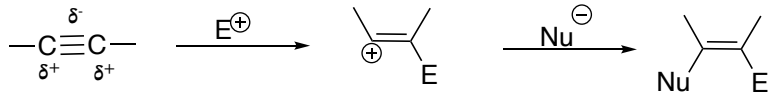
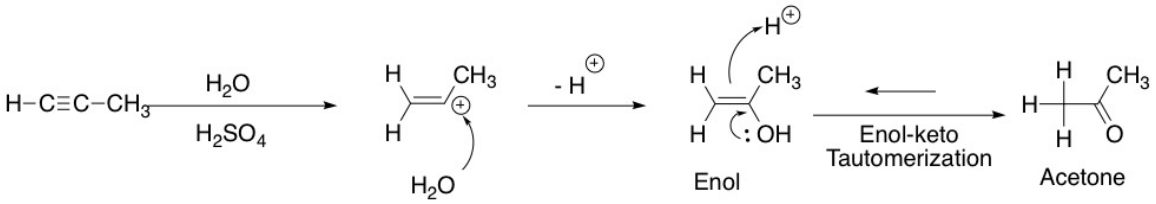
RECALL:



Note: Electrophile like H+ adds in less substituted C (Markovnikov rule) and nucleophile (e.g. Cl^-, H_2O, etc) adds to the more substituted C.

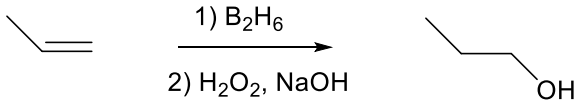
Addition of H_2O to Alkyne

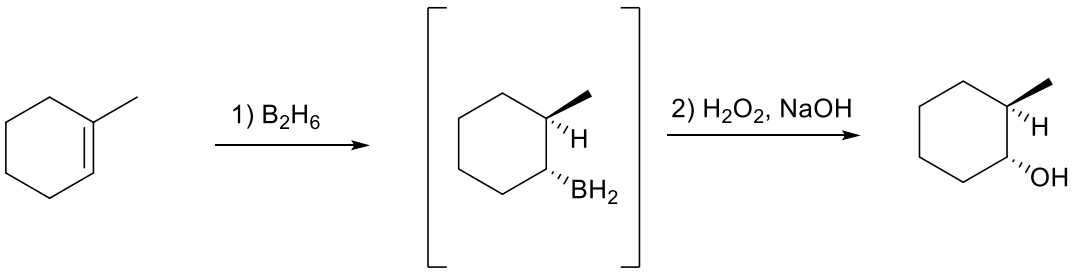


Hydroboration - Oxidation

What if we want addition in anti-Markovnikov fashion?
Then we use a borane reagent!

