CHEM 261 Nov. 23, 2021

Recall:

Alkane Reactions:

-Combustion, Radical Substitution, Nucleophilic Substitution

$$R{-}H \xrightarrow[\Delta]{O_2} CO_2 + H_2O$$

$$R{-}H \xrightarrow{X_2} \underset{\text{Alkyl halide}}{R{-}X} + H{-}X$$

$$\underset{\text{Alkyl halide}}{R{-}X} \xrightarrow{M^{\oplus}\ \ddot{N}u^{\ominus}} R{-}Nu + M^{\oplus}\ X^{\ominus}$$

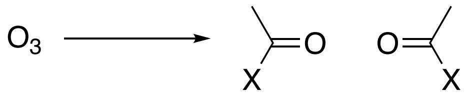
S_N2 occurs on 1°/2° subtrates
S_N1 occurs on 3° substrates

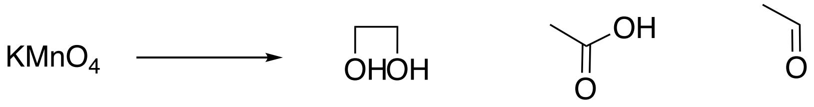
Alkene/Alkyne Reactions:

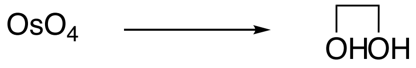
-Addition, Oxidation

C=C C≡C

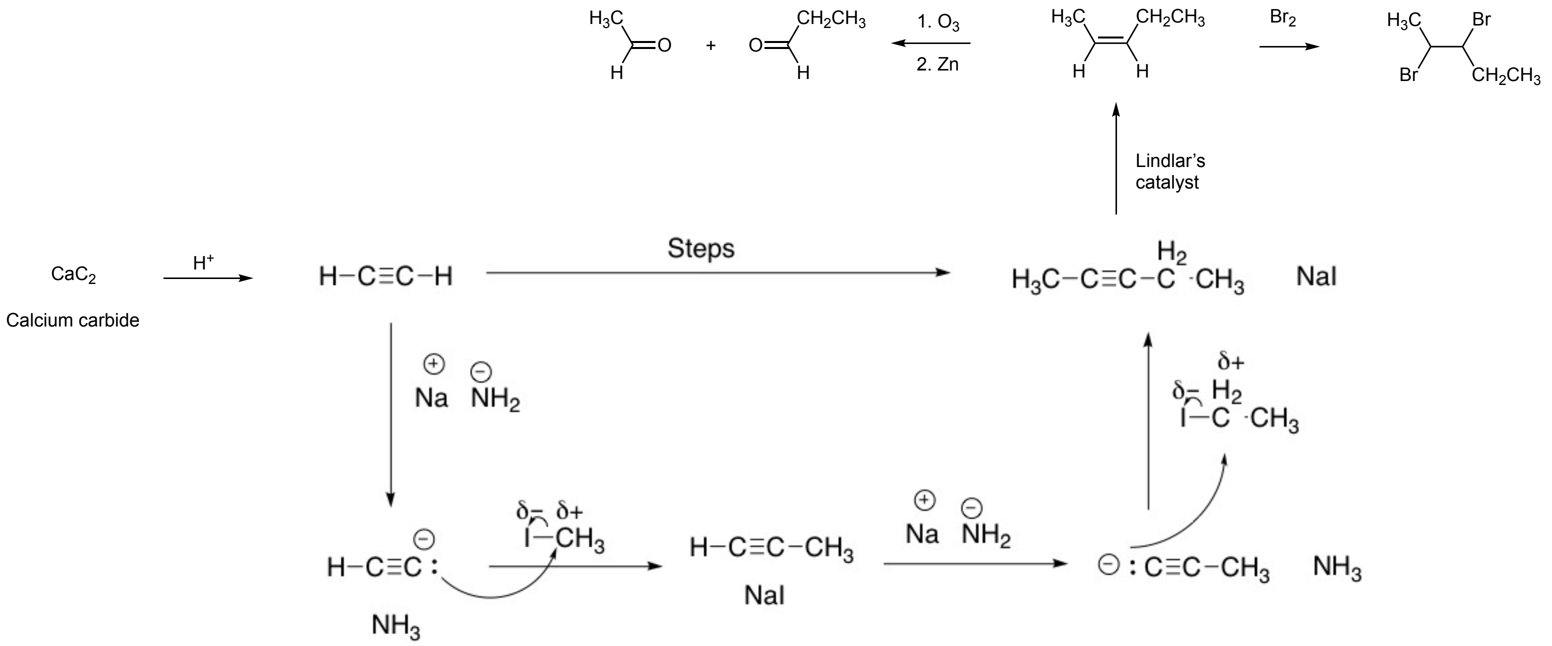
$$\begin{matrix} X_2 \\ HX \\ \left.\begin{matrix} HOH \\ HOR \end{matrix}\right\} H^{\oplus}\ \text{Cat.} \end{matrix}$$





