CONCEPT MAP

SURE SHOT TOPICS OF ORGANIC CHEMISTRY

(ORGANIC COMPOUNDS CONTAINING HALOGENS, OXYGEN AND NITROGEN)

Haloalkanes and Haloarenes

Haloalkanes

Nucleophilic Substitution Reactions

S_N1 reaction

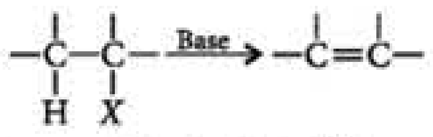
- It is first order reaction.
- Generally carried out in polar protic solvents like water, alcohol and acetic acid.
- Takes place in two steps through carbocation as the intermediate.
- Rate of reaction : 3° > 2° > 1° > Methyl halides
- Tends to proceed with weak nucleophiles, *e.g.*, CH_3OH, H_2O, CH_3CH_2OH, etc.
- Both retention and inversion of configuration takes place, racemic mixture is obtained.

S_N2 reaction

- It is second order reaction.
- Carried out in polar aprotic solvents like acetone, DMSO, acetonitrile or DMF.
- Takes place in one step through transition state.
- Rate of reaction : $CH_3- > 1° > 2° > 3°$ halides
- Lesser the steric hindrance in transition state, faster will be the reaction.
- Tends to proceed with strong nucleophiles, *e.g.*, CH_3O^-, CN^-, OH^-, etc.
- Inversion of configuration takes place (Walden inversion).

Chemical Properties

- **Dehydrohalogenation :**



$$-\underset{H}{\overset{|}{C}}-\underset{X}{\overset{|}{C}}- \xrightarrow{\text{Base}} -\overset{|}{C}=\overset{|}{C}-$$

$$H_3C-\underset{CH_3}{CH}-Cl + KOH(\text{alc.}) \longrightarrow H_3C-CH=CH_2$$

- **Friedel–Crafts reaction :**

$$C_6H_6 + CH_3Cl \xrightarrow{\text{Anhy. } AlCl_3} C_6H_5CH_3 + HCl$$

- **Wurtz reaction :**

$$R\boxed{-X + 2Na + X-}R \xrightarrow{\text{Ether}} R-R + 2NaX$$

Elimination reactions

E1 : In 2 steps: Reactivity of alkyl halides 3° > 2° > 1°

E2 : In 1 step: Via transition state. Favourable → 1° alkyl halide.

Haloarenes

- The aryl halides are relatively less reactive towards nucleophilic substitution reactions as compared to alkyl halides. This low reactivity can be attributed due to the following factors :

  The C—X bond in halobenzene has a partial double bond character due to involvement of halogen electrons in resonance with benzene ring.
- The C—X bond in aryl halides is less polar as compared to that in alkyl halides as sp^2 hybridised carbon is more electronegative than sp^3 hybridised carbon.

Alcohols, Phenols and Ethers

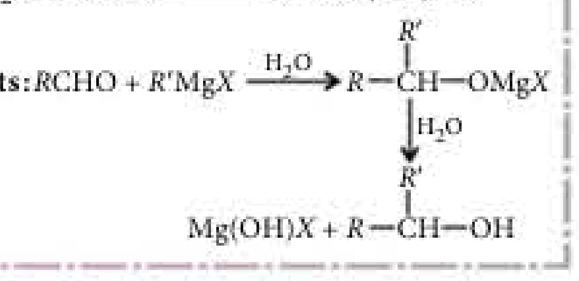
Alcohols

Preparation

- **By acid catalysed hydration :**

  $$CH_3CH=CH_2 + H_2O \overset{H^+}{\rightleftharpoons} CH_3-CH(OH)-CH_3$$
- **By reduction of aldehydes and ketones :**

  $$RCHO + H_2 \xrightarrow{Pd} RCH_2OH;\ RCOR' \xrightarrow{NaBH_4} R-CH(OH)-R'$$
- **From Grignard reagents :** $RCHO + R'MgX \xrightarrow{H_2O}$

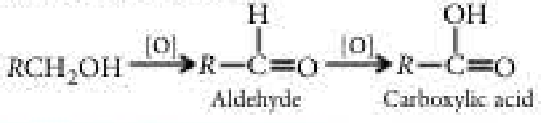


$$R-\overset{R'}{\overset{|}{C}H}-OMgX \xrightarrow{H_2O} Mg(OH)X + R-\overset{R'}{\overset{|}{C}H}-OH$$

Chemical Properties

- **Dehydration :** $C_2H_5OH \xrightarrow[443\text{ K}]{H_2SO_4} CH_2=CH_2 + H_2O$

