# Organic Chemistry

**Alkenes**

**Alkynes**

**Alkanes**

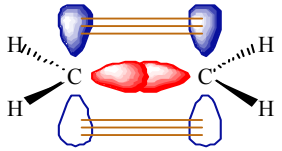
**Benzene**



## Reactions

### General Reactivity

- π bond is electron rich and physically accessible
  - Behave as **nucleophiles**




- Reacts with something electron poor (electrophile)

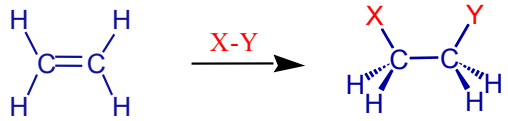


## Reactions

### Addition

- Electrophiles add across the double bond

  *ie.* the π bond breaks and an atom adds to each of the carbons






## Reactions

### 1. Addition of HX

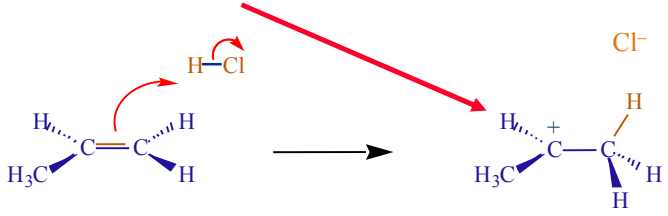
- HCl, HBr and HI readily add to alkenes
  - Order of reactivity = HI > HBr > HCl

# Alkenes

## Mechanism

Step 1

- Nucleophile 'attacks' electrophile
  - a **carbocation** is formed

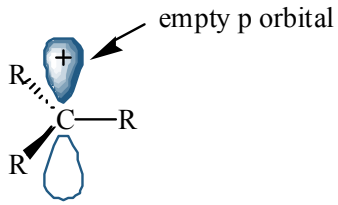





# HX Addition

## Carbocations

- V. reactive species (similar to radicals)
- 6 valence e- in 3 σ bonds
  1 empty p-orbital
- $sp^2$ hybridised

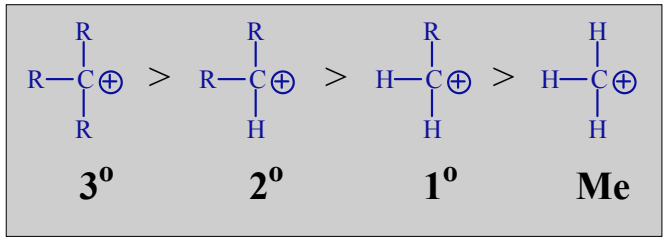





# Alkenes

## Carbocations

- carbocation stability
  - More alkyl groups = more stable (inductive effect)



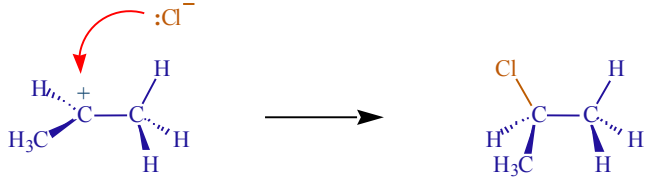



# Alkenes

## Mechanism

Step 2

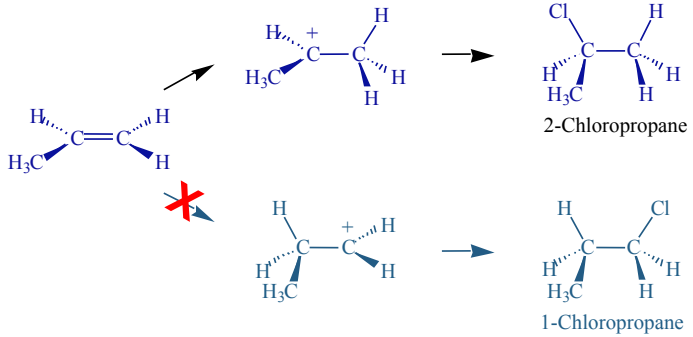
- Nucleophile 'attacks' the electrophile
  - An **alkyl halide** is formed



# Alkenes

## Mechanism

- Two possibilities:






# HX Addition

- Addition of HX is Regioselective

## Markovnikov's Rule

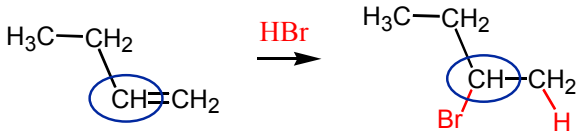
In the addition of HX to an unsymmetrical alkene, the H becomes attached to the least substituted carbon and the X becomes attached to the most substituted carbon



