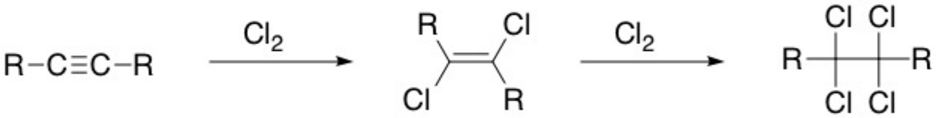
CHEM 261 Notes November 21, 2023

Recall

Addition reactions of Alkynes

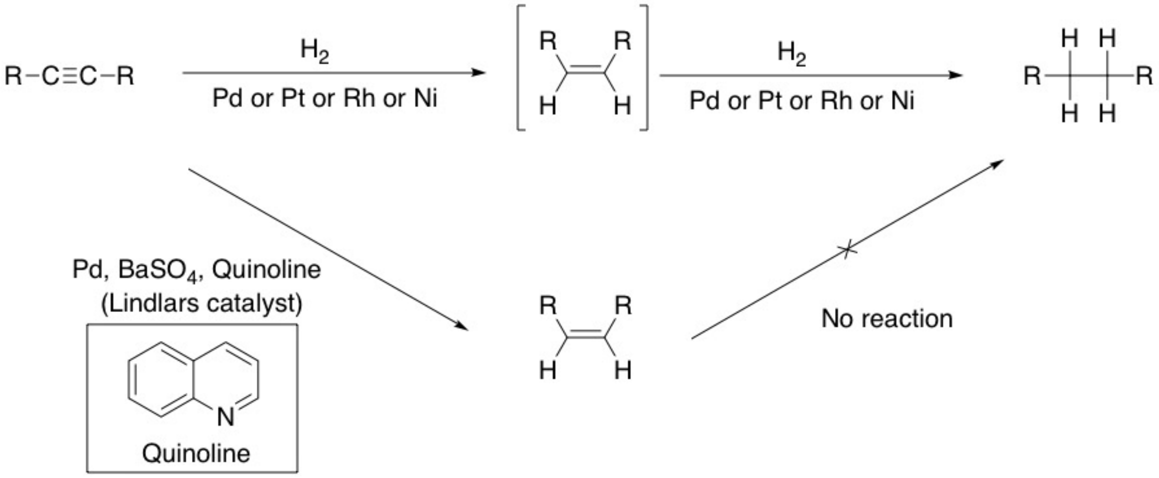
Alkynes are more polar as they have more negative charge between the two carbons. They are always more reactive than alkenes and so can be utilized in all addition reactions that alkenes can, except react faster.

The carbon-carbon triple bond is composed of two pi bonds and a sigma bond



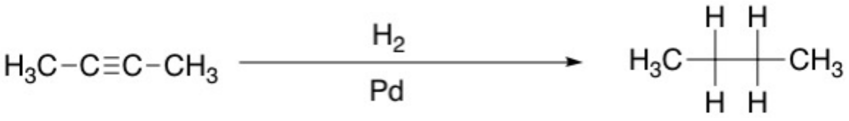
The first addition to the alkyne is anti, which forms the trans alkene.

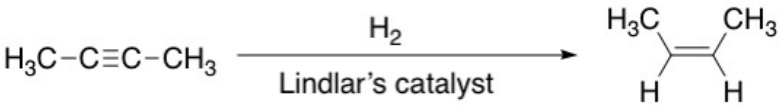
Hydrogenation of Alkynes



- **Lindlar's catalyst –** quinoline complexes with the metal and deactivates it. Hence, the hydrogenation reaction stops at the alkene.