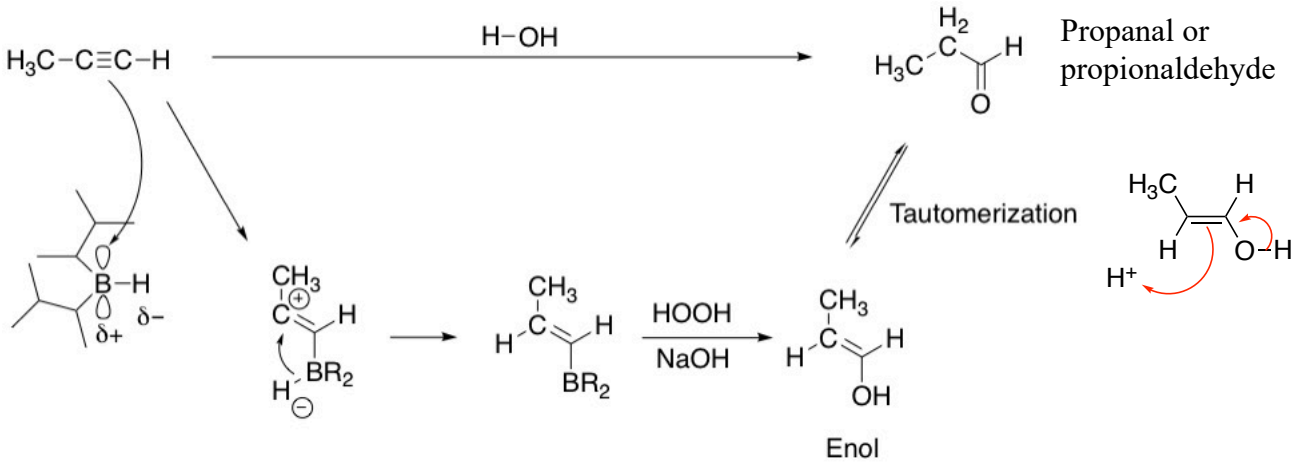
RECALL: Hydroboration of alkenes





- Cis/syn addition
- Oxidation with H_2O_2/NaOH replaces the C–B bond with retention of configuration

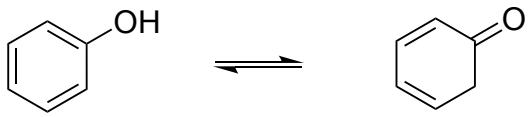
Hydroboration of Alkynes



- Can use diborane, but generally use sterically hindered organoborane to prevent multiple additions across the multiple bond

Note: Notice how in the above examples with 1-propyne, depending on which reagents are used one can carry out a Markovnikov addition leading to a ketone or an anti-Markovnikov addition leading to an aldehyde.

Unique Example where the enol is favored is phenol



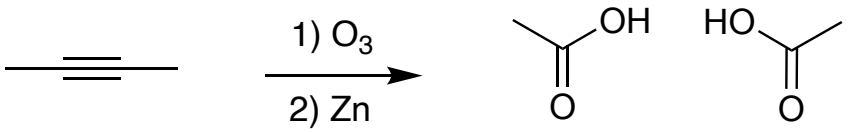
phenol
ϕ-OH
enol is favored

ketone is disfavored

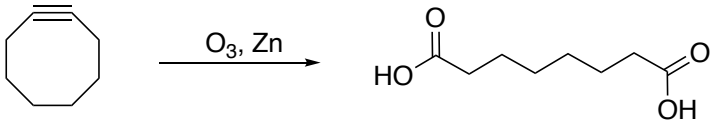
tautomers are structural isomers, not resonance structures

Oxidations of Alkynes

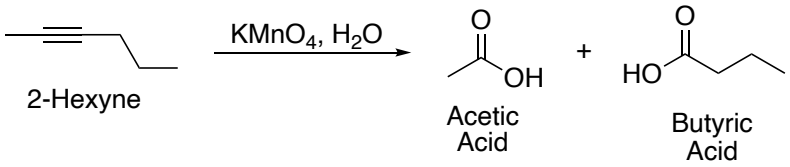
Example 1: Ozonolysis of 2-butyne



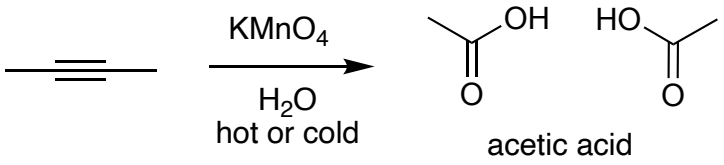
Example 2: Ozonolysis of Cyclooctyne



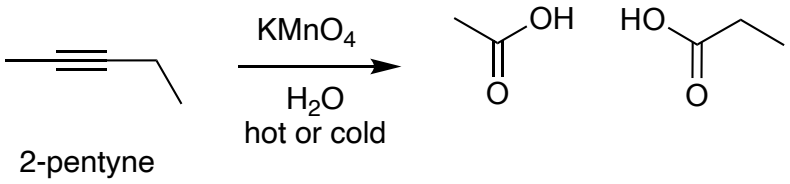
Example 3:



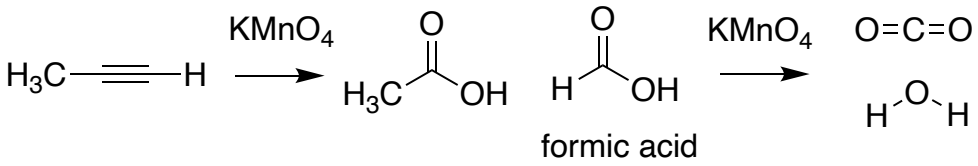
Example 4: 2-butyne



Example 5: 2-pentyne

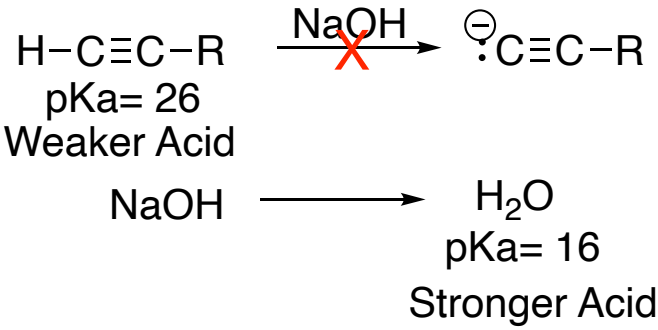


Example 6: propyne



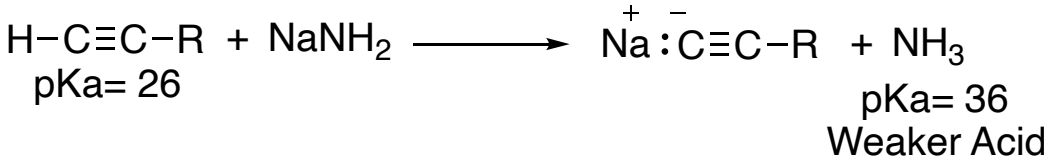
Special Reaction for Terminal Alkynes

Recall:

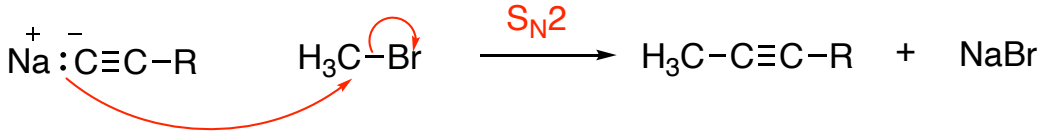


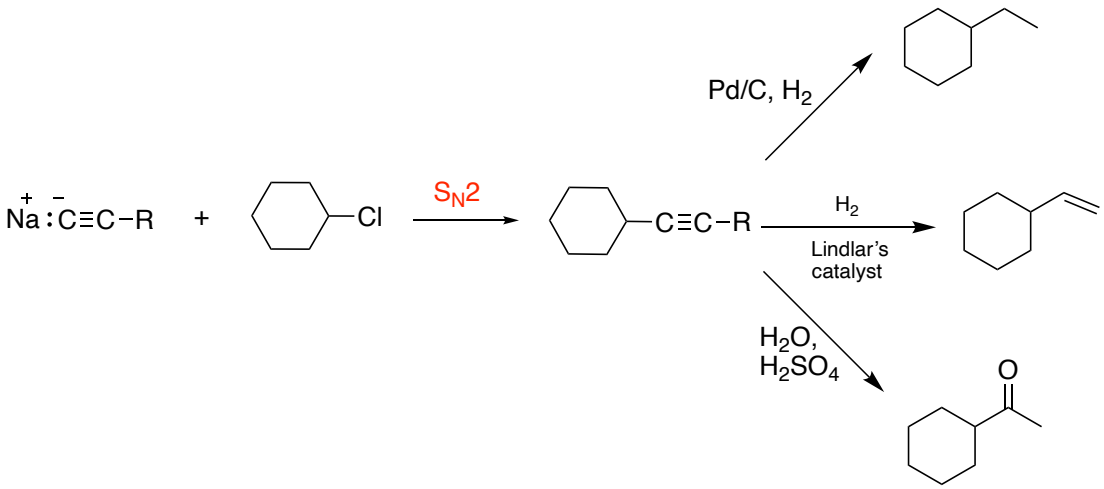
Note: this reaction will not occur because the reaction will form a stronger acid (H_2O) as compared to acetylene