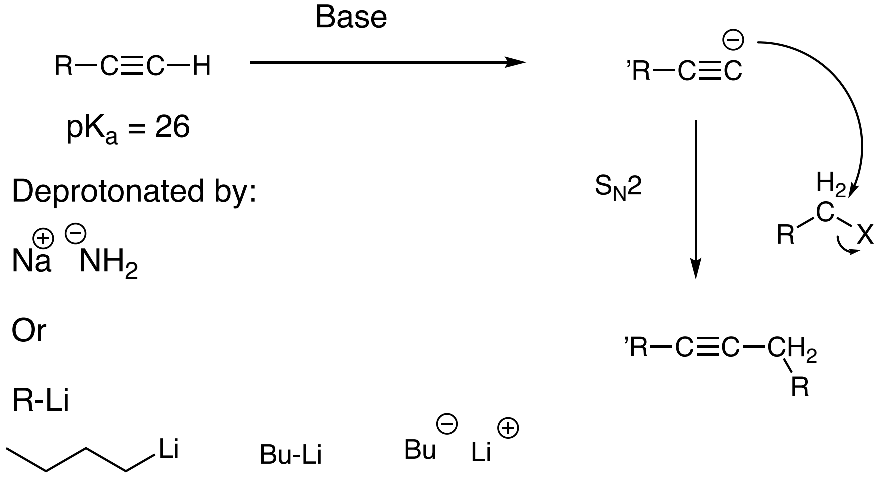


Organic synthesis example:



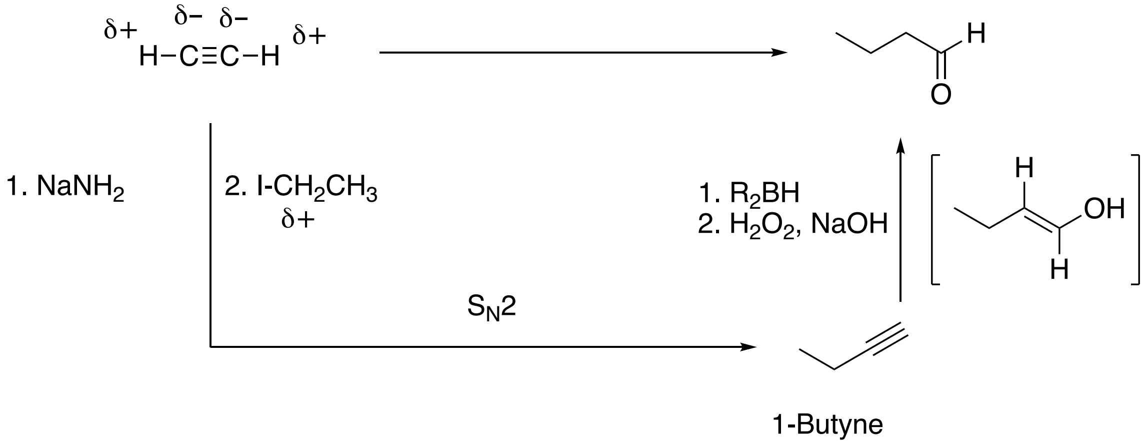
Both substitution reactions involving methyl iodide and ethyl iodide are S_N2, as the primary and secondary carbons will not hold the positive charge that is characteristic of an S_N1 intermediate (tertiary carbocation).

