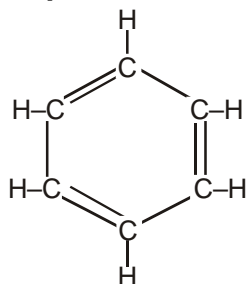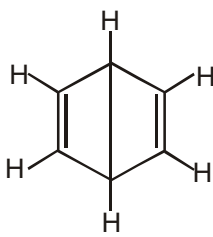<div align="center">**AROMATIC COMPOUNDS**</div>

1. INTRODUCTION :

All organic compounds classify into two broad classes, aliphatic compounds and aromatic compounds. Aromatic compounds are those that resemble with benzene in chemical behaviour.
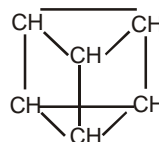
1.1. Proposed structure of benzene :

Kekule benzene   Dewar's benzene   [Prism like structure proposed by Albert Ladenberg]

* Benzene mostly represents by Kekule structure.

1.2. Huckel's (4n + 2) rule for aromaticity :

An aromatic compound must have cyclic clouds of delocalised (4n+2) π electrons above and below the plane of the molecule.

Comparison between Aromatic, Anti-aromatic and Non- aromatic compounds :

Characteristics	Aromatic	Anti-aromatic	Non-aromatic
1. Structure	Cyclic	Cyclic	Cyclic or Acyclic
2. Shape	Planar	Planar	Planar or Non Planar
3. Conjugation	Close cyclic	Close cyclic	Any Kind of conjugation
4. Hybridization	All atoms of the ring is sp^2 or sp	All atoms of the ring is sp^2	Any Kind of Hybridization
5. Number of delocalised electrons	2, 6, 10, 14 ...... (4n+2)	4, 8, ... (4n)	Any number of electrons
6. Resonance energy	High	Zero	Normal

**Stability : aromatic > nonaromatic > antiaromatic**

1.3. Some noteworthy points :

- Some other aromatic species are Pyridine, Furan, Pyrrole, Thiophene, Ferrocene (sandwich compound) Dipotassium cyclooctatetraenide anion, Buckminster fullerene.
- Antiaromatic compounds are paramagnetic in character.
- [10] annulene is not aromatic, although 1, 6-methano [10] annulene is aromatic.
- Aromatic compound has the ability to sustain an induced ring current.
- Azulene is highly coloured and polar although its isomer naphthalene does not have significant zwitter ionic character.

- Fullerene has been called the most symmetrical possible molecule, its buck side salt becomes a super conductor when cooled below 18 K.

- In pyrrole the sp^2 hybridized nitrogen must contribute two electrons to give an aromatic sextet.

- Aromatic hydrocarbons contain higher percentage carbon content so burn with sooty flame.

1.4. Comparison of Aromatic compounds with alkenes :

Benzene is not as reactive as alkenes. Alkene gives addition reaction while benzene gives substitution reaction.
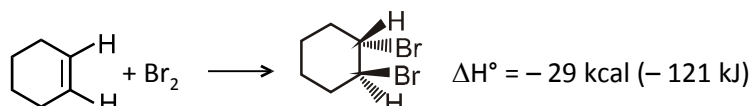
The analogous addition of bromine to benzene is endothermic because it requires the loss of aromatic stability. The addition is not seen under normal circumstances. The substitution of bromine in place of hydrogen atom gives an aromatic product. The substitution requires a Lewis acid catalyst to convert bromine into a stronger electrophile.
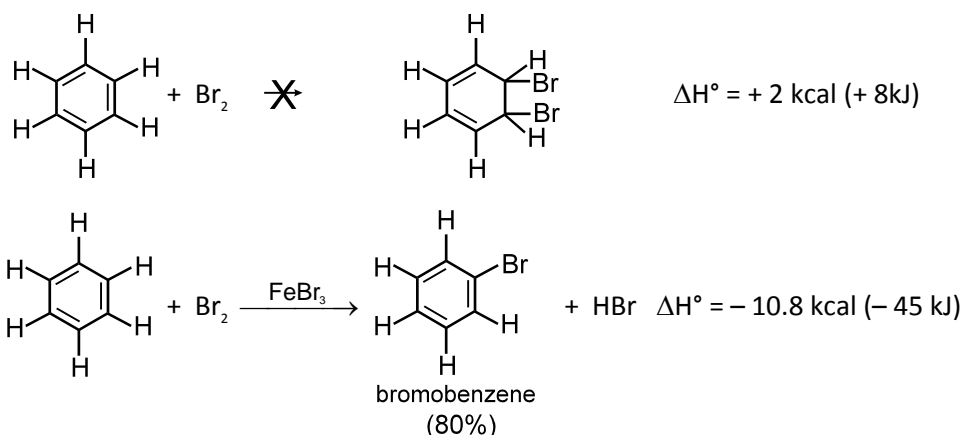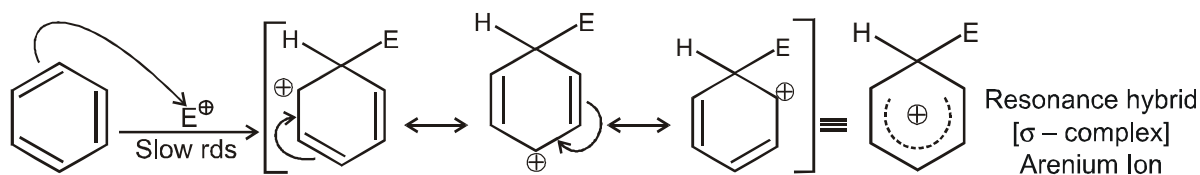

