

A blue spiral-bound notebook with silver metal rings along the top edge. The cover has a fine, woven texture.

# Substitution vs Elimination

UCI Chem 51A  
Dr. Link

# Goals

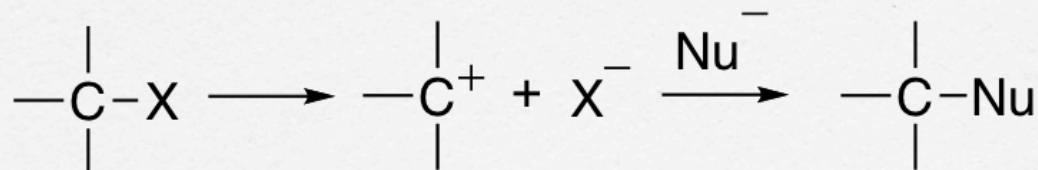
- After this lesson you should be able to
  - Determine what reaction conditions to choose to favor one mechanism over another
  - Predict the product or products of an alkyl halide reacting under a specific set of conditions

# Two Types of Reactions...Four Pathways!

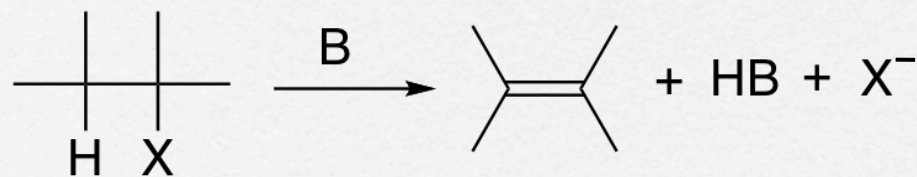
All at Once:  $S_N2$



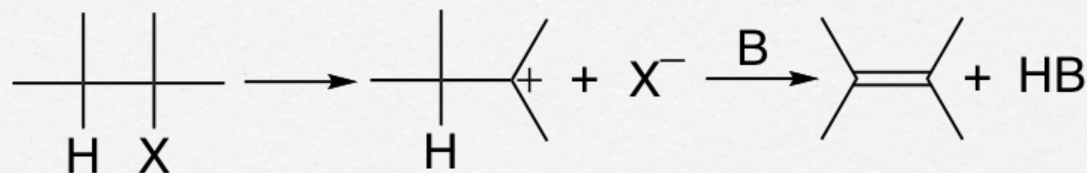
One Step at A Time:  $S_N1$



All at Once:  $E2$



One Step at A Time:  $E1$



# $S_N2$ Refresher

- Rate = 2nd order
- Mechanism = 1 steps
- LG = good LG required
- R-X = Me > 1° > 2°
  - no 3°
- Nu = Strong nucleophile favors  $S_N2$
- Solvent = polar aprotic solvent favors  $S_N2$
- Stereochemistry = backside attack, inversion

# $S_N1$ Refresher

- Rate = 1st order
- Mechanism = 2 steps
- LG = good LG required
- R-X = Benzylic, allylic,  $3^\circ > 2^\circ$ 
  - no  $1^\circ$ , no methyl
- Nu = Weak nucleophile favors  $S_N1$
- Solvent = polar protic solvent favors  $S_N1$
- Stereochemistry = racemization of stereocenter

# E2 Refresher

- Rate = 2nd order
- Mechanism = 1 step
- LG = good LG required
- R-X =  $\beta$ -H required,  $3^\circ > 2^\circ > 1^\circ$
- Base = Strong base favors E2
- Solvent = polar aprotic solvent favors E2
- Regioselectivity = usually most stable alkene favored\*
- Stereochemistry = antiperiplanar TS<sup>‡</sup>
- can be used to make alkynes

# E1 Refresher

- Rate = 1st order
- Mechanism = 2 steps
- LG = good LG required
- R-X =  $\beta$ -H required. Benzylic, allylic,  $3^\circ > 2^\circ$ 
  - no  $1^\circ$
- Base = weak base favors E1
- Solvent = polar protic solvent favors E1
- Regioselectivity = most stable alkene favored

# Which Mechanism Dominates?

- Alkyl Halide
- Nucleophile/Base
- Solvent



# The R-X

□ Start here!