However,

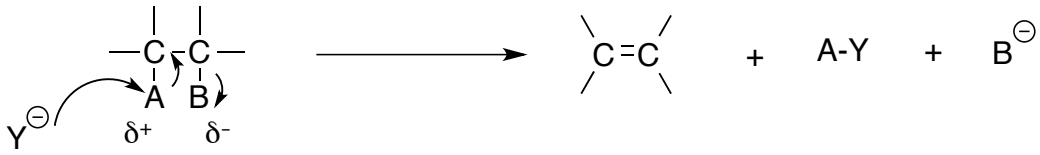


Reaction of Acetylide anion

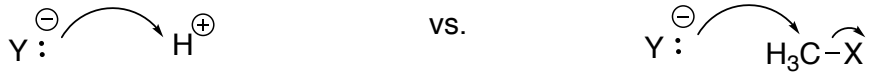




Elimination Reactions:



Base vs. Nucleophile:



Base

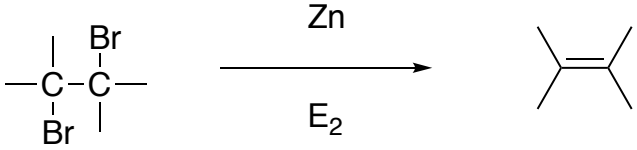
Nucleophile

Elimination (E_1 and E_2)

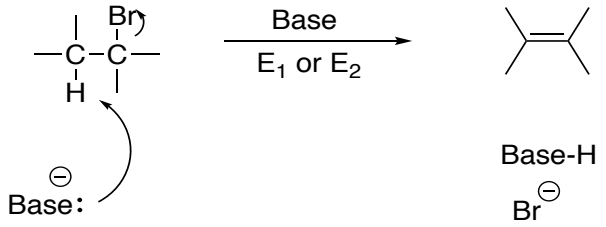
Substitution (S_N1 and S_N2)

Types of Elimination Reactions:

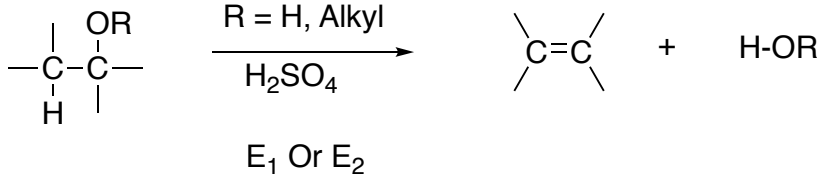
1) Dehalogenation



2) Dehydrohalogenation



3) Dehydration



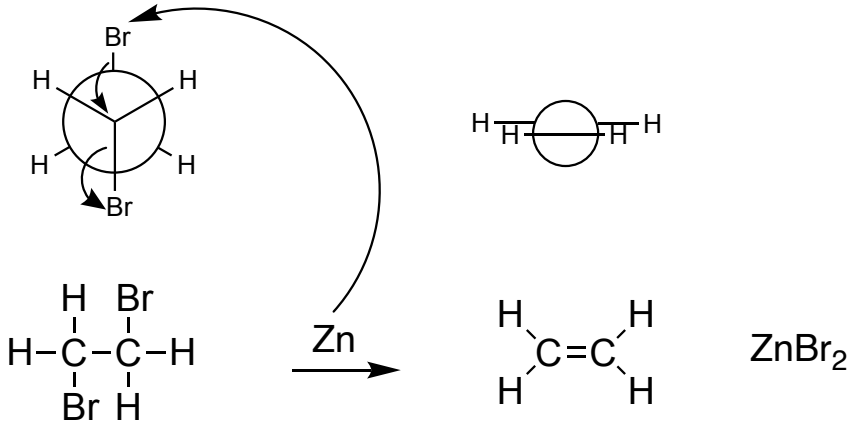
2 Types of Mechanisms: E_1 and E_2

<u>E_2 Reaction</u> (E=Elimination)**:**

- Rate depends on two concentrations
- Stereospecific
- Concerted (bonds being formed and broken at the same time)
  - No intermediate
- follows Zaitsev Rule: most substituted alkene will be the major product
- Anti-periplanar geometry
- 1º, 2º, 3º, but especially primary and secondary

