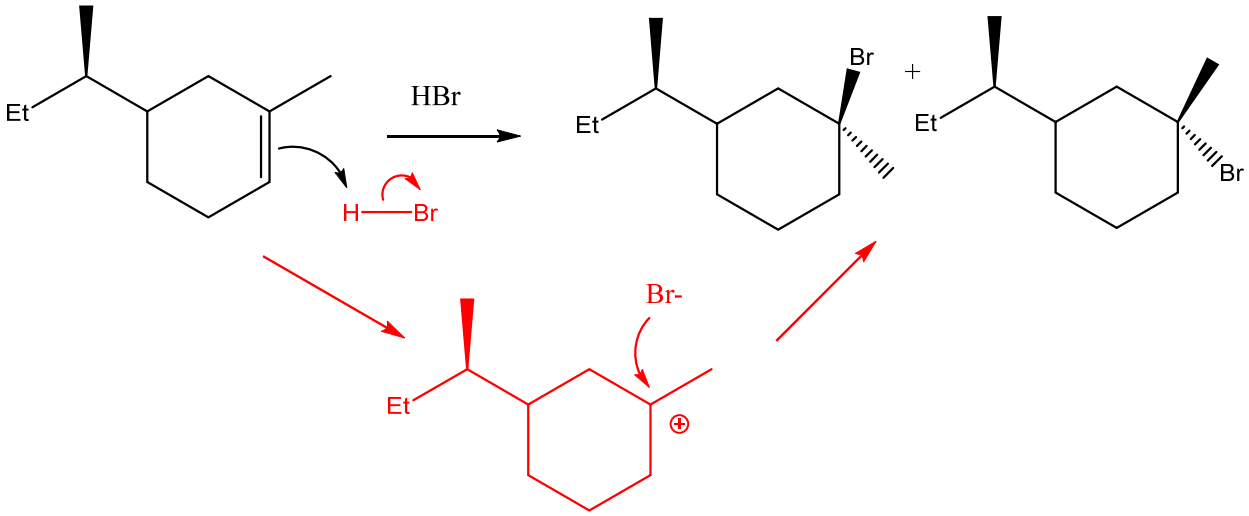
Discussion Worksheet #10
Electrophilic Additions

Skill 1: Draw arrow mechanisms of electrophilic addition of HX and H_3O^+

- A mechanism is an explanation of how and why a reaction happens like it does
- It has to explain the regiochemistry outcome
- It has to explain the stereochemistry outcome
- It has to explain rearrangements.
- The identity of the starting materials and reagents dictate the mechanism because every molecule has a way of reacting in a most energetically favorable way.
- Use arrows by drawing from the nucleophile (most reactive pair of electrons) to the electrophile (most partially positive atom)

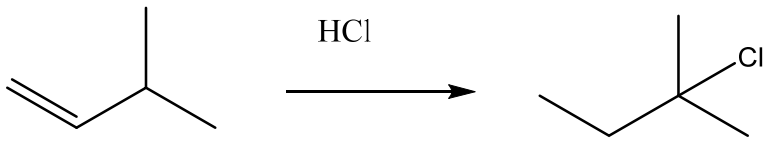
Problem 1. Draw an arrow mechanism with all intermediates for this reaction. In once sentence, how does this mechanism explain the regiochemical outcome? In one sentence, how does this mechanism explain the stereochemical outcome?

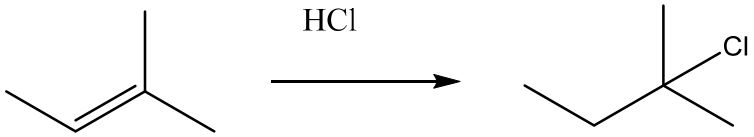


Regiochemistry: The proton is added to the less substituted carbon of the double bond because the more stable tertiary carbocation forms faster.