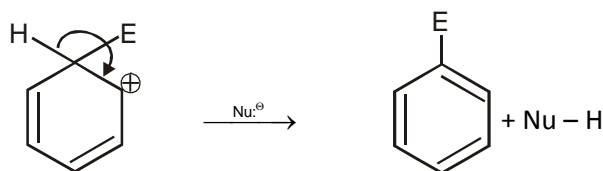# 2. AROMATIC ELECTROPHILIC SUBSTITUTION (ARS$_E$2) REACTIONS IN BENZENE RING

2.1. Mechanism of Electrophilic subtitution :

It is a two step reaction, In Ist step sigma complex is formed in slow step. Formation of the sigma complex is rate determining and the transition state leading to it occupies the highest-energy point on the energy diagram.
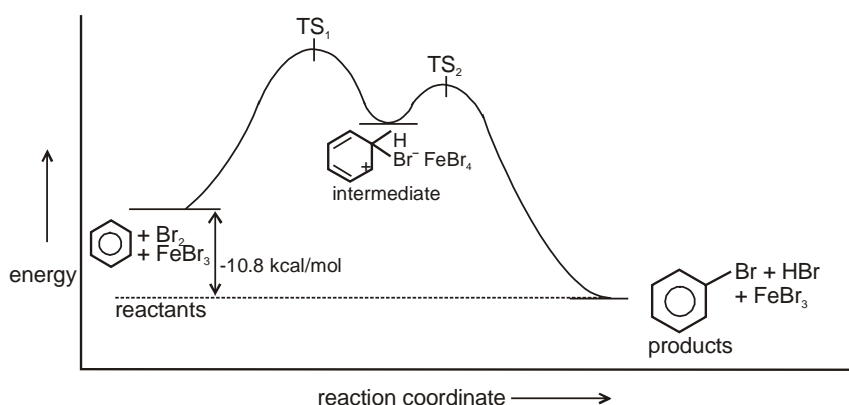
Step 1 : Attack of an electrophile on benzene ring forms the sigma complex

Step 2 : Loss of a proton gives the substitution product.

Energy diagram : For bromination reaction, electrophile is bromonium ion (Br⁺)

Electrophilic aromatic substitution reaction to overcome the high activation energy that charaterizes the first step, the electrophile must be a fairly reactive one. Many of the electrophilic reagents that react rapidly with alkenes do not react at all with benzene. For example peroxy acids and diborane , fall into this category, others such as bromine react with benzene only in presence of catalysts that increases their electrophilicity.

Note :

- Aromatic rings have stable pi electrons still they are available to attack on a strong electrophile to give a carbocation.
- This resonance-stabilized carbocation is called a **sigma complex** because the electrophile is joined to the benzene ring by a new sigma bond.
- The sigma complex (also called an arenium ion) is not aromatic because the sp^3 hybrid carbon atom interrupts the ring of p orbitals.
- This loss of aromaticity contributes to the highly endothermic nature of this first step. The sigma complex regains aromaticity either by a reversal of the first step (returning to the reactants) or by loss of the proton on the tetrahedral carbon atom, leading to the substitution product.
- The overall reaction is the substitution of an electrophile $(\overset{\oplus}{E})$ in place of a proton $(\overset{\oplus}{H})$ on the aromatic ring. **(i.e. electrophilic aromatic substitution)**
- Electrophilic substitution occurs preferentially in the 5-membered ring of azulene.

2.2. Effect of substituent groups in monosubstituted benzene :

2.2.1 Ortho-para directing and activating groups :
All electron releasing groups (+m, +I) are ortho-para directing groups and activating towards electrophilic reactions.

2.2.2 Ortho para directing but deactivating groups :
Halogens are deactivating but ortho-para directing groups.

Reactivity of benzene decreases by –I effect of halogens and ortho-para directing nature decided by +m effect of halogens.