Example: 2-butyne

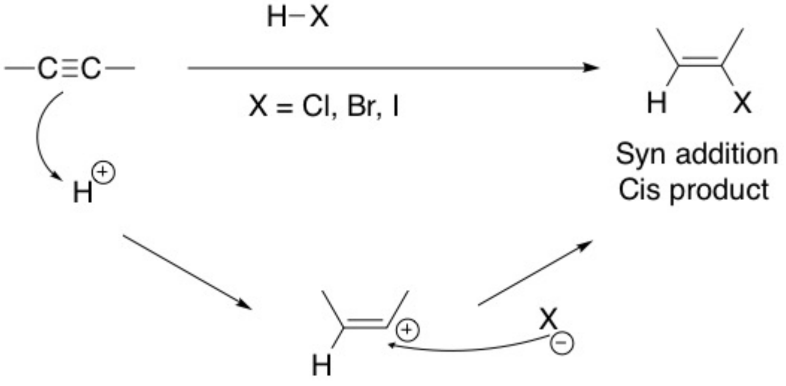




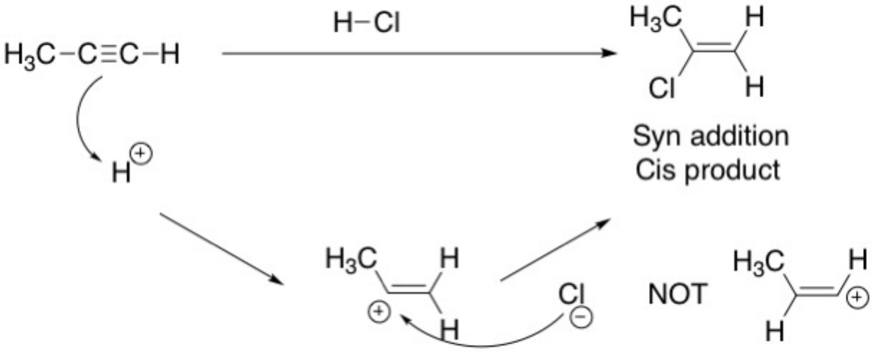
- Reaction is stereospecific – H atoms are added on the same side of the double bond

HX Addition

Example 1: 2-butyne



Example 2: 1-propyne

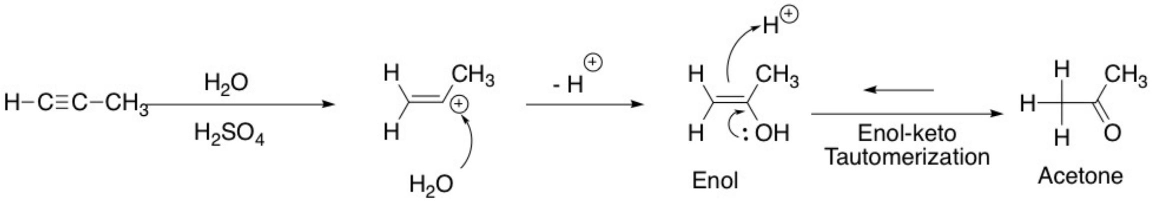


RECALL: Addition of HX across the double bond occurs in Markovnikov fashion– the H^+ adds to the least substituted end of a multiple bond, and Cl- to the most substituted end to form 2-chloro-1-propene

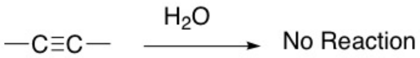
<u>Addition of H_2O</u>

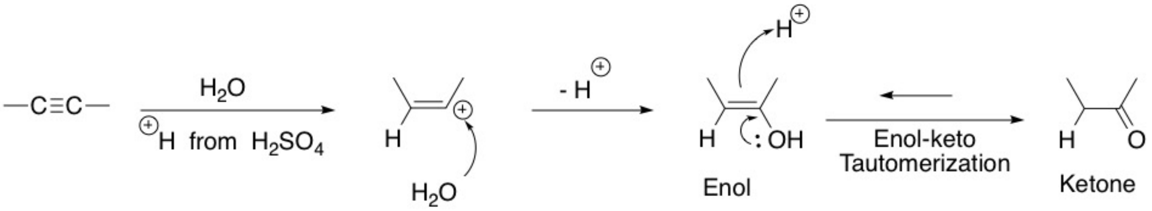
Example 1: 1-propyne

- H_2O or ROH by itself cannot add to the double bond. Need an acid (H^+) to pull the electrons from the double bond.
- H_2SO_4 (H^+) is a catalyst, meaning that it is not transformed or used up in the reaction but is present to lower the activation energy.



