#### **Alkane**

Wurtz reaction (Reagent: Na, ether) 1° & 2° alkyl halides give this reaction.

$$R - X + 2Na \xrightarrow{\text{ether}} R - R;$$
  $R - X + R' - X + 2Na$   
 $\xrightarrow{\text{ether}} R - R' + R - R + R' - R'$   
 $Br \longrightarrow Br + 2Na \xrightarrow{\text{ether}} \bigodot$ 

# Alkene & Alkyne

#### Characteristic reaction of Alkene & Alkyne is Electrophilic addition reaction.

Mechanism

Step 1 : Attack of the electrophile on  $\pi$  bond forms a carbocation.

$$C = C + E \rightarrow -C - C^{\oplus}$$
+ on the more substituted carbon

Step 2: Attack by a nucleophile gives the product of addition.

(b) Addition of hydrogen halides (where HX = HCI, HBr, HI)

$$R - C \equiv C - R' \xrightarrow{H-X} R - CH = CX - R' \xrightarrow{H-X} R - C - C - R'$$
(Markovnikov addition)

(Markovnikov

orientation)

Note: When electrophiles are: Cl<sup>+</sup>, Br<sup>+</sup>, I<sup>+</sup>, NO<sub>2</sub><sup>+</sup> or Hg<sup>2+</sup> then stereochemistry is important and major product is formed by anti addition.

## Alkyl halide

## Nucleophilic substitution Reaction (S<sub>N</sub>1, S<sub>N</sub>2)

 $S_N 1$  reaction:

$$R-X + H_2O \xrightarrow{AgNO_3} R^+ + AgX \downarrow \longrightarrow ROH$$
 (R may rearrange)

Alkylhalide are hydrolysed to alcohol very slowly by water, but rapidly by silver oxide suspended in boiling water.

#### S<sub>N</sub>2 reaction:

Mechanism : 
$$HO^{-}$$
  $R-X \longrightarrow HO \cdots R \cdots X^{\delta-} \longrightarrow HO-R+X^{-}$ 

$$HO^{-} + \underset{b}{\overset{a}{\bigvee}} \underset{d}{\overset{A}{\bigvee}} \underset{X}{\overset{\delta_{-}}{\bigvee}} \underset{b}{\overset{a}{\bigvee}} \underset{d}{\overset{\delta_{-}}{\bigvee}} \underset{HO}{\overset{\delta_{-}}{\bigvee}} \underset{d}{\overset{A}{\bigvee}} \underset{b}{\overset{A}{\bigvee}} \underset{d}{\overset{A}{\bigvee}} \underset{d}{\overset$$

### **Alcohol**

#### $S_N 1$ reaction :

$$R-OH \xrightarrow{H^{\oplus}} R-OH_2 \xrightarrow{-H_2O} R \xrightarrow{\oplus} R \xrightarrow{X^{\ominus}} R-X(R \text{ may rearrange})$$

Reactivity of HX: HI > HBr > HCI

Reactivity of ROH: allyl, benzyl > 3° > 2° > 1° (Carboocation)

#### S<sub>N</sub>2 reaction:

ROH + 
$$PCI_5 \longrightarrow RCI + POCI_3$$
  
ROH +  $PCI_3 \longrightarrow RCI + H_3PO_3$   
ROH +  $SOCI_2 \longrightarrow RCI + SO_2 + HCI$ 

#### Williamson's synthesis:

It is the reaction in which sodium or potassium alkoxide is heated with an alkyl halide  $(S_N 2)$ .

$$\bigcap_{R_1O^- + R^2 - X} \stackrel{\delta_-}{\longleftarrow} R^{\frac{\delta_-}{1}}O.....R^2.....R^2 \longrightarrow R^1OR^2 + X^-(g)$$

This method is particularly useful for preparing mixed ethers.

# Nucleophilic Aromatic Substitution of aryl halides(S<sub>N</sub>2Ar):

 An electron withdrawing group at ortho or para positions with respect to a good leaving groups are necessary conditions for S<sub>N</sub>2 Ar.

$$\begin{array}{c|c}
X \\
+ Nu^{\Theta} \xrightarrow{Step-I} & Nu \\
\hline
RDS
\end{array}$$

$$\begin{array}{c|c}
X \\
\hline
-X^{\Theta} \text{ (fast)} \\
\hline
Step-II
\end{array}$$

Intermediate ion is stabilized by resonance. and are stable salts called Meisenheimer salts.

$$\begin{bmatrix} \mathsf{Nu} & \mathsf{X} & \mathsf{Nu} & \mathsf{X} & \mathsf{Nu} & \mathsf{X} \\ \vdots & & & & \vdots \\ \vdots & & & & \vdots \\ \end{bmatrix}$$

 A group that withdraws electrons tends to neutralize the negative charge of the ring and this dispersal of the charge stabilizes the carbanion.

$$X$$
 $G$  G withdraws electrons : stabilizes carbanion, activates the  $Ar-S_N^2$  reaction.  $(-N(CH_3)_3, -NO_2, -CN, -SO_3H, -COOH, -CHO, -COR, -X)$ 

 A group that releases electrons tends to intensify the negative charge, destabilizes the carbanion, and thus slows down reaction.

G ( $-NH_2$ , -OH, -OR, -R) releases electrons : destabilizes carbanion, deactivates the Ar-S<sub>N</sub>2 reaction.

### Element effect :

Reactivity order towards  $S_N 2Ar$  with different halogens Ar-F > Ar-Cl > Ar-Br > Ar-I