

Chapter 3: Elimination Reactions (E1 and E2)

In an elimination reaction two atoms on adjacent carbons are eliminated to form a pi bond. In first semester organic chemistry this normally means breakage of C-H and C-X on adjacent carbons.



Elimination reactions follow one of two mechanistic pathways: a pathway where the rate-determining step is unimolecular (E1) and a pathway where the rate determining step is bimolecular (E2).

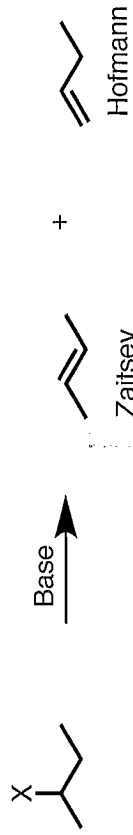
E1 Reactions



Starting material rate of reactivity (LG degree of substitution) 3° (fastest) $> 2^\circ \gg 1^\circ$ (slowest)

- Weak base
- Polar solvent (protic or aprotic)
- Carbocation intermediate formed
- Step-wise mechanism
- First order kinetics: rate depends solely on concentration of substrate
- Typically forms the most stable alkene (Zaitsev product)
- No stereochemical requirements for the starting material

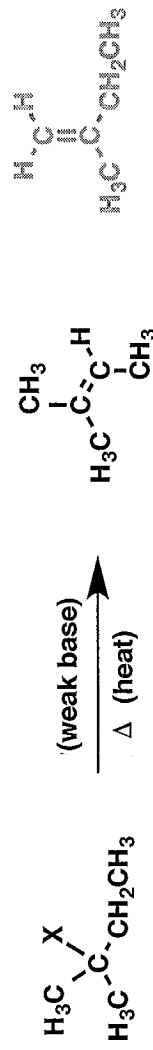
E2 Reactions



- Strong charged bases (e.g. alkoxides, RO^-)
- Polar solvent (often the conjugate acid of the base)
- Concerted mechanism; no carbocation intermediate
- Second order kinetics - rate depends on size of base and degree of substitution of leaving group
- The H and the X group must be anti co-planar in order to undergo elimination
- The ratio of Zaitsev to Hofmann elimination products is based on the size of the base and the degree of substitution of the leaving group

E1 Elimination With A Halide Leaving Group

General Reaction:



X = halide

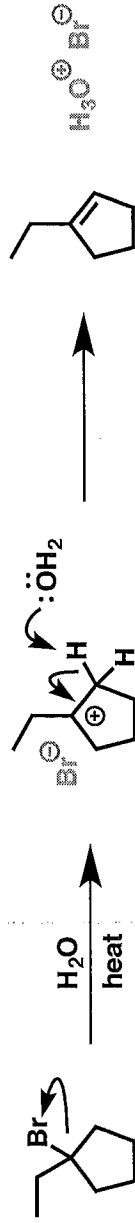
Favored product ("Zaitsev") has the most substituted double bond

Typical bases are protic solvents like H₂O and ROH

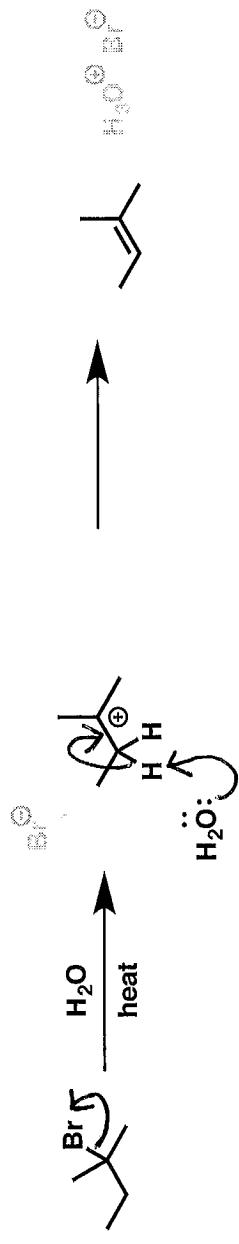
Mechanism Basics Box:

- Leaving groups (X) include halogens such as Cl, Br, and I in addition to alkyl sulfonates
- May or may not require heat to push the equilibrium towards heat
- The starting material (substrate) has a leaving group that is typically tertiary (3°), allylic (3°, 2° or 1°) and to a lesser extent 2°
- The reaction proceeds via a carbocation which can rearrange to become more stable
- The Zaitsev rule applies to this elimination; the more stable alkene is formed preferentially
- E1 under these conditions often competes with S_N1 solvolysis reactions
- May be a poor yielding reaction

