistry

- Stereochemistry deals with *stereoisomers*
  - **Syn** and **Anti** products are terms used to describe *stereochemistry*



- Regiochemistry deals with *constitutional isomers*
  - **Markovnikov** and **Anti-Markovnikov** products are terms used to describe *regiochemistry*



Advice for reactions

- Concentrate on how to create on **stability**
  - Certain reactions follow the Markovnikov Rule because it is more stable for them
  - H and methyl shifts occur to increase stability

Anti-Markovnikov Additions

- Results to H being added to more substituted C on alkene
- Example: alkene + HBr with trace peroxides (HOOR)

- Mechanism involves radicals-do not worry about memorizing it
- We will cover more anti-markovnikov additions later this week