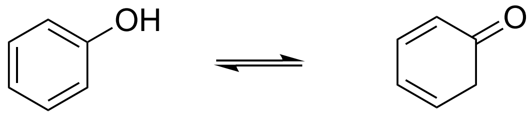
Example 2: 2-butyne





- **Enols** are generally unstable and tend to isomerize to the **<u>keto form (generally favored over the enol</u>** – less thermodynamically energetic) – this process is called **tautomerization**
- **Tautomers** are rapidly interconverting structural isomers. In the above example, the ketone and enol are tautomers. **Note**: these are not resonance forms since the position of the H atom is changed.

Unique Example where the enol is favored is phenol



phenol

enol is favored

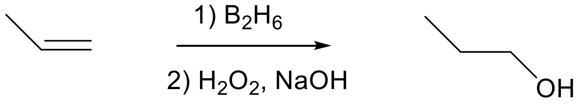
ketone is disfavored

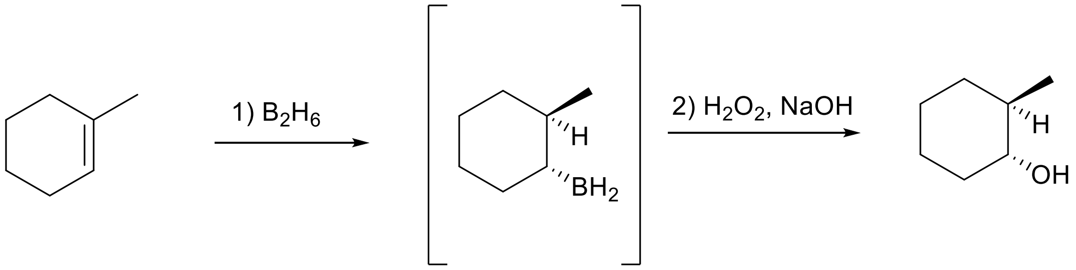
tautomers are structural isomers, not resonance structures

Hydroboration - Oxidation

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

RECALL: Hydroboration of alkenes

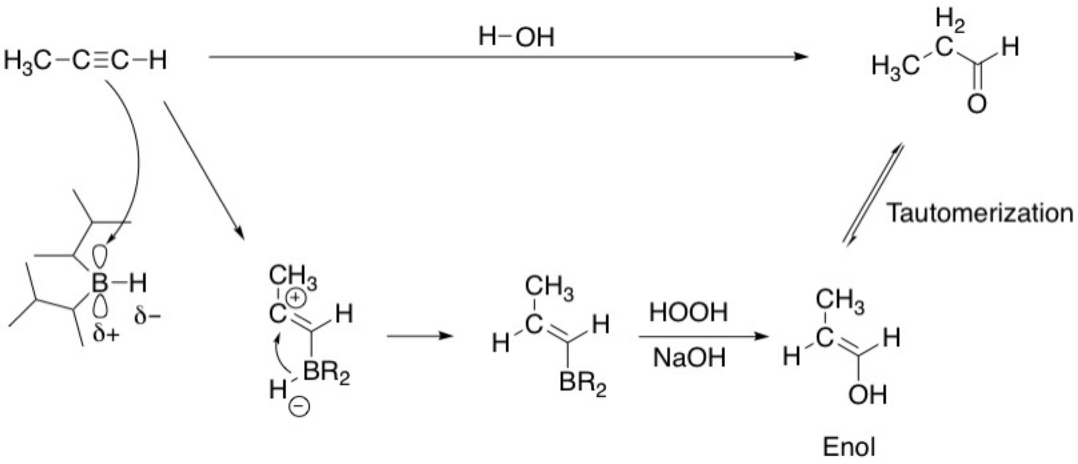




- Cis/syn addition
- Oxidation with H_2O_2/NaOH replaces the C–B bond with retention of configuration