# HX Addition

## Stereochemistry

- Some additions produce a *new chiral centre*:



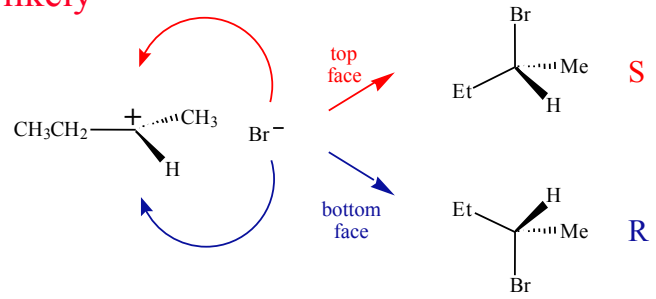

- The carbon of the alkene is said to be **pro**chiral
- It gives rise to the formatino of a new chiral compound after the reaction.
- Usually formed in 50:50 mixture! Why?



# HX Addition

## Stereochemistry

- Attack from either face is equally likely




- Produces a mixture of enantiomers

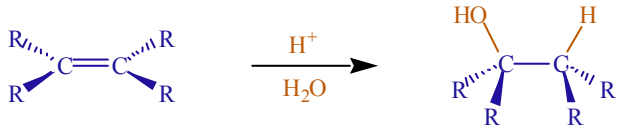
# Alkenes

## Reactions

Other Additions

- Addition of water (HO-H)
  - alkene is treated with aqueous acid

*eg.*



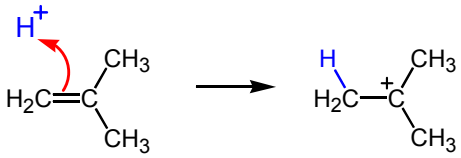



# Addition of Water

## Mechanism

- almost identical to HX addition

Step 1

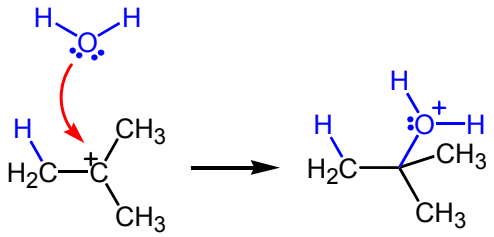





# Addition of Water

## Mechanism

Step 2

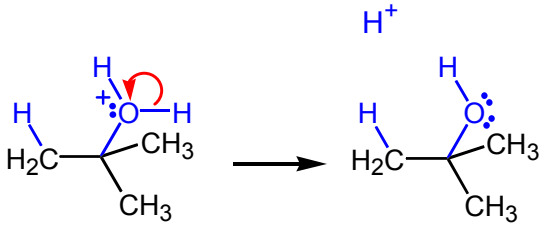





# Addition of Water

## Mechanism

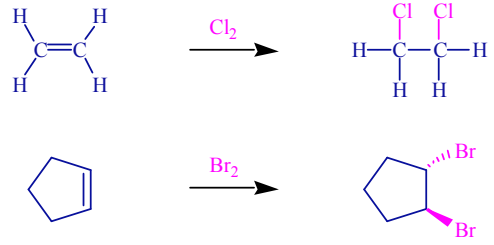
Step 3



# Reactions

## Addition of Halogens

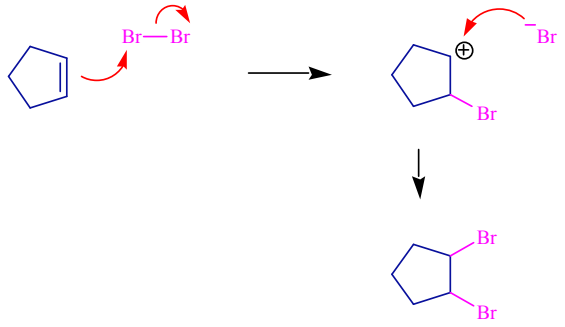
- $Cl_2$ and $Br_2$ add readily to alkenes