Generating an Acetylide anion:

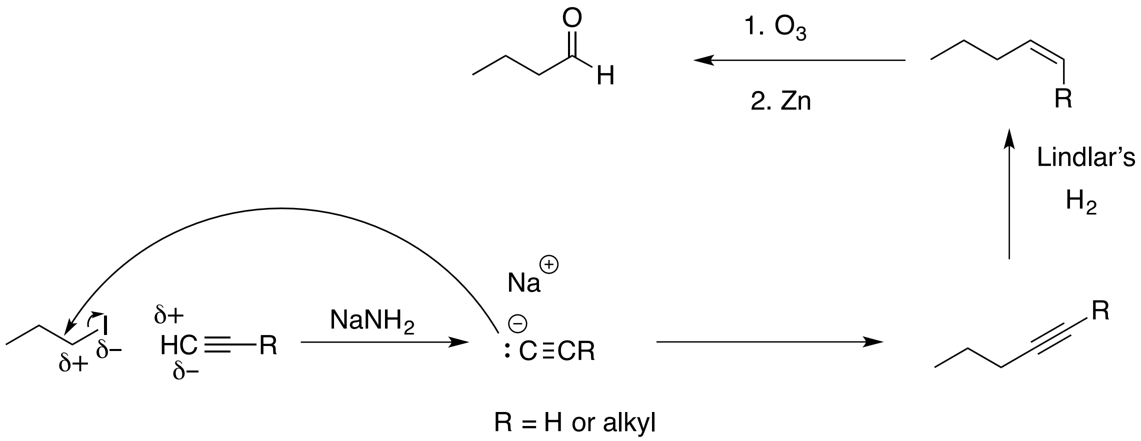


The resulting acetylide anion can be used in the synthesis of other acetylenes by substitution reactions.

Example:

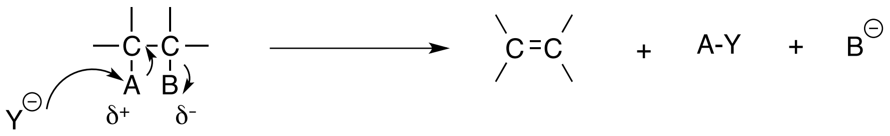


Alternative solution to above problem:

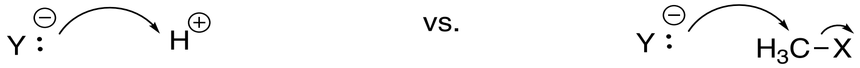


Elimination Reactions:

2 Types of Mechanisms: E_1 and E_2



Base vs. Nucleophile:



Base

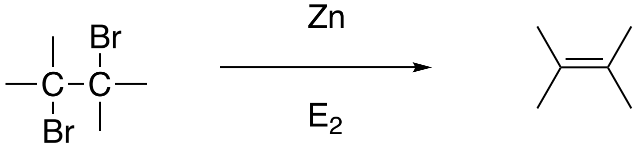
Nucleophile

Elimination (E_1 and E_2)

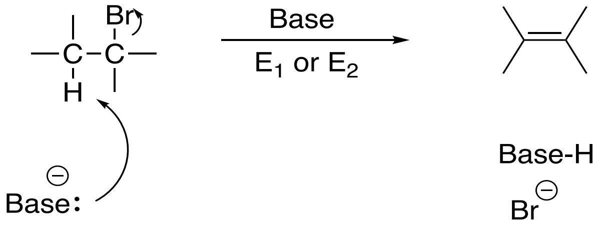
Substitution (S_N1 and S_N2)

Types of Elimination Reactions:

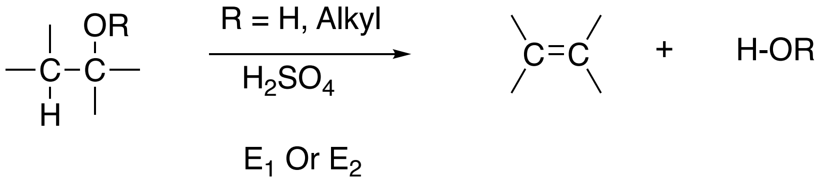
1) Dehalogenation (Removal of X_2, X = halide)