  Acid catalysed dehydration of alcohols follows carbocation mechanism. Thus, relative ease of dehydration of alcohols follows the following order: 3° > 2° > 1°
- **Oxidation :**

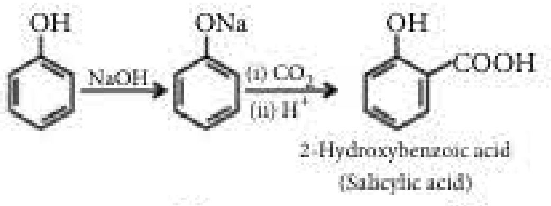


$$RCH_2OH \xrightarrow{[O]} \underset{\text{Aldehyde}}{R-\overset{H}{\overset{|}{C}}=O} \xrightarrow{[O]} \underset{\text{Carboxylic acid}}{R-\overset{OH}{\overset{|}{C}}=O}$$

Phenols

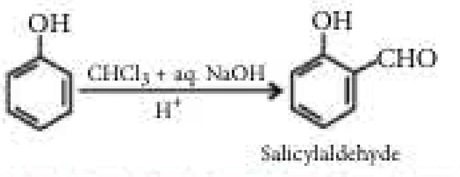
Preparation

- **Kolbe's reaction :**



2-Hydroxybenzoic acid (Salicylic acid)

- **Reimer-Tiemann reaction :**



Salicylaldehyde

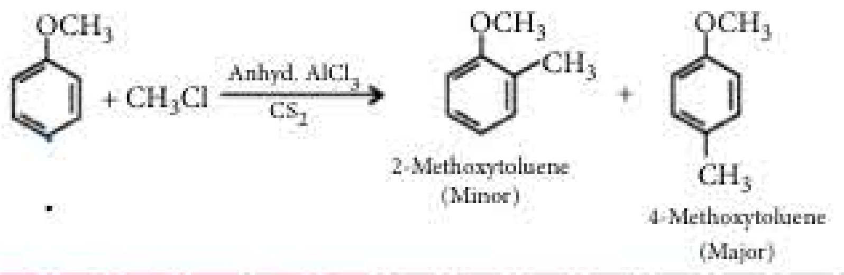
Ethers

Preparation

- **From alcohols by dehydration :** $2ROH \xrightarrow{H_2SO_4,\ 413\text{ K}} ROR$
- **From alkyl halide :** $R-X + RONa \xrightarrow[-NaX]{\Delta} ROR$ **(Williamson synthesis)**

Chemical Properties

- **Friedel-Crafts reaction :**



2-Methoxytoluene (Minor)

4-Methoxytoluene (Major)

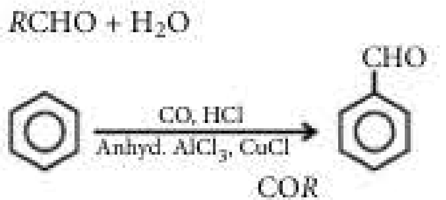
Aldehydes, Ketones and Carboxylic acids

Aldehydes and Ketones

Preparation

- **Oxidation of alcohols :**

  $$RCH_2OH + [O] \xrightarrow[H_2SO_4\text{ (dil.)}]{K_2Cr_2O_7} RCHO + H_2O$$
- **Gatterman-Koch reaction :**



- **Friedel-Crafts acylation :**

- **Etard reaction :**

- **Rosenmund reduction :** $RCOCl + H_2 \xrightarrow[\text{boiling xylene}]{Pd\text{-}BaSO_4,\ S} RCHO + HCl$

Chemical Properties

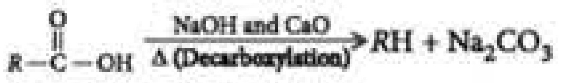
- **Nucleophilic addition reactions :** Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons.
- **Haloform reaction :** Given by compounds having CH_3CO- group or $CH_3CH(OH)-$ group.

  $$RCOCH_3 \xrightarrow{NaOX} RCOONa + \underset{\text{Haloform}}{CHX_3}$$
- **Aldol condensation :**
  - Aldehydes and ketones having at least one α-H atom undergo a reaction in the presence of dilute alkali as catalyst to form β-hydroxy aldehydes (aldols) or β-hydroxy ketones (ketols), respectively.
  - The aldol and ketol readily lose water to give α, β-unsaturated carbonyl compounds.
- **Cannizzaro reaction :** Aldehydes which do not have α-H atom undergo disproportionation on heating with concentrated alkali.