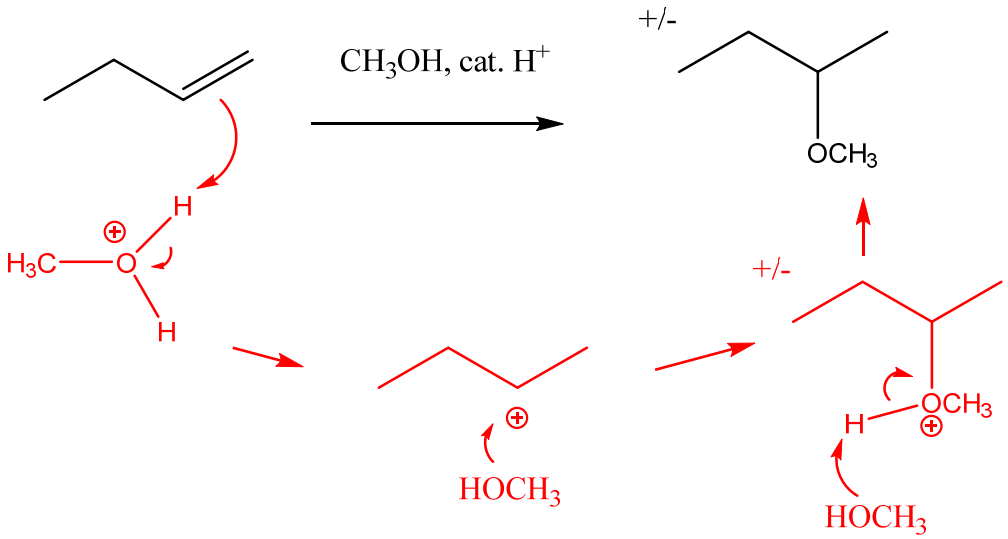
Stereochemistry: Two diastereomers form because the bromide can add to either side of the planar carbocation giving a mix of stereochemistry at that chiral center.

Problem 2. Draw the high energy intermediate for each of these reactions. Explain why the two different alkenes give the same product.