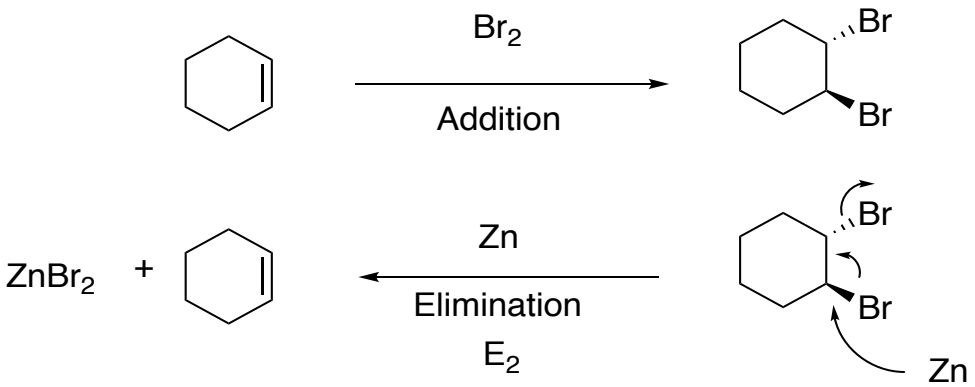
Dehalogenation

Example 1:

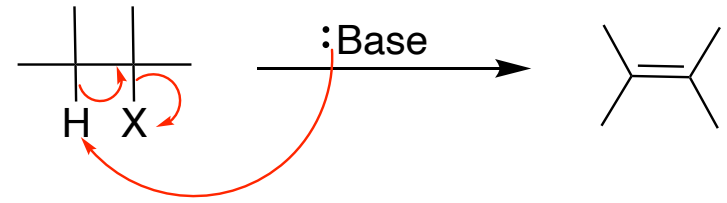


Example 2:

- Zinc mechanism always proceeds via E_2

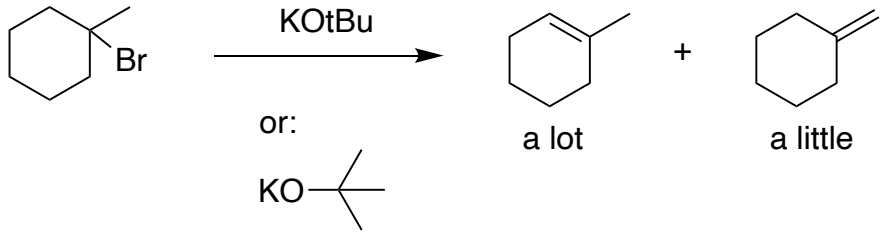


Dehydrohalogenation

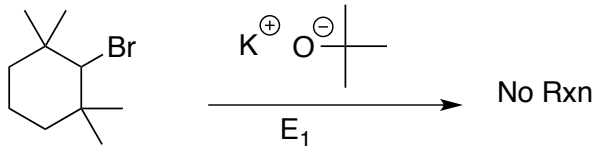


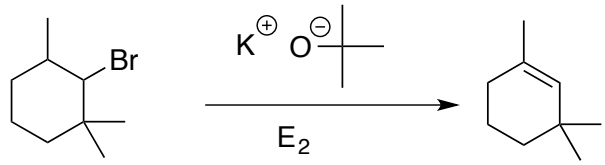
X= Cl, Br, I

Example 1:



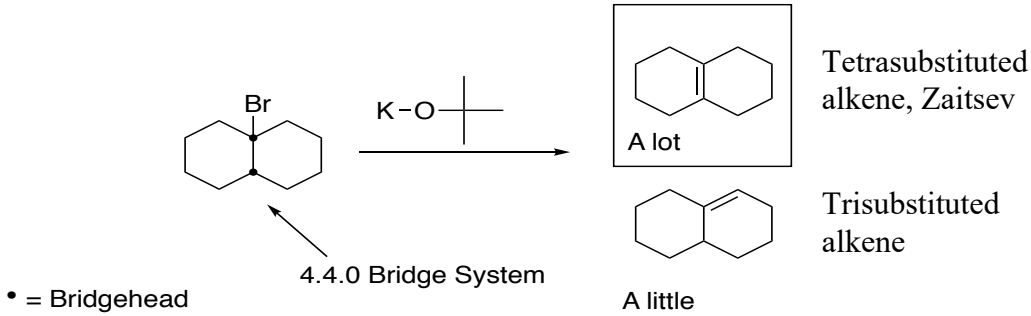
Example 2:





need hydrogen on adjacent carbon for loss of HBr

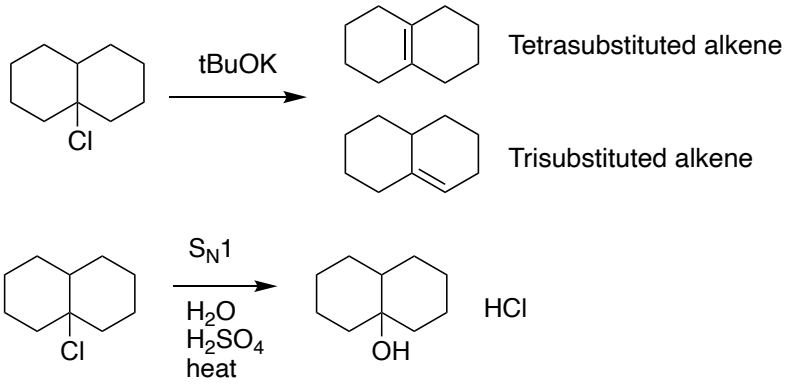
Example 3:



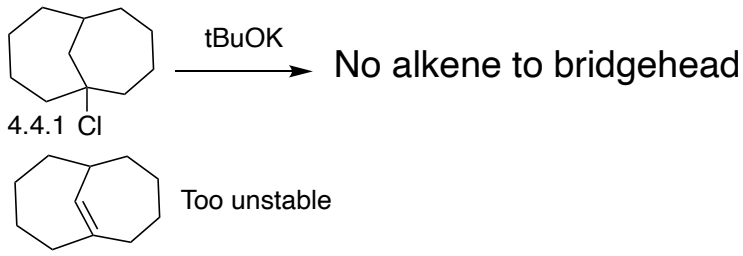
Zaitsev Rule: Get the more substituted alkene

Bredt Rule: Bridged alkenes are only okay if one of the bridges is a "zero" (0) bridge in small rings <9

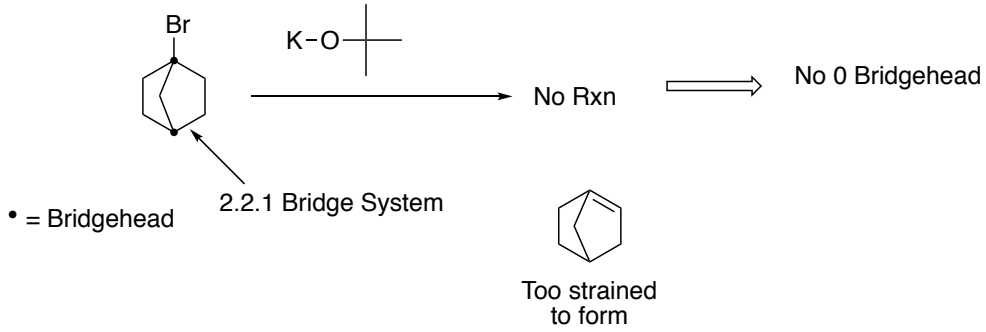
Example 4:



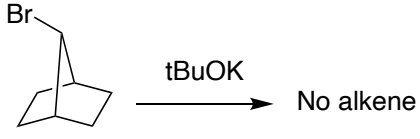
Example 5:



Example 6:

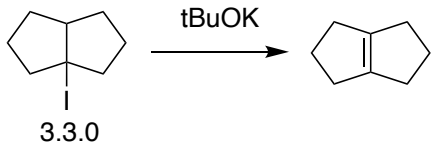


Example 7:

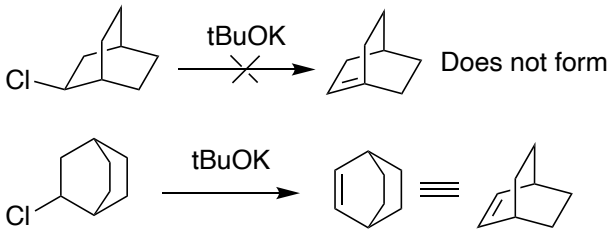


(too unstable – will not form according to Bredt's rule

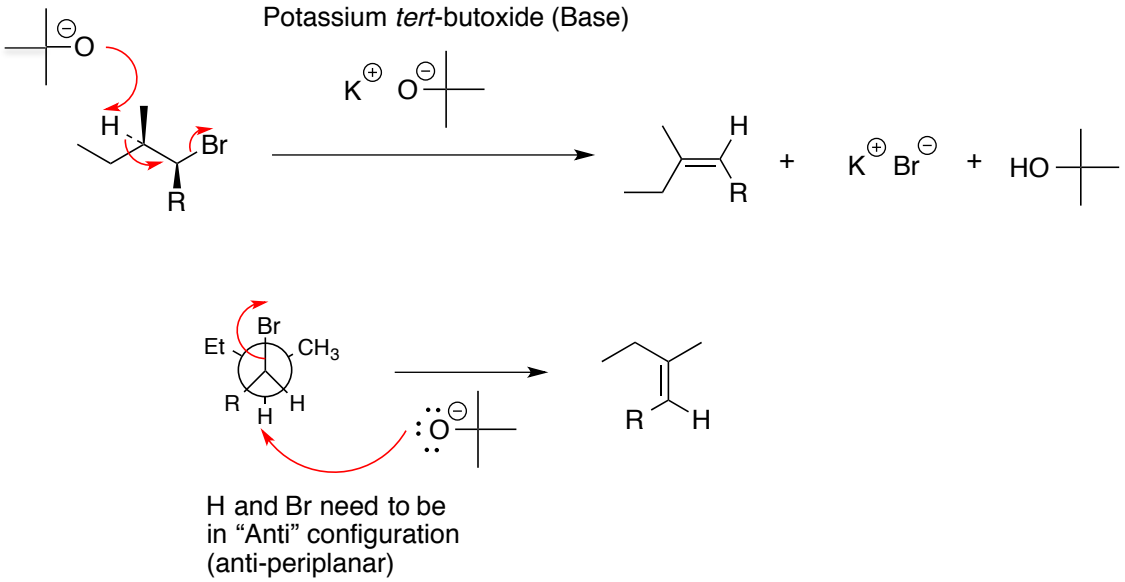
Example 8:



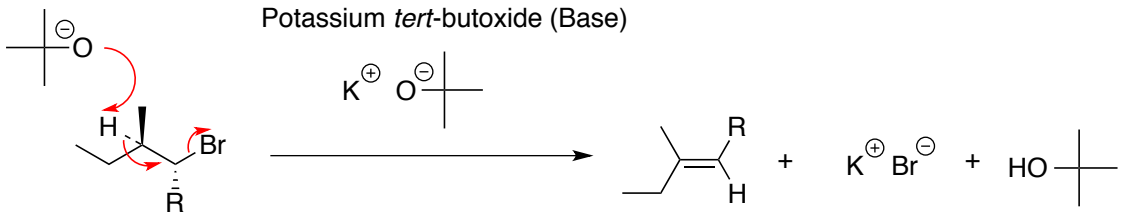
Example 9:

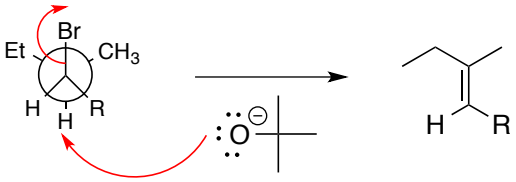


Example 10 A:



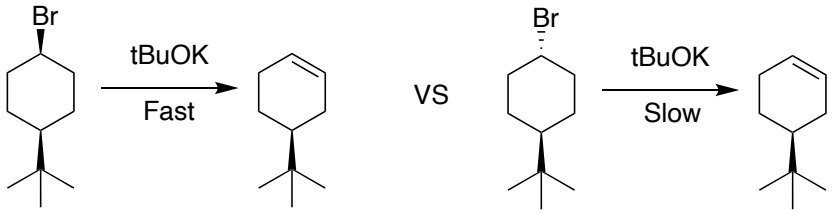
Example 10 B: Start with different stereochemistry get different product stereochemistry (a diastereomer)





H and Br need to be in "Anti" configuration (anti-periplanar)

Example 11:



The *tert*-butyl group must be placed in the equatorial position