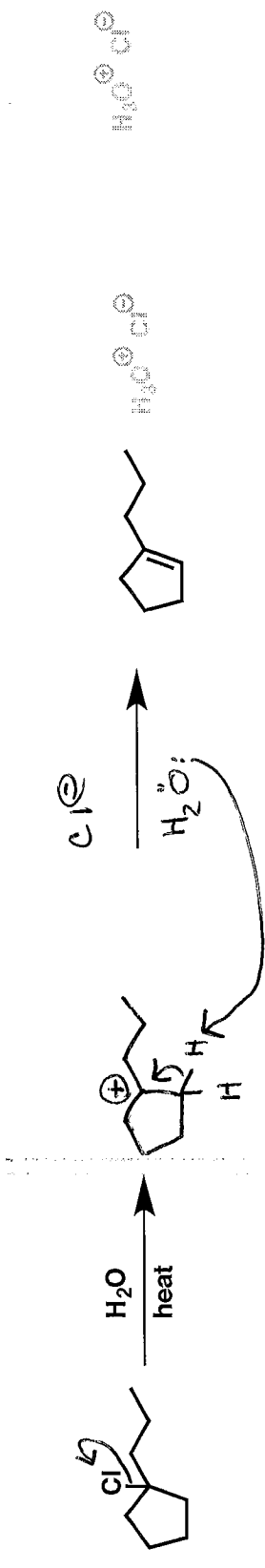
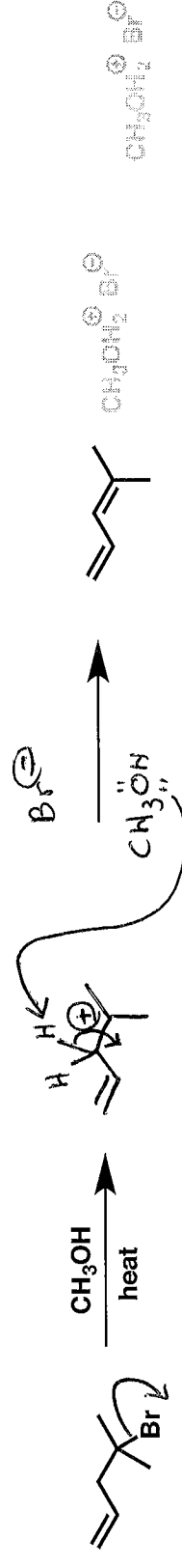
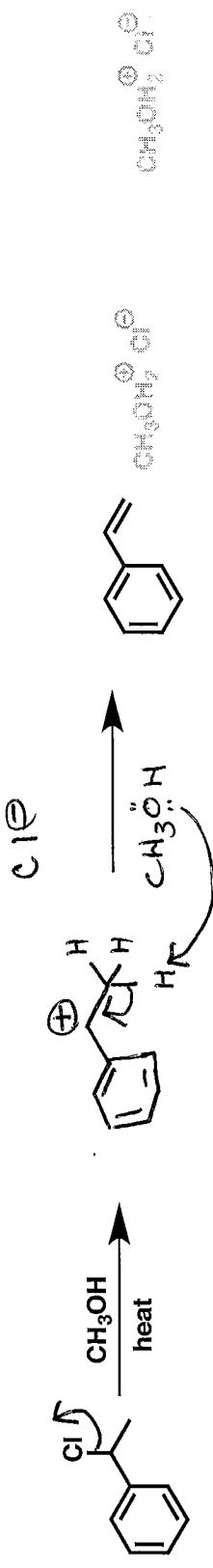
General Mechanism:



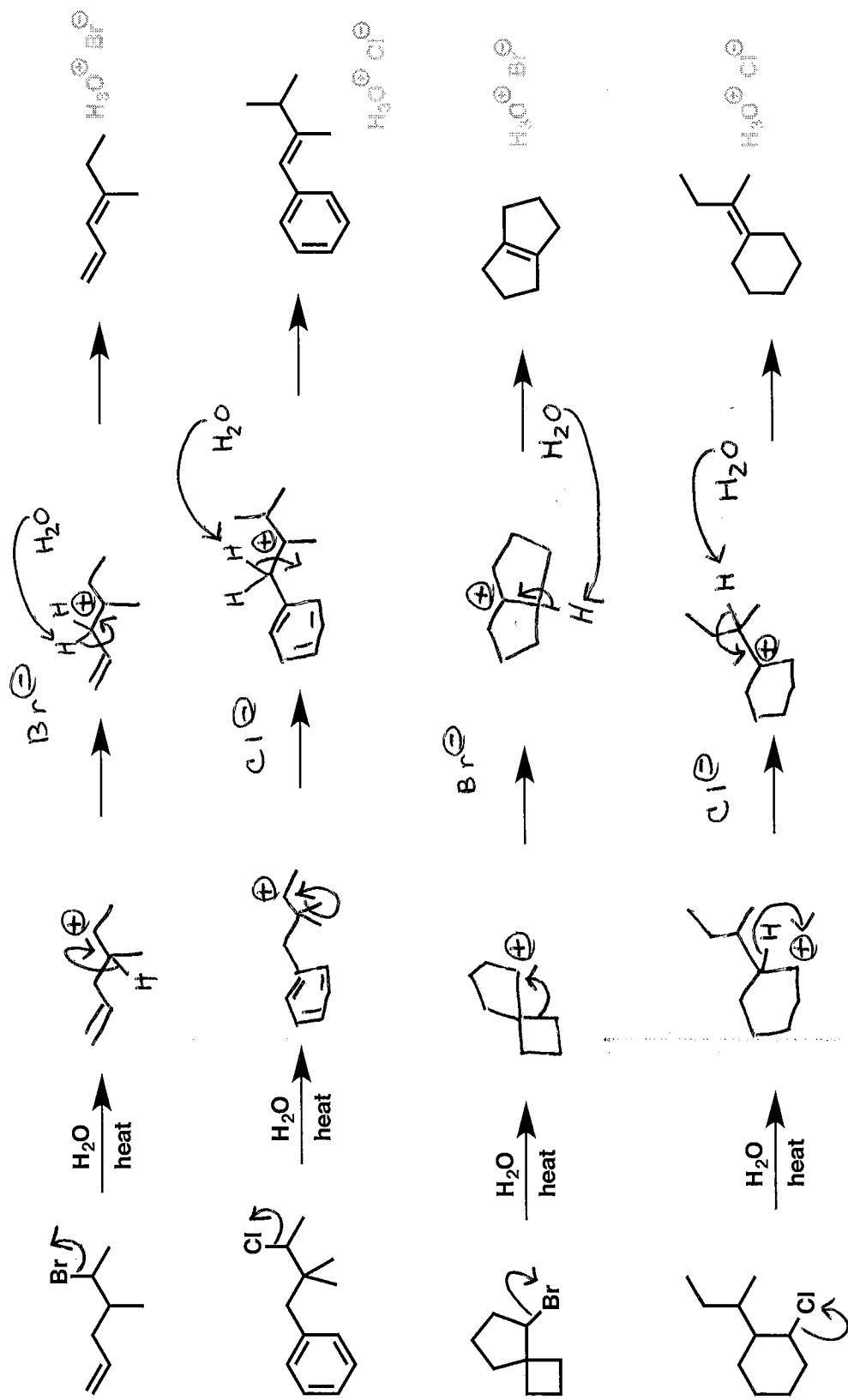
Fill in the missing arrows.



Complete the mechanism by following the pattern (draw arrows and intermediate).

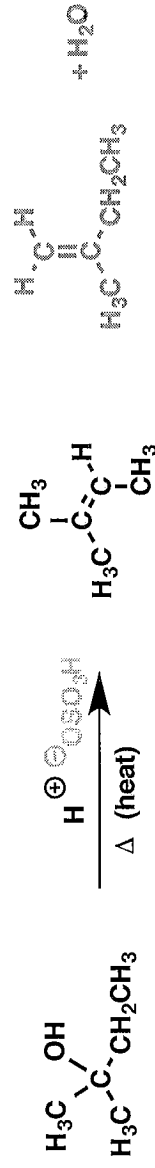


Provide missing mechanism arrows and intermediates. Keep an eye out for hydride shifts, methide shifts, ring expansions and contractions that are common for carbocations.



E1 Elimination With An Alcohol Leaving Group

General Reaction:

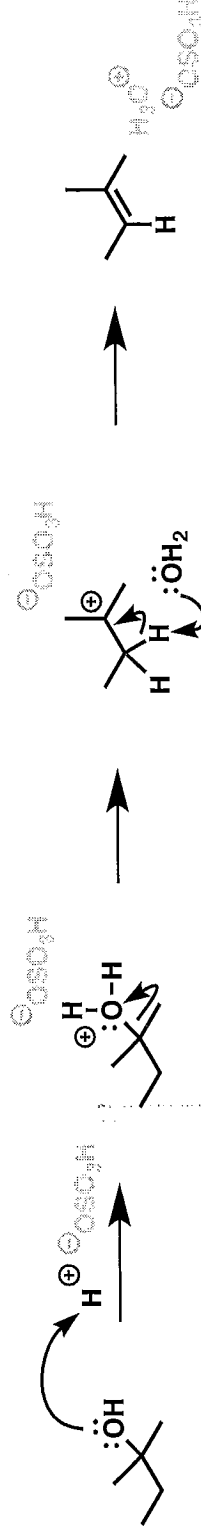


Acids that can be used include H_2SO_4 , TsOH , and H_3PO_4

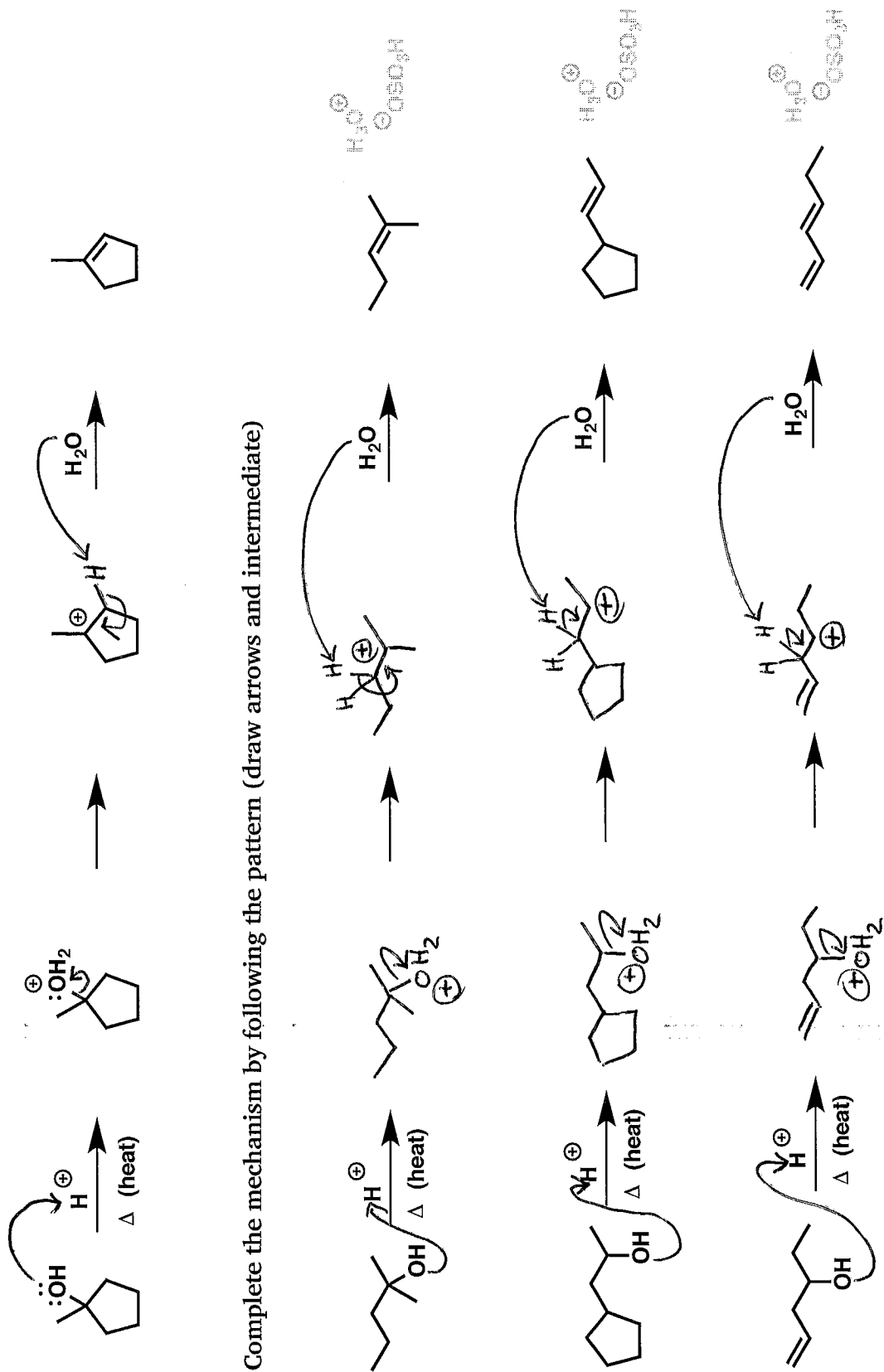
Mechanism Basics Box:

- See mechanism box for E1 with a halide leaving group
- The alcohol will not act as a leaving group unless it is protonated
- Use mineral acids such as H_2SO_4 , TsOH , or H_3PO_4 to protonate the alcohol (HCl , HBr , or HI will convert the alcohol to a halide via $\text{S}_{\text{N}}1$)
- The more substituted alkene will be preferentially formed (“Zaitsev’s rule”)