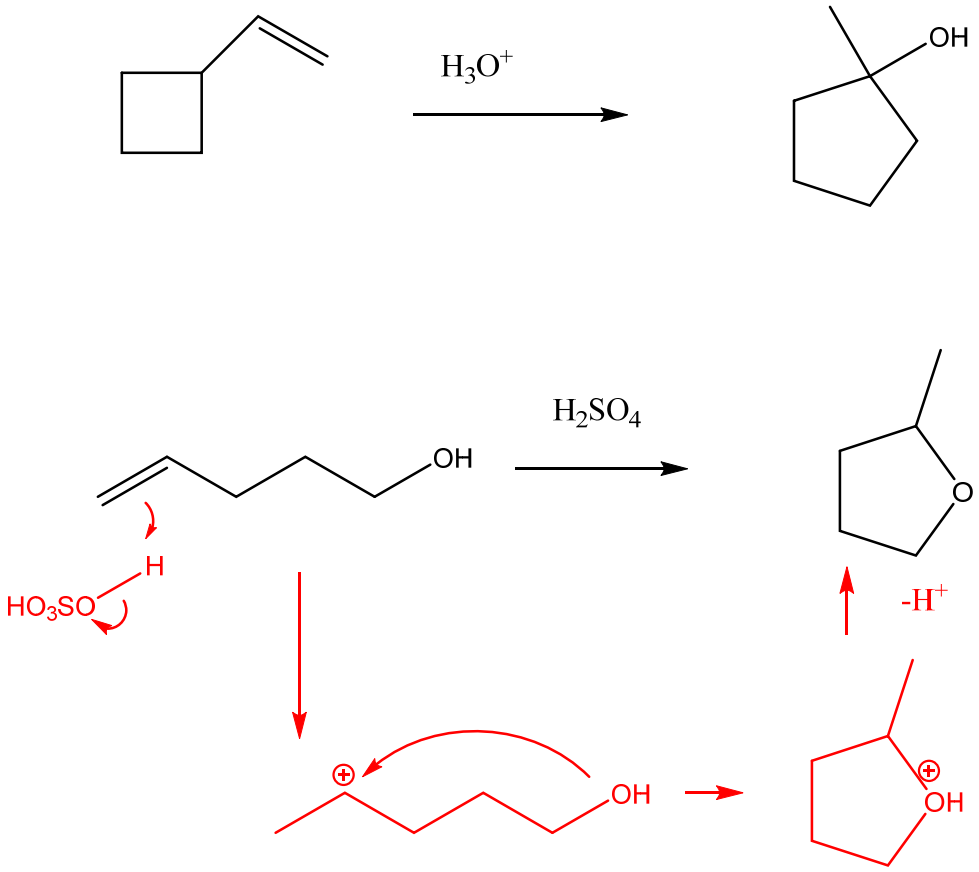




Problem 3. Draw an arrow mechanism with all intermediates. Use the mechanism to explain the observed regiochemistry and stereochemistry.



Problem 4. Draw arrow mechanisms with all intermediates.



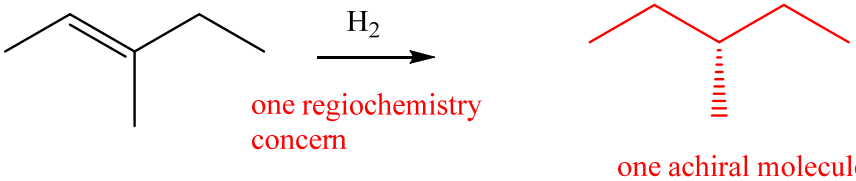
Skill 3: Predict the products of addition: regioselectivity and stereospecificity

- Regiochemistry: First, look at the starting material
  - If it is symmetrical, regiochemistry is not applicable
  - If it is asymmetrical, regiochemistry is applicable—consider the reagent
- Second, look at the reagent
  - If it is symmetrical, regiochemistry is not applicable
  - If it is asymmetrical, regiochemistry is dictated by the mechanism

- Stereochemistry: First, look at the new carbon centers formed in the product
  - If it has no chiral centers form, only one, molecule will be produced with no stereochemistry designated at those centers
  - If it has one chiral center produced, it will form two products with both possible stereochemistries at that center
  - If it has two chiral centers produced, it can form up to 4 different stereoisomers (Then see rule two)
- Second, look at the reagent
  - If it produces a mix of stereochemistries, all possible stereoisomers form
  - If it only produces *syn* or *anti* products, then only two of the possible stereoisomers (a pair of enantiomers) form

Problem 5. Apply regioselectivity and stereospecificity principles. How many distinct major products are formed in each of these reactions? Draw them all out.

A.



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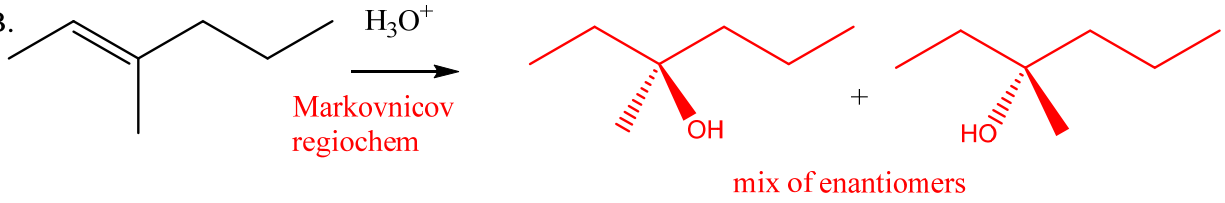

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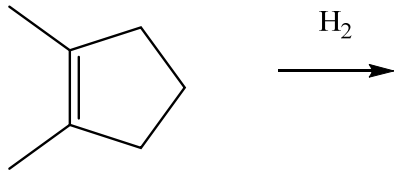

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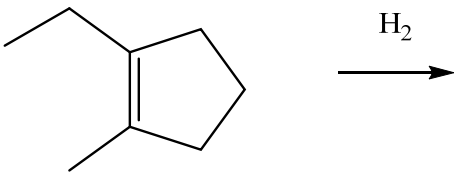

Problem 6. Predict the major product(s) of the following reactions.