2) Dehydrohalogenation



3) Dehydration

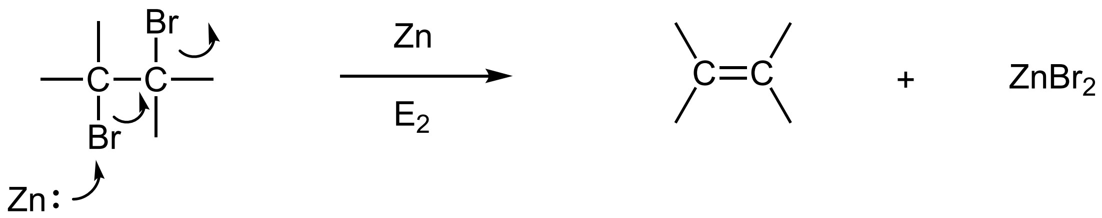


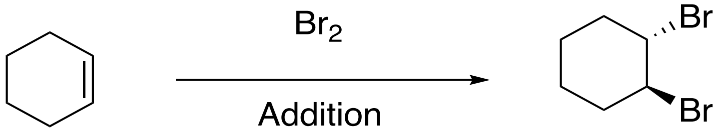
E_2 Reaction (E=Elimination)**:**

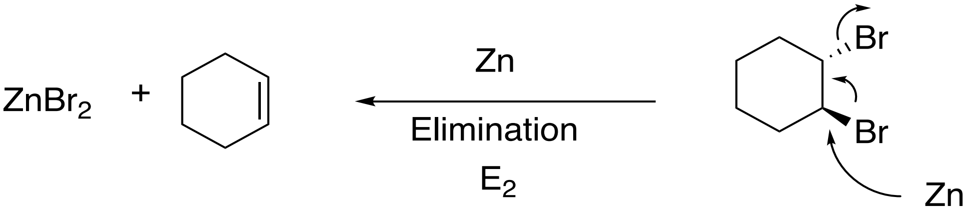
- Rate depends on two concentrations
- Stereospecific
- Concerted (bonds being formed and broken at the same time)
    - No intermediate
- Anti-periplanar geometry

Example #1:

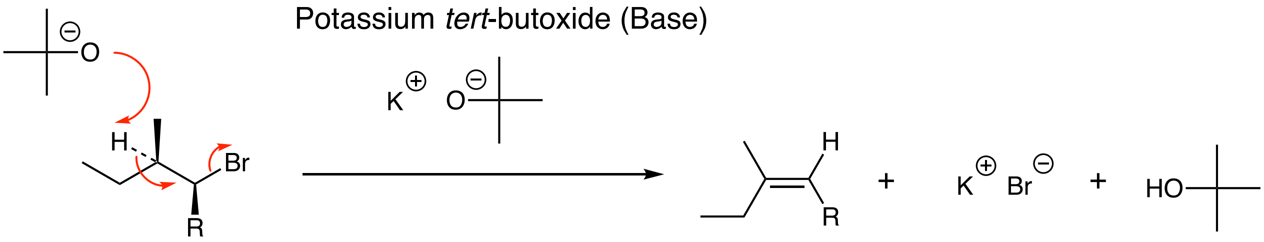
- Zinc mechanism always proceeds via E_2