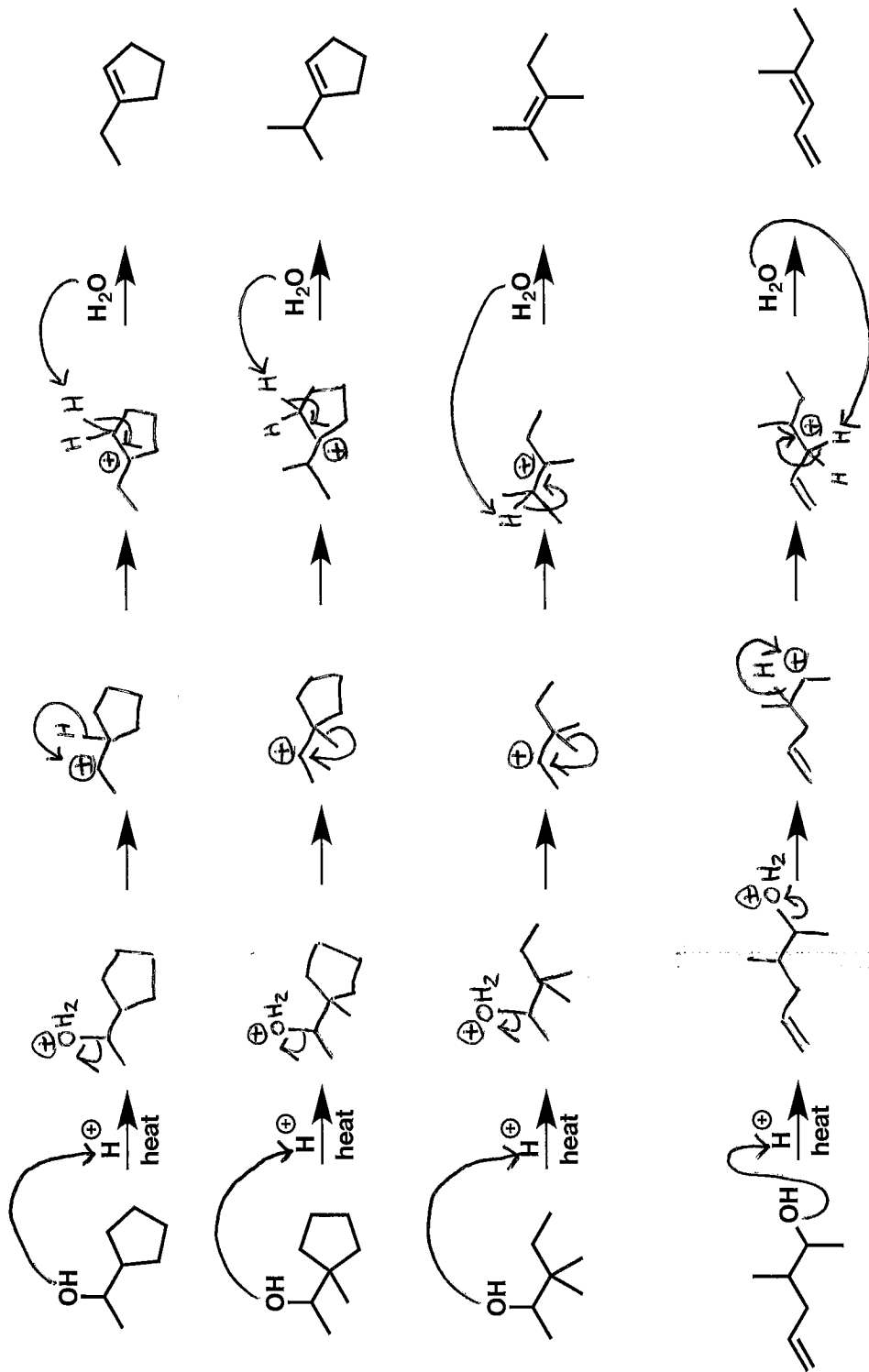
General Mechanism:



Fill in the missing arrows.

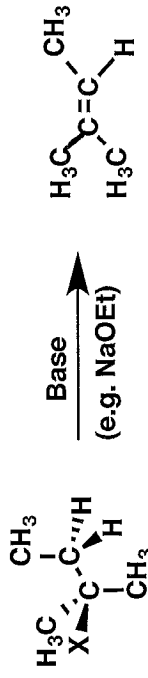


Fill in the missing arrows and intermediates. Keep an eye out for hydride shifts, methide shifts, ring contractions and ring expansions that may occur with carbocations.



E2 (Elimination Bimolecular)

General Reaction:

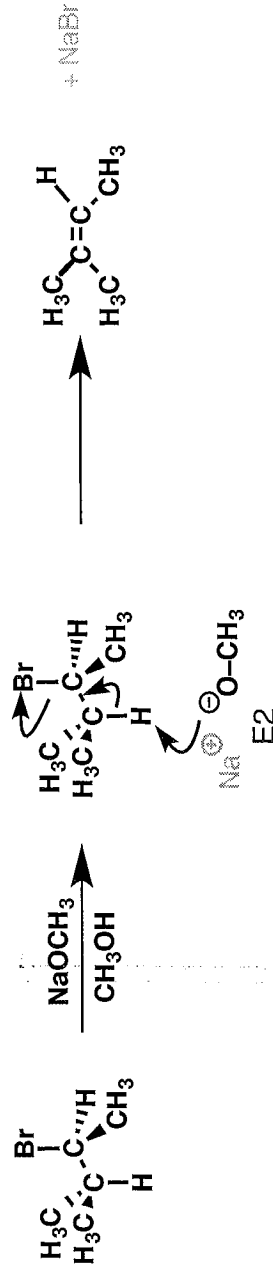


Typical bases: $\ominus\text{OCH}_3$, $\ominus\text{OCH}_2\text{CH}_3$, $\ominus\text{OC}(\text{CH}_3)_3$