# $X_2$ Addition

## Possible Mechanism

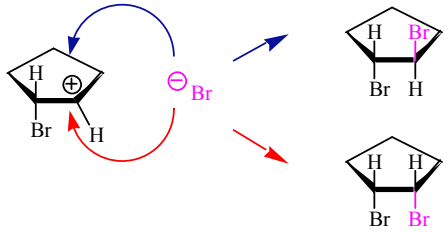





# $X_2$ Addition

## Stereochemistry

- Expect a *cis* (*syn*) –*trans* (*anti*) mixture

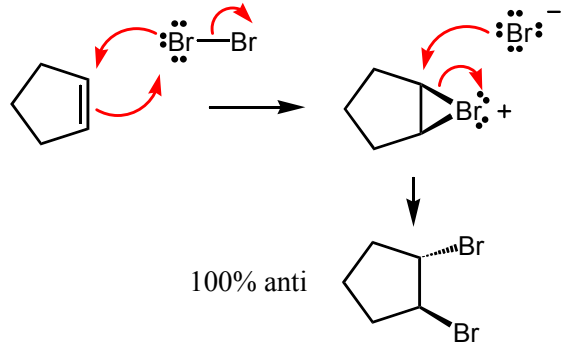



- However, only *trans* is observed! Why??



# $X_2$ Addition

## Actual Mechanism

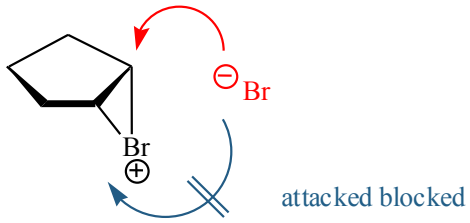



- Intermediate is a **bromonium ion**

# $X_2$ Addition

## Stereochemistry

- proceeds with *trans* (*anti*) - stereochemistry

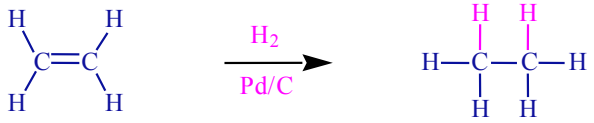





# Reactions

## Addition of Hydrogen

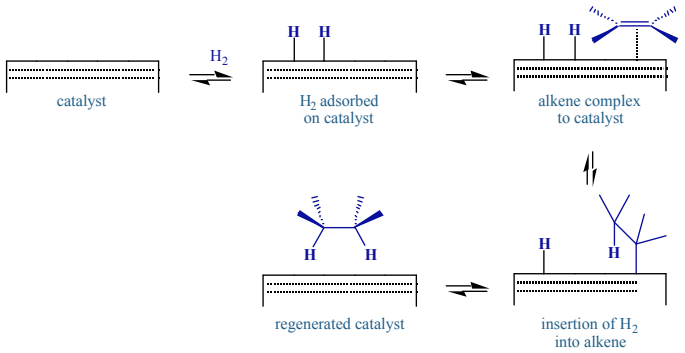
- Requires $H_{2\,(g)}$ and a metal catalyst
  - Pd on C
  - $PtO_2$






# Addition of Hydrogen

## Mechanism

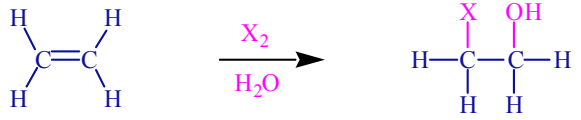





# Reactions

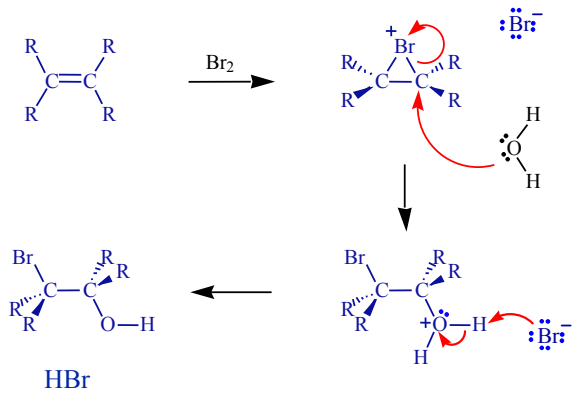
## Halohydrin Formation

- 'HOBr' and 'HOCl' add to alkenes
  - A halogen X adds to one carbon and the -OH adds to the other