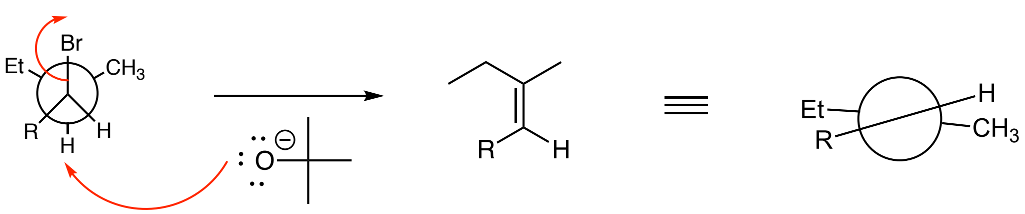






Example #2 A: Dehydrohalogenation

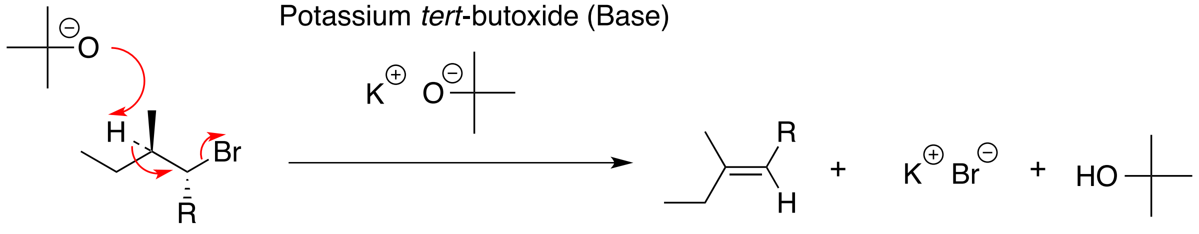


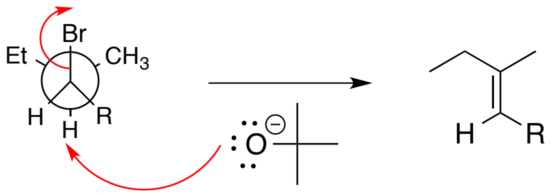


H and Br need to be
in “Anti” configuration
(anti-periplanar)

alkene

Example #2 B: Start with different sterochemistry get different product stereochemistry (a diasteromer)

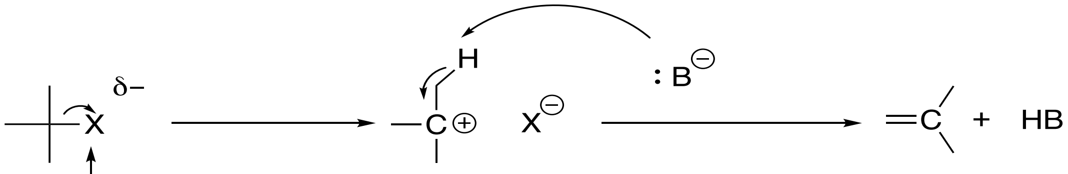




H and Br need to be
in "Anti" configuration
(anti-periplanar)

E$_1$ Reaction:

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

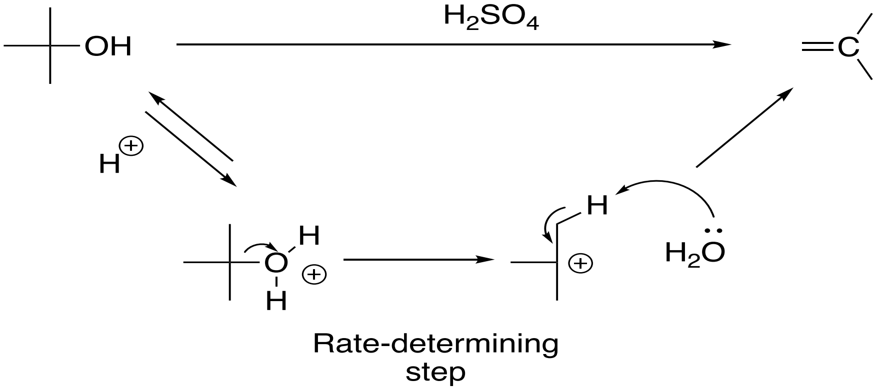


Leaving
group

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

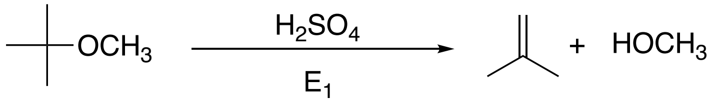
Planar
carbocation
intermediate
(sp^2)

Example #1:



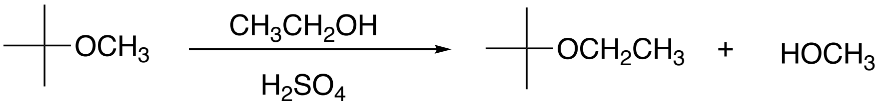
Example #2:

E$_1$



vs.

