# CONCEPT MAP

## SURE SHOT TOPICS OF ORGANIC CHEMISTRY
(ORGANIC COMPOUNDS CONTAINING HALOGENS, OXYGEN AND NITROGEN)

### Haloalkanes and Haloarenes

#### Haloalkanes

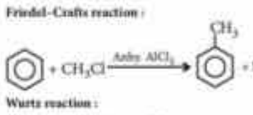
**Nucleophilic Substitution Reactions**

**$S_N1$ 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 :** $-\underset{H}{\overset{|}{C}}-\underset{X}{\overset{|}{C}}- \xrightarrow{\text{Base}} -\overset{|}{C}=\overset{|}{C}-$

  $H_3C-\underset{CH_3}{CH}-Cl + KOH(\text{alc.}) \longrightarrow H_2C=CH-CH_3$
- **Friedel-Crafts reaction :**

  
- **Wurtz reaction :**

  $R\overset{X}{\overset{|}{C}}H_2 + 2Na + X\overset{|}{C}H_2R \xrightarrow{\text{Ether}} R-R + 2NaX$

**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 :**

  $CH_2CH=CH_2 + H_2O \xrightarrow{H^+} CH_3-CH(OH)-CH_3$
- **By reduction of aldehydes and ketones :**

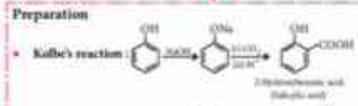
  $RCHO + H_2 \xrightarrow{Pd} RCH_2OH$; $RCOR' \xrightarrow{NaBH_4} R-CH(OH)-R'$
- **From Grignard reagents :** $RCHO + R'MgX \xrightarrow{H_2O} R-\overset{R'}{\overset{|}{C}H}-OMgX \xrightarrow{H_2O} R-\overset{R'}{\overset{|}{C}H}-OH + Mg(OH)X$

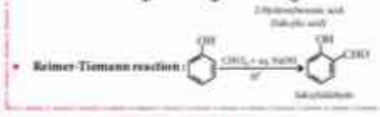
**Chemical Properties**
- **Dehydration :** $C_2H_5OH \xrightarrow[443\,K]{H_2SO_4} CH_2=CH_2 + H_2O$

  Acid catalysed dehydration of alcohols follows carbocation mechanism. Thus, relative ease of dehydration of alcohols follows the following order : 3° > 2° > 1°
- **Oxidation :** $RCH_2OH \xrightarrow{[O]} R-\overset{H}{\overset{|}{C}}=O$ (Aldehyde) $\xrightarrow{[O]} R-\overset{OH}{\overset{|}{C}}=O$ (Carboxylic acid)

#### Phenols

**Preparation**
- **Kolbe's reaction :**

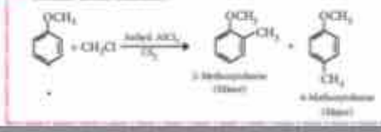
  
- **Reimer-Tiemann reaction :**

#### Ethers

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

**Chemical Properties**
- **Friedel-Crafts reaction :**

### Aldehydes, Ketones and Carboxylic acids

#### Aldehydes and Ketones

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

- **Friedel-Crafts acylation :**

- **Etard reaction :**

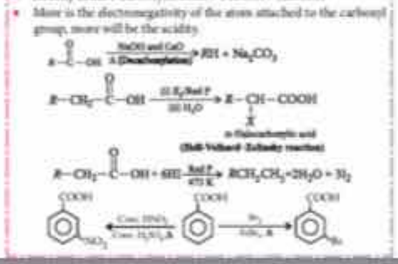
- **Rosenmund reduction :** $RCOCl + H_2 \xrightarrow[\text{boiling xylene}]{Pd\,BaSO_4,\,S} RCHO + HCl$

**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.

  $RCOCH_3 \xrightarrow{NaOX} RCOONa + CHX_3$ (Haloform)
- **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 carbonyl group, more will be the acidity.



### Amines

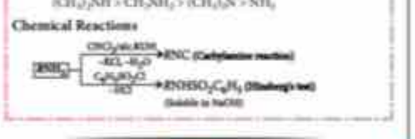
#### Aliphatic Amines

**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**



#### Aniline

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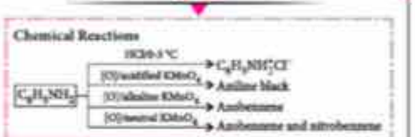
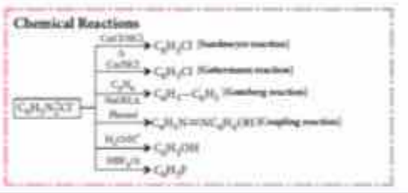


#### Diazonium Salts

**Preparation**

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

**Chemical Reactions**

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  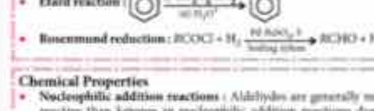
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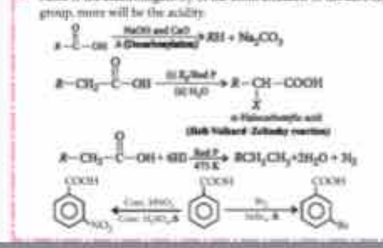

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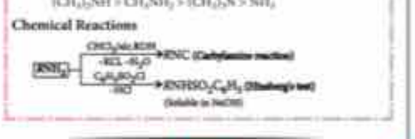

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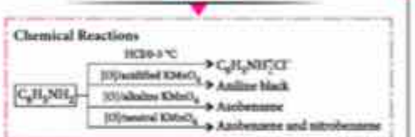

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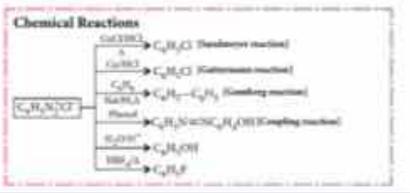
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