1°

$S_N1$   $S_N2$  E1 E2

methyl

$S_N1$   $S_N2$  E1 E2

2°

$S_N1$   $S_N2$  E1 E2

allyl

$S_N1$   $S_N2$  E1 E2

3°

$S_N1$   $S_N2$  E1 E2

benzyl

$S_N1$   $S_N2$  E1 E2

# The Base/Nucleophile

Strong Base/Nu

\_\_\_\_\_

\_\_\_\_\_

Weak Base/Nu

\_\_\_\_\_

\_\_\_\_\_

# Ways to Avoid Unwanted Reactions

## Avoiding Elimination

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

## Avoiding $S_N2$

\_\_\_\_\_

\_\_\_\_\_

## How do we avoid $S_N1/E1$ mix?

\_\_\_\_\_

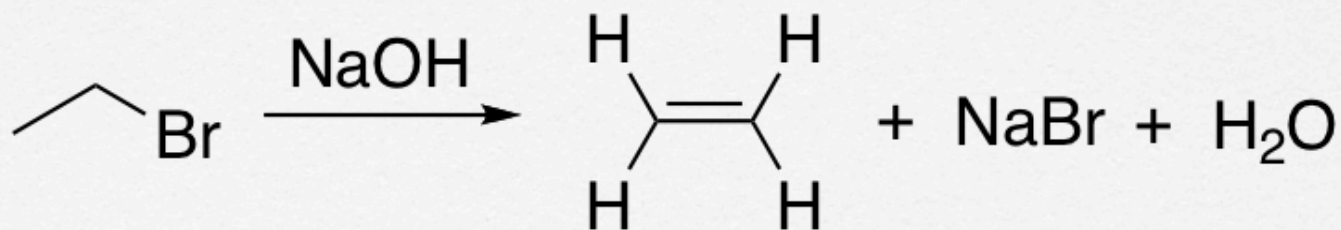
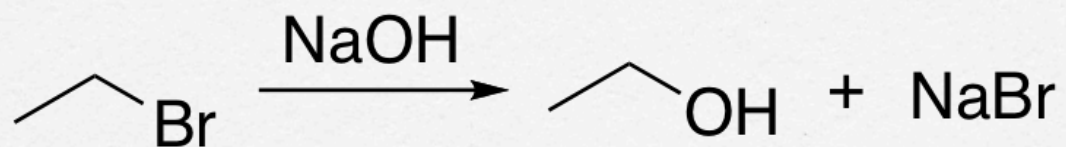
## Favoring Elimination over Substitution

\_\_\_\_\_

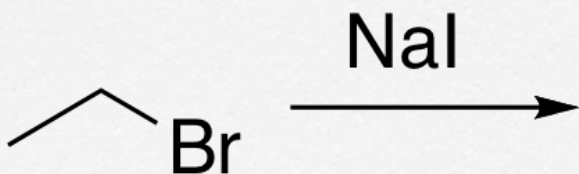
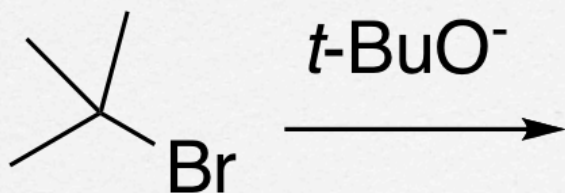
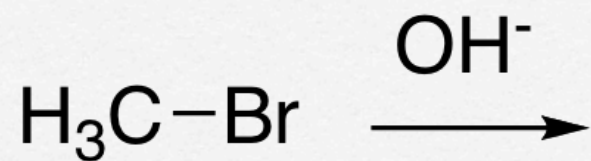
# Heat Favors Elimination

□ Entropy &  $\Delta G$ !

$$\Delta G = \Delta H - T\Delta S$$



# Examples



# Wrapping Up

- Practice predicting which mechanism or mechanisms will dominate for an alkyl halide under a set of reaction conditions
- Practice choosing mechanisms that will allow one mechanism to be dominant for an alkyl halide where possible