# Halohydrin Formation

## Mechanism



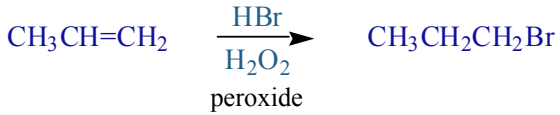



# Reactions

## Radical Addition to Alkenes

- Normally


- But



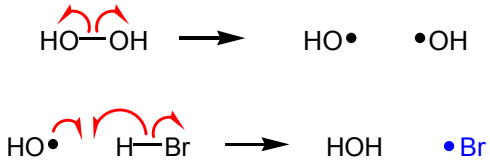



# Radical Addition

## Mechanism

- Peroxides are **radical initiators**

## 1. Initiation

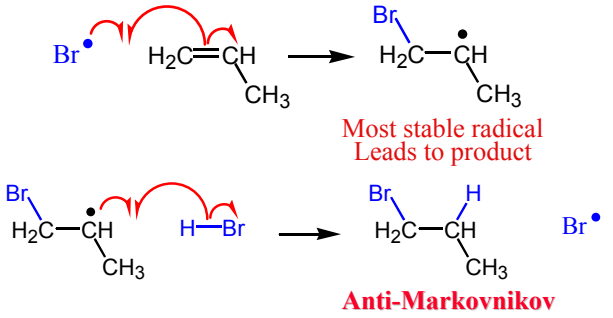





# Radical Addition

## Mechanism

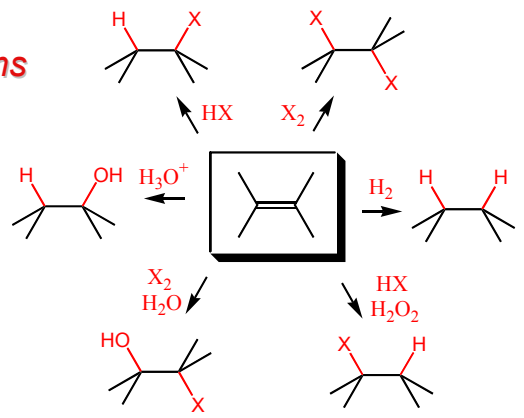
## 2. Propagation



# Alkene Reactions

## Summary

*Addition Reactions*






# Organic Chemistry

**Alkanes**

**Alkenes**

**Alkynes**

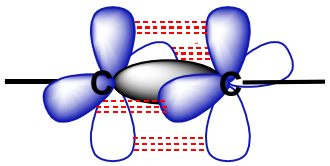
**Benzene**



# Structure

## Electronic Structure

- carbons are sp hybridised
- linear
  - The C≡C triple bond consists of 1 x σ bond and 2 x π bonds






# Reactions

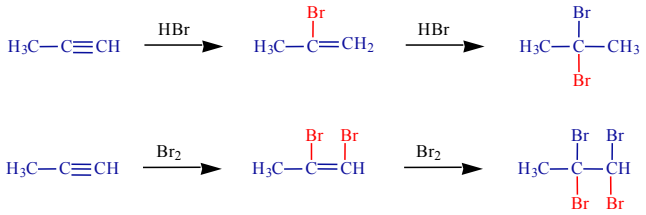
## Generally

- alkynes commonly undergo addition
  - addition of HX, XX
  - addition of water
  - addition of hydrogen
- similar to alkenes
- also undergo
  - alkylation

# Reactions

## Addition of HX, XX

- as for alkenes (but twice)

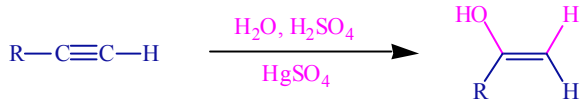





# Reactions

## Addition of Water

Mercuric Ion Catalysed




alkene and alcohol

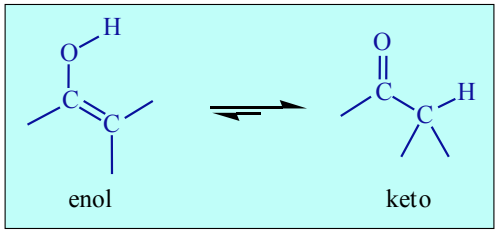
**enol**



# Addition of Water

Enol-Keto Tautomerism

- an enol can tautomerise
- tautomerism = movement of bond and H



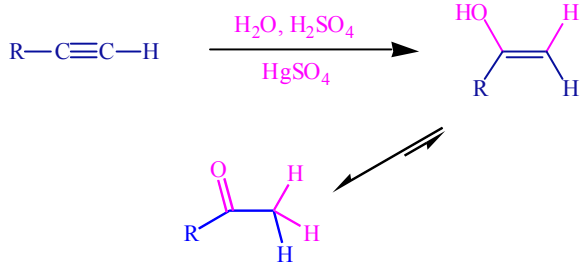

- the keto-tautomer is favoured (more stable)