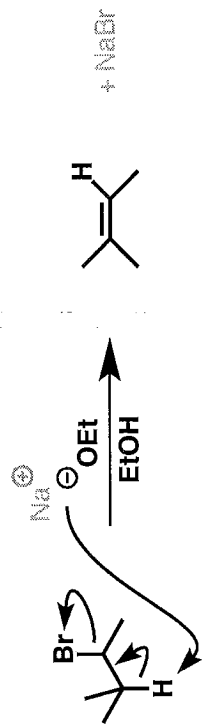
Mechanism Basics Box:

- Good leaving groups (X) are weak bases, such as halides (Cl, Br, I) and sulfonates (TsO, MsO)
- Works best with "strong" bases, generally negatively charged species such as $\ominus\text{OR}$ and $\ominus\text{OH}$
- Solvent is usually conjugate acid of the base (e.g. CH_3OH or t-BuOH)
- Reaction requires anti orientation of leaving group and hydrogen
- Formation of more substituted alkene is favored (Zaitsev's rule) [exception: with bulky base or leaving group]
- Rate law is bimolecular; depends both on concentration of base and substrate
- Reaction is favored by heat (more than substitution)

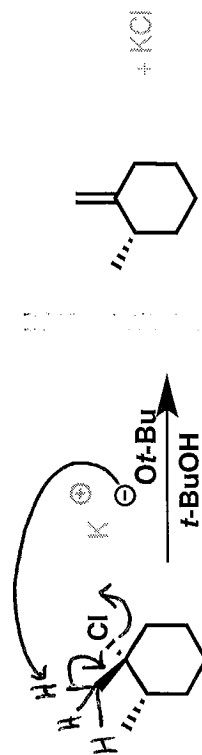
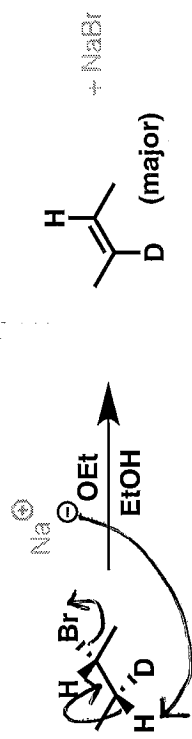
General Mechanism:



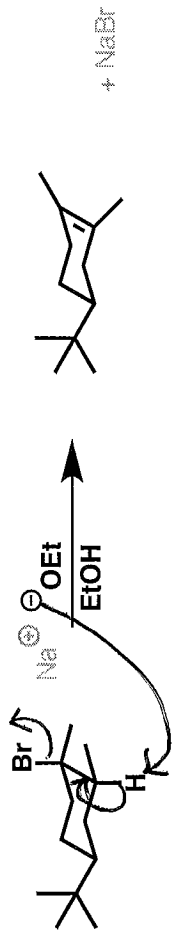
Given this example, fill in the arrows for the remaining examples.



Fill in the missing arrows.



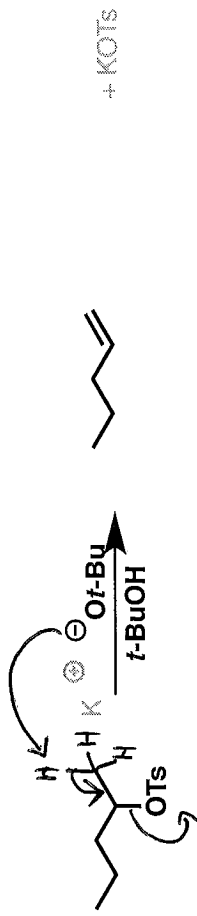
Fill in the missing arrows.



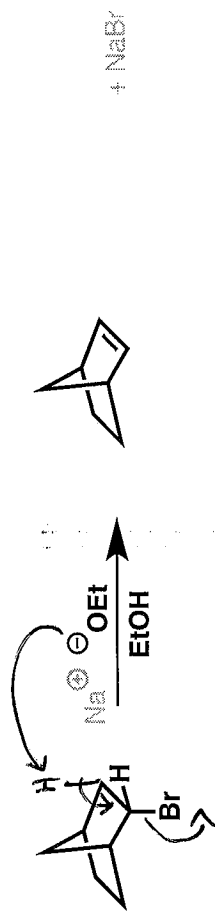
+ NaBr



+ KBr



+ KOTs



+ NaBr

Why not this product? Big bulky bases favor Hofmann elimination

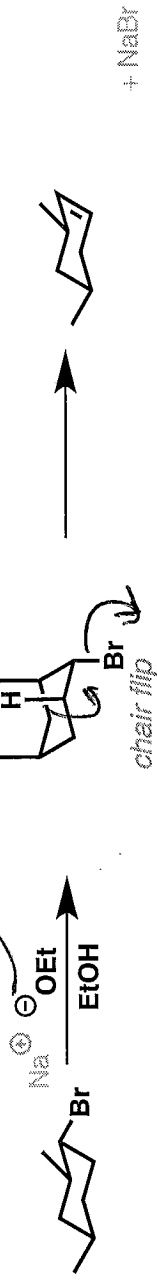


Why not this product?