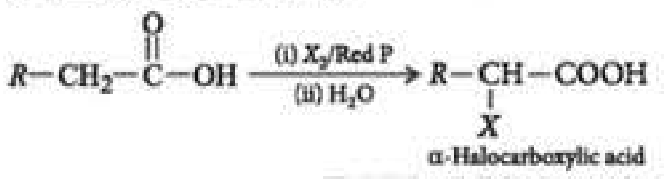
Carboxylic Acids

Chemical Properties

- Hydroxyl group of acids is more acidic than the hydroxyl group of alcohols and phenols.
- **Acidity order :** Carboxylic acids > Phenols > Alcohols
- More is the electronegativity of the atom attached to the carboxyl group, more will be the acidity.



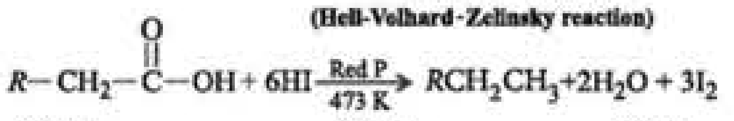
$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\Delta\text{ (Decarboxylation)}]{\text{NaOH and CaO}} RH + Na_2CO_3$$



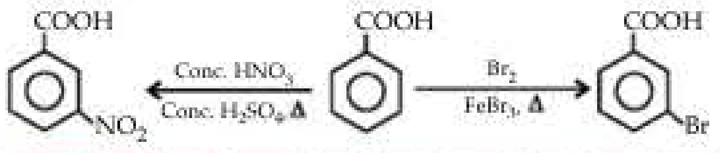
$$R-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2\text{/Red P}} R-\underset{X}{\underset{|}{CH}}-COOH$$

α-Halocarboxylic acid

(Hell-Volhard-Zelinsky reaction)



$$R-CH_2-\overset{O}{\overset{\|}{C}}-OH + 6HI \xrightarrow[473\text{ K}]{\text{Red P}} RCH_2CH_3 + 2H_2O + 3I_2$$



Amines

Aliphatic Amines

Chemical Properties

- **Basic character of amines :**
  - Amines are basic in nature due to the presence of lone pair of electrons on nitrogen atom.
  - Aliphatic amines are stronger bases than ammonia due to +*I* effect of alkyl groups present in amines.
  - Aromatic amines are weaker bases than ammonia due to –*I* effect of aryl group.
  - Beside inductive effect, there are other effects like steric effect, solvation effect, resonance effect which affect the basic strength of amines.
  - In gaseous phase, the order of basicity of amines is 3° amine > 2° amine > 1° amine > NH_3.
  - In aqueous phase, despite of inductive effect, solvation effect and steric hindrance also play an important role. Thus, the order of basicity of amines is

    $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$ and

    $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

Chemical Reactions

$\boxed{RNH_2} \xrightarrow[-KCl,\ -H_2O]{CHCl_3\text{/alc.KOH}} RNC$ **(Carbylamine reaction)**

$\boxed{RNH_2} \xrightarrow[-HCl]{C_6H_5SO_2Cl} RNHSO_2C_6H_5$ **(Hinsberg's test)** **(Soluble in NaOH)**

Aniline

Chemical Reactions

$\boxed{C_6H_5NH_2} \xrightarrow{HCl\text{/0-5 °C}} C_6H_5NH_3^+Cl^-$

$\boxed{C_6H_5NH_2} \xrightarrow{[O]\text{/acidified } KMnO_4}$ Aniline black

$\boxed{C_6H_5NH_2} \xrightarrow{[O]\text{/alkaline } KMnO_4}$ Azobenzene

$\boxed{C_6H_5NH_2} \xrightarrow{[O]\text{/neutral } KMnO_4}$ Azobenzene and nitrobenzene

Diazonium Salts

Preparation

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{0-5°C} C_6H_5N_2^+Cl^- + NaCl + 2H_2O$$

Chemical Reactions

$\boxed{C_6H_5N_2^+Cl^-} \xrightarrow[\Delta]{CuCl/HCl} C_6H_5Cl$ [Sandmeyer reaction]

$\boxed{C_6H_5N_2^+Cl^-} \xrightarrow{Cu/HCl} C_6H_5Cl$ [Gattermann reaction]

$\boxed{C_6H_5N_2^+Cl^-} \xrightarrow[NaOH,\Delta]{C_6H_6} C_6H_5-C_6H_5$ [Gomberg reaction]

$\boxed{C_6H_5N_2^+Cl^-} \xrightarrow{\text{Phenol}} C_6H_5N=NC_6H_4OH$ [Coupling reaction]

$\boxed{C_6H_5N_2^+Cl^-} \xrightarrow{H_2O/H^+} C_6H_5OH$

$\boxed{C_6H_5N_2^+Cl^-} \xrightarrow{HBF_4/\Delta} C_6H_5F$