# Reactions

## Addition of Water

Mercuric Ion Catalysed

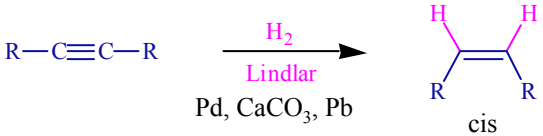



Keto- form

# Reactions

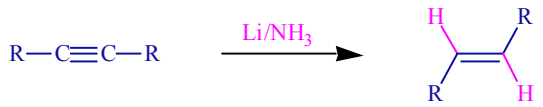
## Addition of Hydrogen

### Hydrogen + Metal Catalyst




cis

### Lithium in Liquid Ammonia

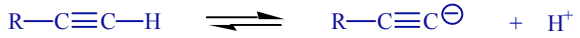



trans



# Acidity of Alkynes

- alkynes are weakly acidic




## Relative Acidity

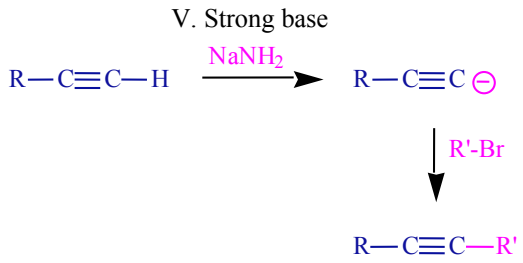
| | |
|---|---|
| $H_3C$-COOH | $pK_a = 5$ |
| HC≡CH | 25 |



# Reactions

## Alkylation

- acetylide anions are nucleophilic
  - react with electrophiles such as alkyl halides

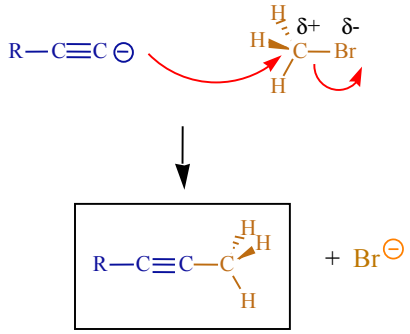





# Alkylation

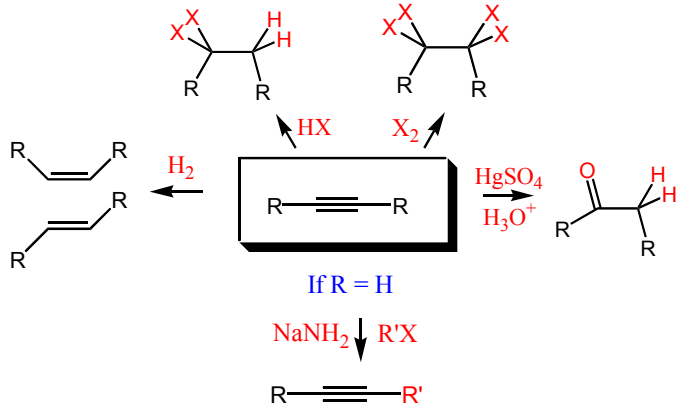
### Mechanism

- one step



# Alkynes

## Summary






# Organic Chemistry

**Alkanes**

**Alkenes**

**Alkynes**

**Alkyl Halides**

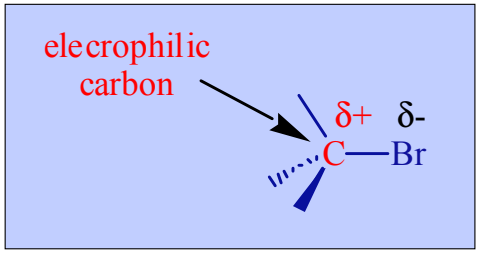
**Benzene**



# Alkyl Halides

## Structure

- $sp^3$ hybridised
- C-X bond is polarised






# Preparation

## From Alkenes

- Alkene + HX
- Alkene + $X_2$

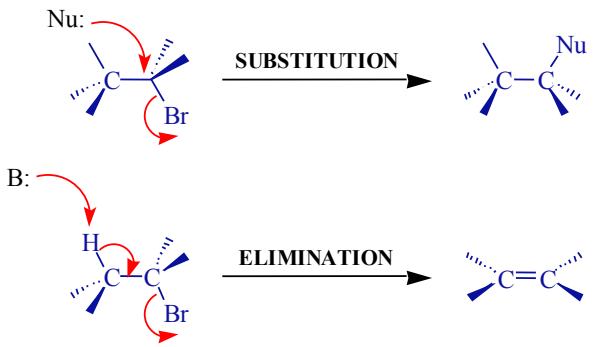
## From Alcohols

- React alcohol with Thionyl Chloride ($SOCl_2$) or Phosphorous tribromide ($PBr_3$)