Too much bond angle strain at the bridgehead

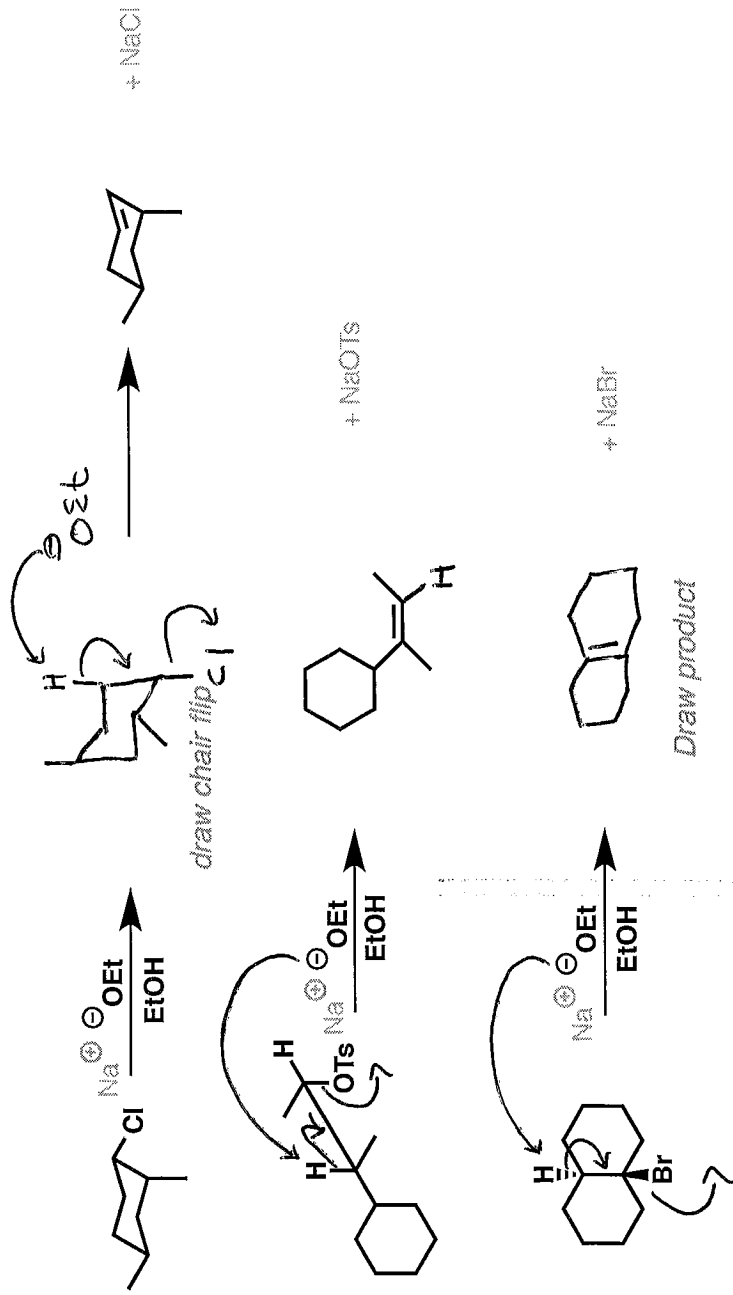
Fill in the missing arrows.



must flip the chair
to make H
C-C
|
X

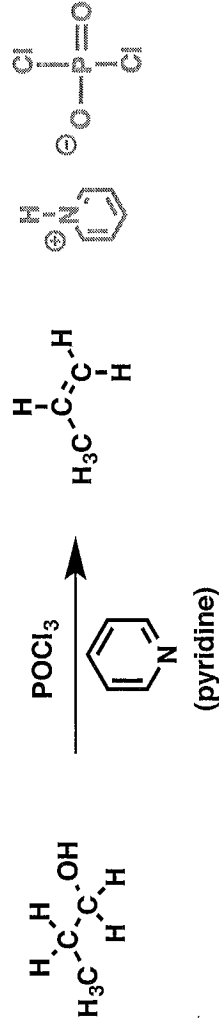
anti-coplanar.

Complete the mechanism by following the pattern (draw arrows and intermediates).