Hydroboration of Alkynes

Propanal or
propionaldehyde

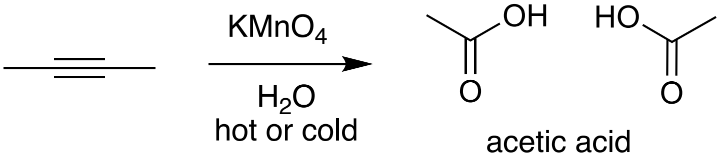


- Can use diborane, but generally use sterically hindered organoborane to prevent multiple additions across the multiple bond

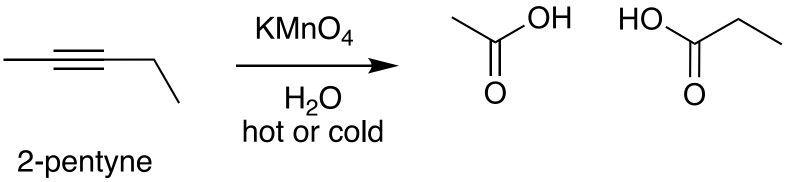
Note: Notice how in the above examples with 1-propyne, depending on which reagents are used one can carry out a Markovnikov addition leading to a ketone or an anti-Markovnikov addition leading to an aldehyde.

Oxidations of Alkynes

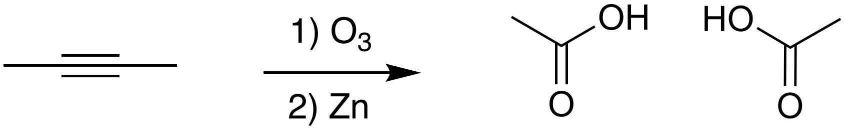
Example 1: 2-butyne



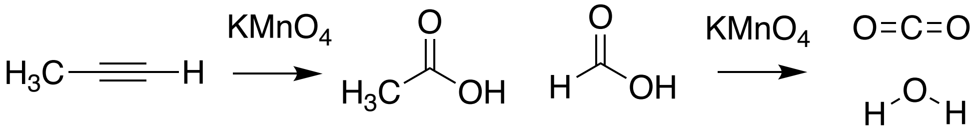
Example 2: 2-pentyne



Example 3: Ozonolysis of 2-butyne

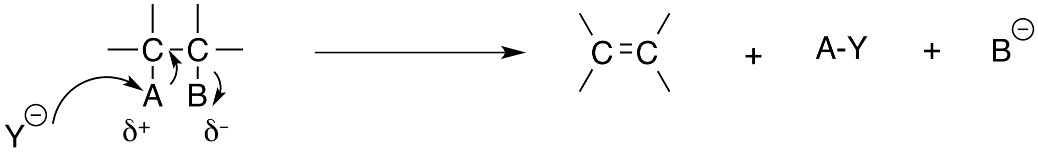


Example 4: propyne

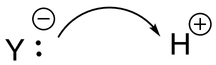


formic acid

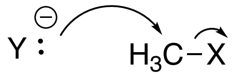
Elimination Reactions:



Base vs. Nucleophile:



vs.



Base

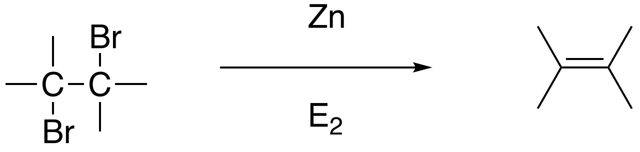
Nucleophile

Elimination (E_1 and E_2)

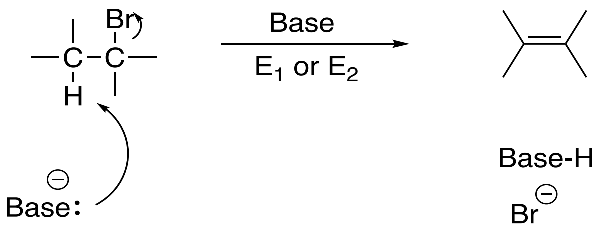
Substitution (S_N1 and S_N2)

Types of Elimination Reactions:

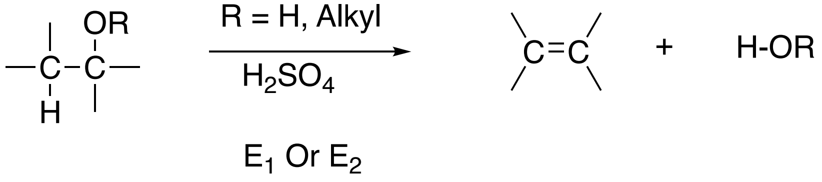
1) Dehalogenation



2) Dehydrohalogenation



3) Dehydration



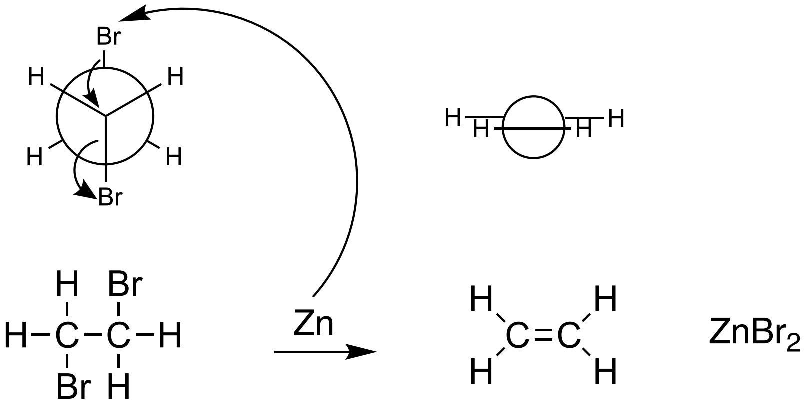
2 Types of Mechanisms: E_1 and E_2

E_2 Reaction (E=Elimination)**:**

- Rate depends on two concentrations
- Stereospecific
- Concerted (bonds being formed and broken at the same time)
    - No intermediate
- Anti-periplanar geometry
- 1°, 2°, 3°, but especially primary and secondary

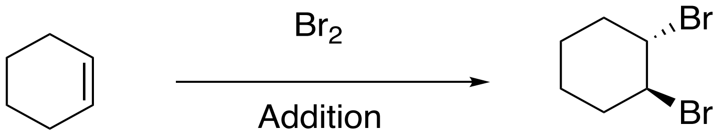
Dehalogenation

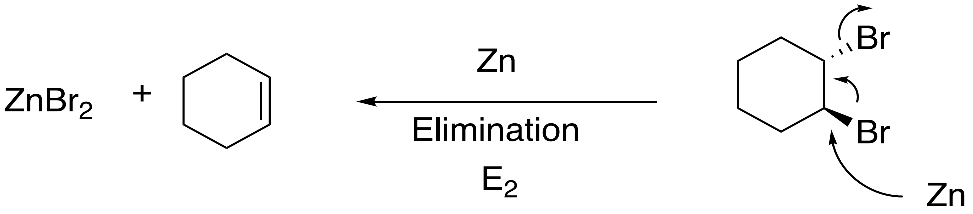
Example 1:



Example 2:

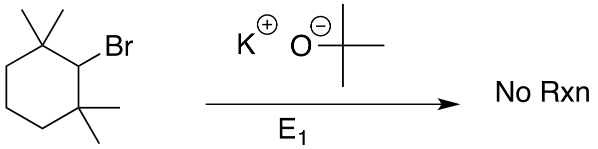
- Zinc mechanism always proceeds via E_2