R-OH → R-X

# Reactions

## General Reaction Types

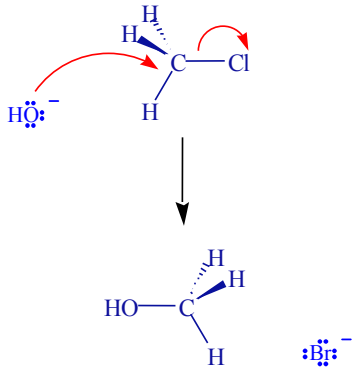





# Reactions

## 1. Nucleophilic Substitution

### Mechanism

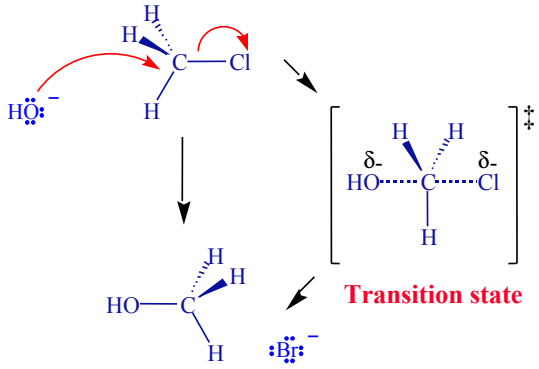





# Reactions

## 1. Nucleophilic Substitution

### Mechanism

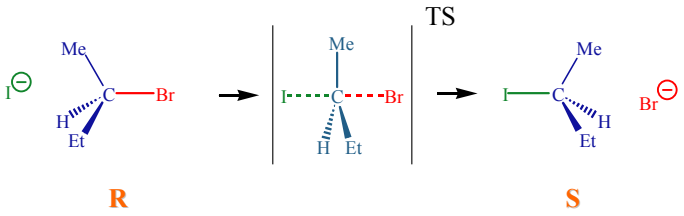





# Nucleophilic Substitution

### Stereochemistry

- Proceeds with inversion of configuration



# $S_N2$

Kinetics

- Relationship between reaction rate and reactant concentrations
- Used to study reaction mechanisms
- rate is dependant on [Nu] and [RX]

rate = k [Nu] [RX]

- **second order** kinetics:

$S_N2$ = Substitution, Nucleophilic, 2nd order



# $S_N2$

The Nucleophile

- **Lewis base**

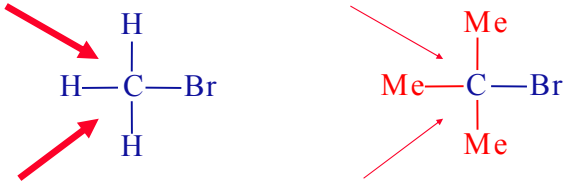
- Nucleophilicity *generally* (but not always) parallels basicity: *i.e.* good base = good nucleophile (*NB!* LDA is a good base but a poor nucleophile)



# $S_N2$

The Alkyl Halide

- Bulky alkyl halides are less reactive for steric reasons



2,000,000 ~1



# $S_N2$

The Leaving Group

- The group which is expelled
  - usually with a negative charge
- Best LG's stabilise a negative charge
  - weak bases

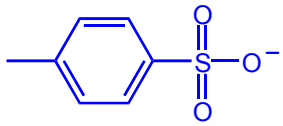
Trend:

- $TosO^- > I^- > Br^- > Cl^- > F^- >> HO^- > H_2N^- > RO^-$

Good LG Poor LG

# $S_N2$

$TosO^-$ =



Tosylate anion (weak base ∴ good LG)

$RO^-$ = Alkoxide anion (formed from alcohol)

$$ROH + B \rightarrow RO^- + BH^+$$

Alkoxide anions are *strong* bases ∴ poor LG's but good Nu



# Reactions

## 2. Elimination

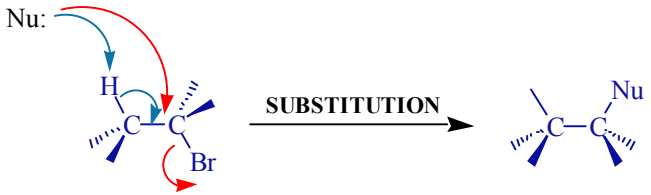
- Alkyl halide is treated with a base




# Reactions

## 2. Elimination

- Often competes with nucleophilic substitution






# Elimination

## Mechanism

- Bimolecular