E2 Elimination With An Alcohol Leaving Group

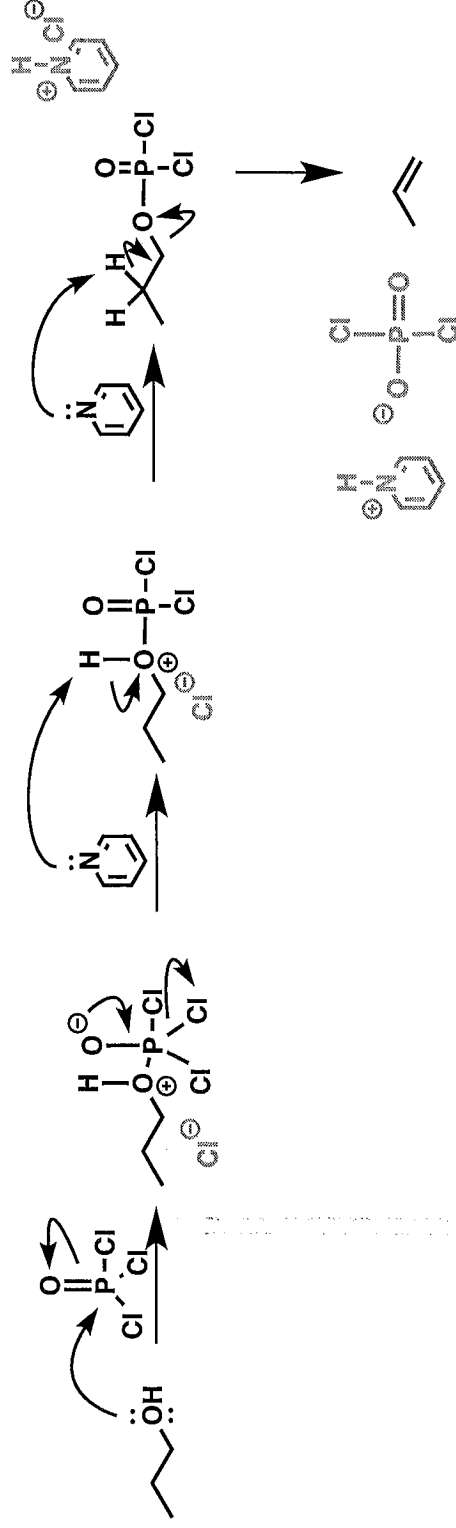
General Reaction:



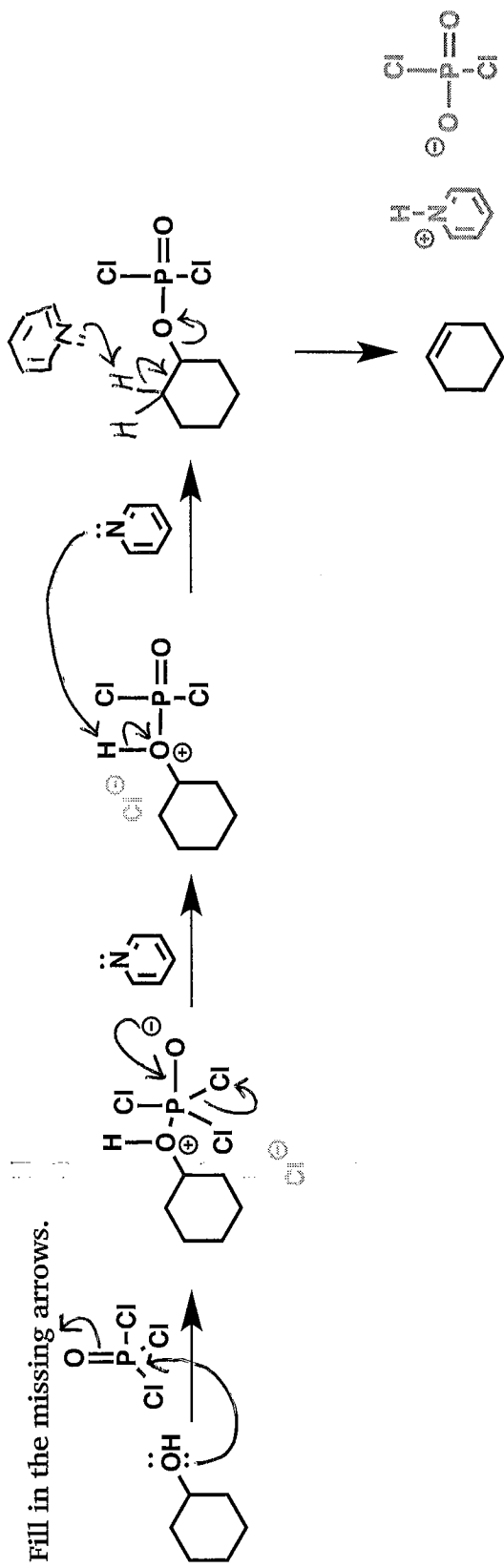
Mechanism Basics Box:

- In order for an elimination (E2) to take place, the alcohol must first be converted into a good leaving group under basic conditions
- This reaction works with any degree of substitution for the alcohol (primary, secondary or tertiary)
- The reaction is generally run with pyridine as solvent, so it's safe to assume an excess is present.

General Mechanism:



Fill in the missing arrows.



Complete the mechanism by following the pattern (draw arrows and intermediates)