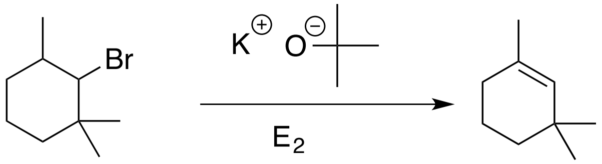




Dehydrohalogenation

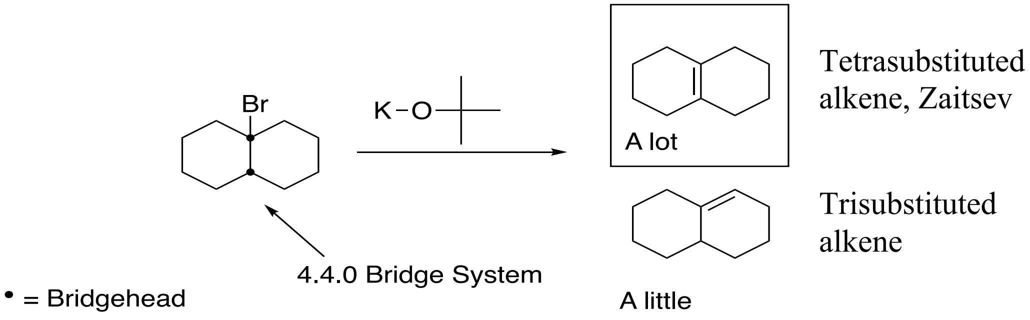
Example 1:





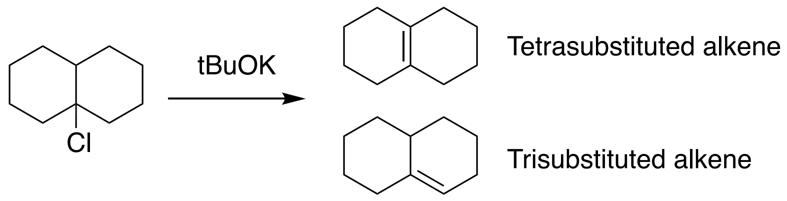
need hydrogen on adjacent carbon for loss of HBr

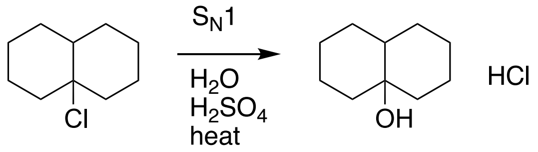
Example 2:



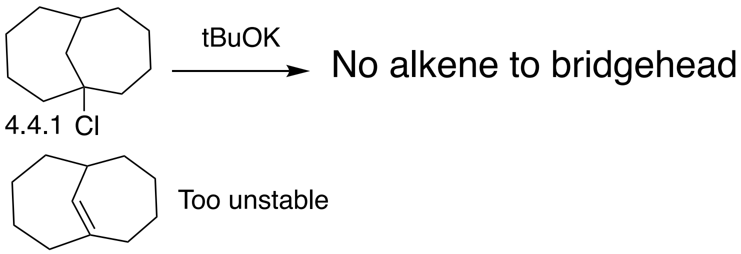
Zaitsev Rule: Get the more substituted alkene

Example 3:



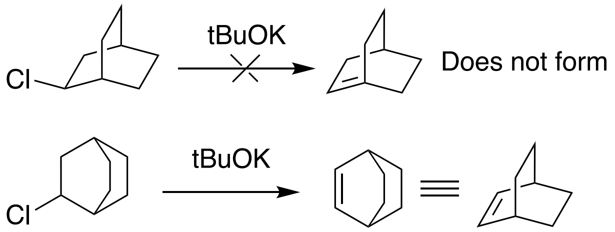


Example 4:

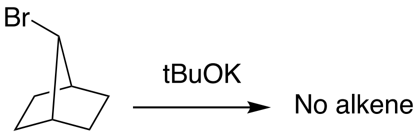


Bredt Rule: Bridged alkenes are only okay if one of the bridges is a “zero” (0) bridge in small rings <9

Example 5:

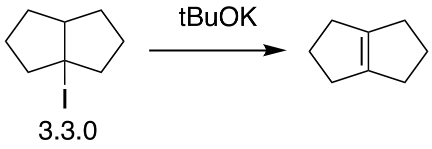


Example 6:

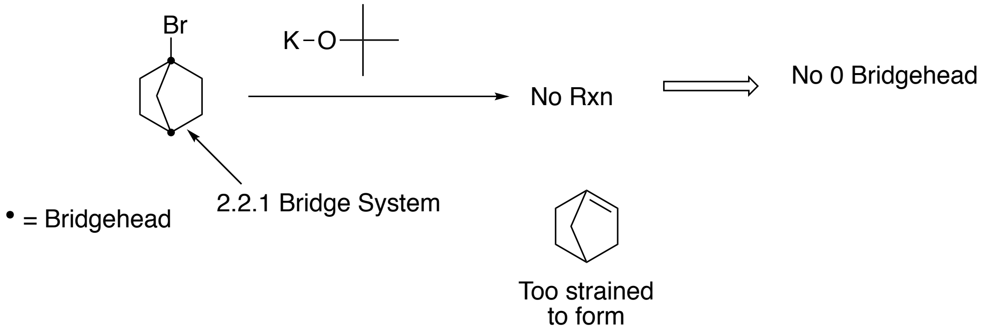


(too unstable – will not form according to Bredt’s rule**)**

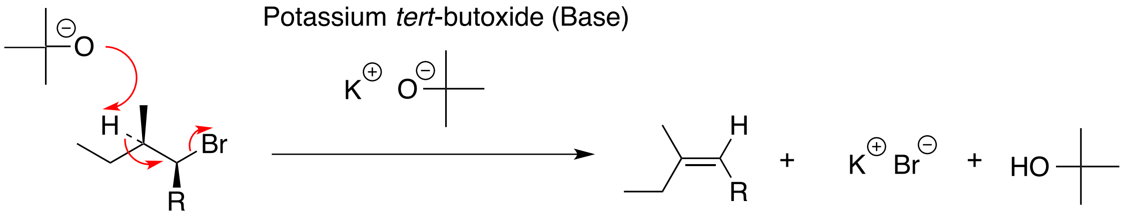
Example 7:

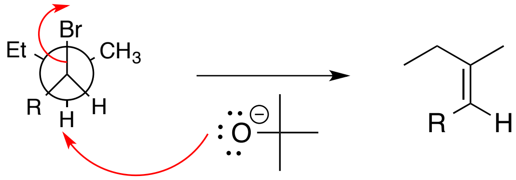


Example 8:



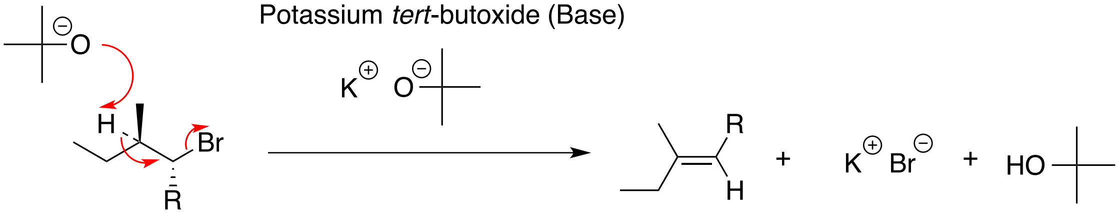
Example 9 A:

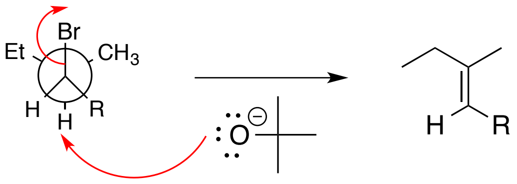




H and Br need to be
in “Anti” configuration
(anti-periplanar)

Example 9 B: Start with different stereochemistry get different product stereochemistry (a diastereomer)





H and Br need to be
in “Anti” configuration
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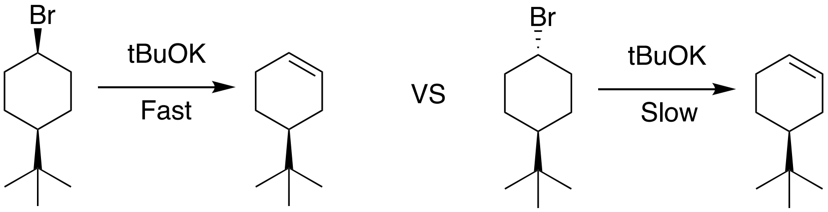
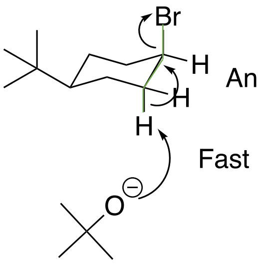
Example 10:

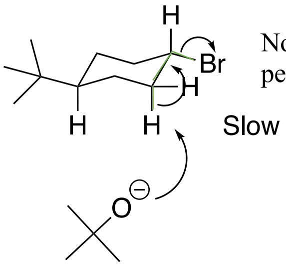


The *tert*-butyl group must be placed in the equatorial position



Anti-periplanar geometry

Fast

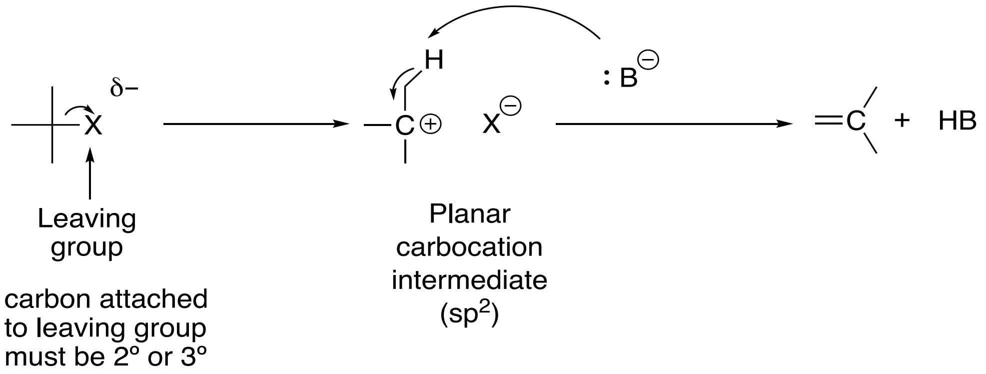


Not in the ideal anti-periplanar geometry

Slow

E$_1$ Reaction:

- Rate depends on one concentration
- Not concerted (carbocation intermediate)
- Not stereospecific
- Favored with leaving group being 3°



Leaving group

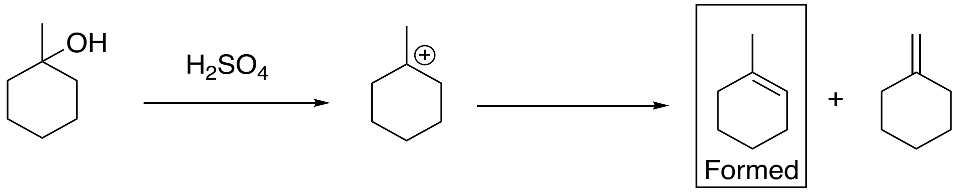
carbon attached to leaving group must be 2° or 3°

Planar carbocation intermediate (sp^2)

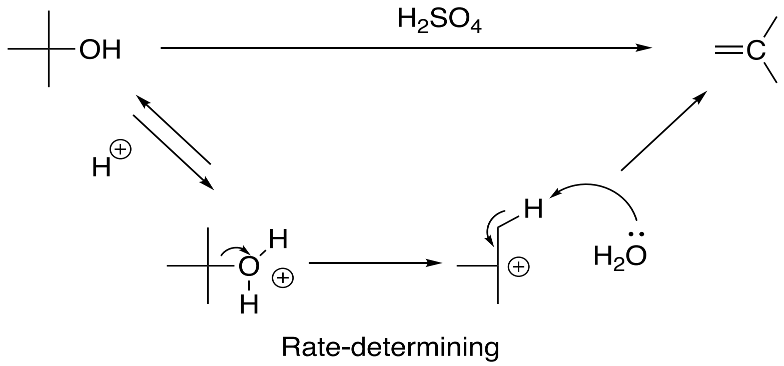
Dehydration

-OH and -OR are not leaving groups, but H-OH and H-OR are okay

Example 1:



Example 2:



Rate-determining step