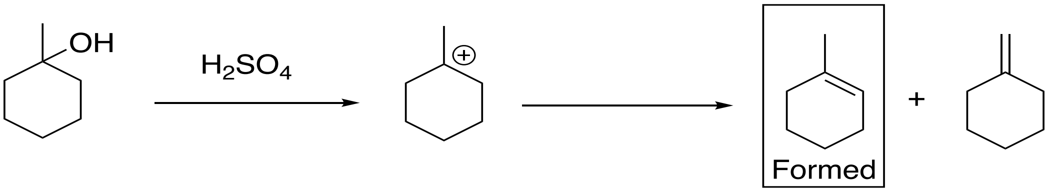
S$_N$1



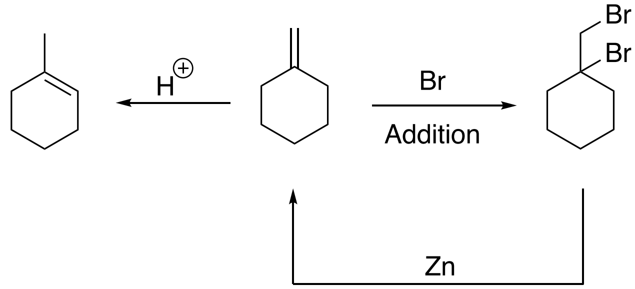
Substitution	vs.	Elimination:
- Low Temp		- High Temp
- Weaker Base		- Stronger Base
- Dilute H$^+$		- Conc. H$^+$
- Leaving group on 1º carbon		- 2º, 3º
- Small Nucleophile		- Large Nucleophile

Zaitsev Rule: Get the more substituted alkene

Example #1:



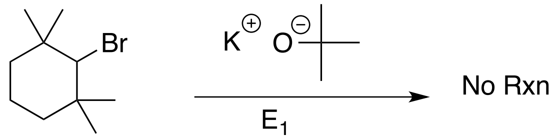
Example #2:

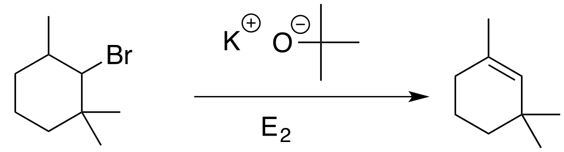


Due to mechanism of Zn, the double bond is stuck at less substituted end.

Double bond can go to more substituted if it is left in aced

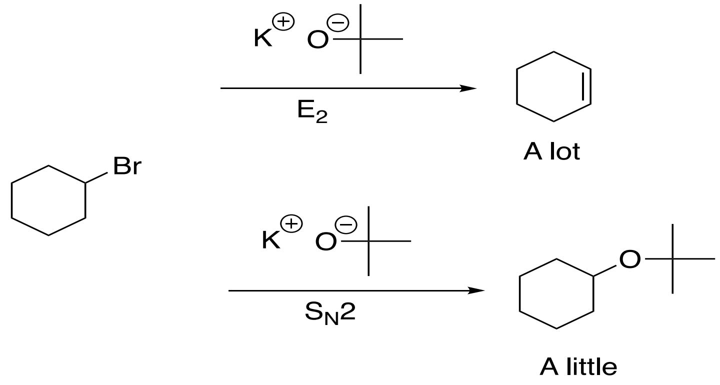
Example #3:



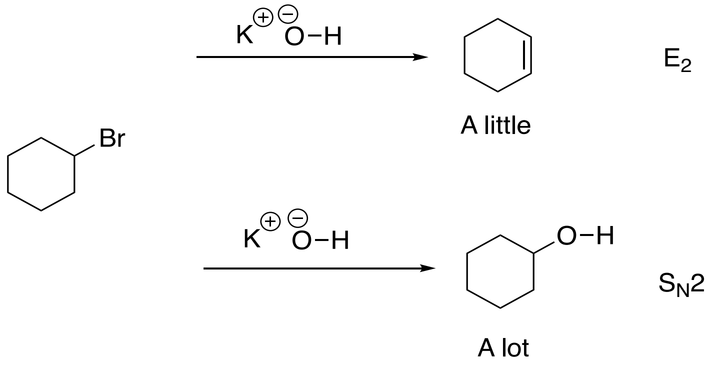


need hydrogen on adjacent carbon for loss of HBr

Example #4: bulky nucleophiles/bases favour elimination

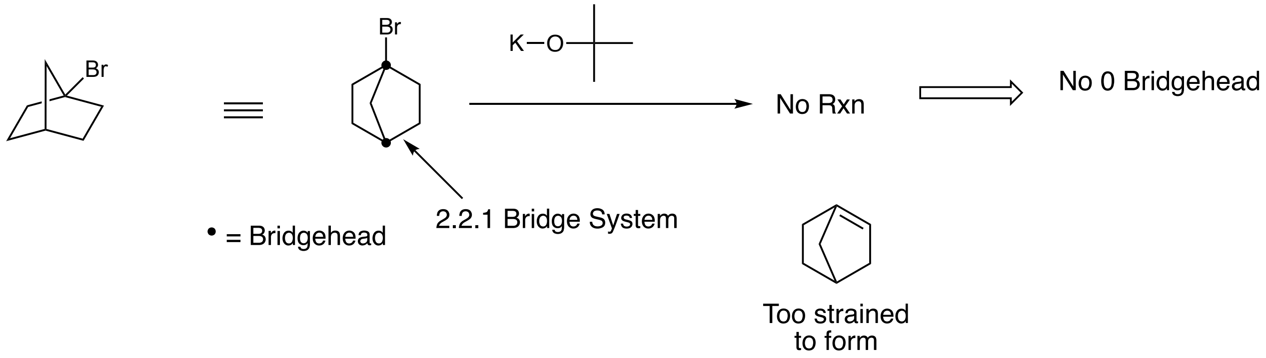


Example #5: small nucleophiles/bases favour substitution

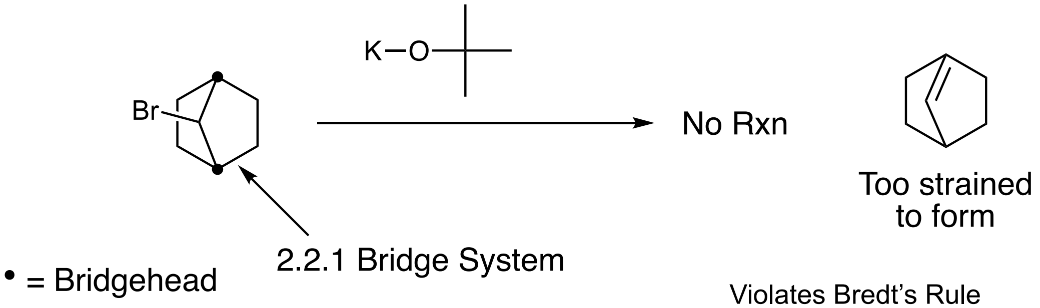


Bredt Rule: Bridged alkenes are only okay if one of the bridges is a “zero” (0) bridge in small rings <9 ; If a bicyclic ring system has all bridges > 0 carbons, then there cannot be an alkene on a bridgehead.

Example:

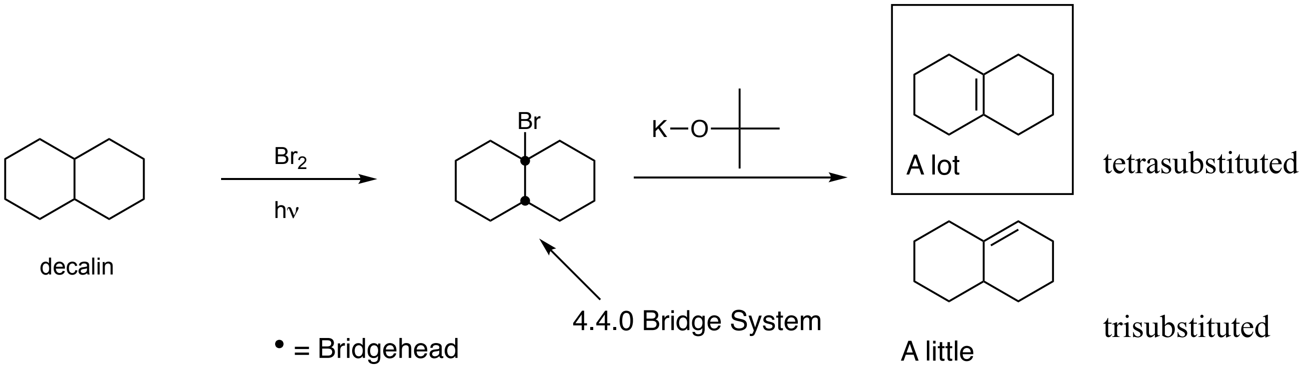


Example:



Violates Bredt’s Rule

Example:



Zaitsev Rule: Get the more substituted alkene