2.2.3 Meta directing and deactivating groups :
Mostly electron withdrawing groups (–m, –I) are meta directing groups and deactivating towards electrophilic reactions.

	Substituent groups	Reactivity (effect on rate)	Directing nature (effect on orientation)
1.	$-O^- > -NH_2 > -NHR > -NR_2 > -OH$	Very strongly activating	Ortho-para directing
2.	$-OR > -NH-\overset{O}{\overset{\|}{C}}-R > -O-\overset{O}{\overset{\|}{C}}-R$	Strongly activating	Ortho-para directing
3.	$-R, -Ar, -CH=CH_2$	Activating	Ortho-para directing
4.	$-X(F, Cl, Br, I), -N=O, -CH_2X, -CHX_2$	Deactivating	Ortho-para directing
5.	$-CHO, -\overset{O}{\overset{\|}{C}}-R, -COOH, -COOR, -COCl, -C\equiv N, -SO_3H$	Strongly deactivating	Meta directing
6.	$-NO_2, -\overset{+}{N}R_3, -\overset{+}{S}R_2, -CF_3$	Very strongly deactivating	Meta directing

## 2.3. Effect of substituent groups in disubstituted benzene :
1) If activating and deactivating both groups are present in a system then position of electrophile will be determined by activating group.
2) If both groups present in a system are deactivator then position of electrophile will be determined by stronger deactivator.
3) If both the groups are activating group then position of electrophile will be determined by stronger activator.
4) There is often little substitution between two groups that are meta to each other.

e.g Nitration product of (image: benzene ring with Cl, Br, 37%, 1%, 62%) (% nitro product)
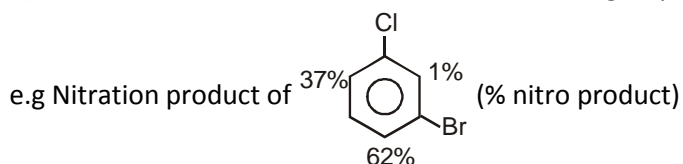
2.4. Halogenation

- Bromine or chlorine itself is not sufficiently electrophilic to react with benzene so a strong Lewis acid such as $FeBr_3$ or $AlCl_3$ catalyzes the reaction.

- Iodination takes place in presence of oxidising agents like HNO_3 or HIO_3. Kinetic isotope effect is also observed in iodination reaction of benzene.
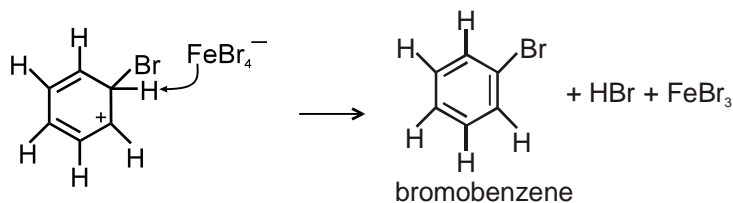
Step 1 : Formation of a stronger electrophile.

$$:\ddot{B}r - \ddot{B}r: \ + \ FeBr_3 \ \rightleftharpoons \ \left[:\ddot{B}r - \overset{\delta^+}{\ddot{B}r} - \overset{\delta^-}{FeBr_3} \right]$$
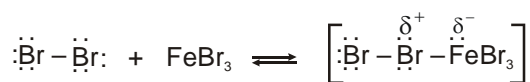
Step 2 : Electrophilic attack and formation of the sigma complex.

sigma complex
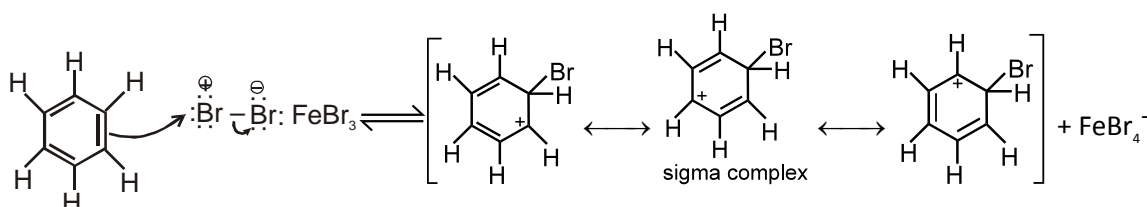
Step 3 : Loss of a proton gives the products.

bromobenzene

Other halogenating agents are ICl, HOCl etc.

order of effectiveness – Cl_2 > BrCl > Br_2 > ICl > I_2

2.5. Nitration

- HNO_3 alone is a weak nitrating agent where as the mixture of concentrated HNO_3 and concentrated H_2SO_4 is strong nitrating mixture. In this mixture HNO_3 is act as base.
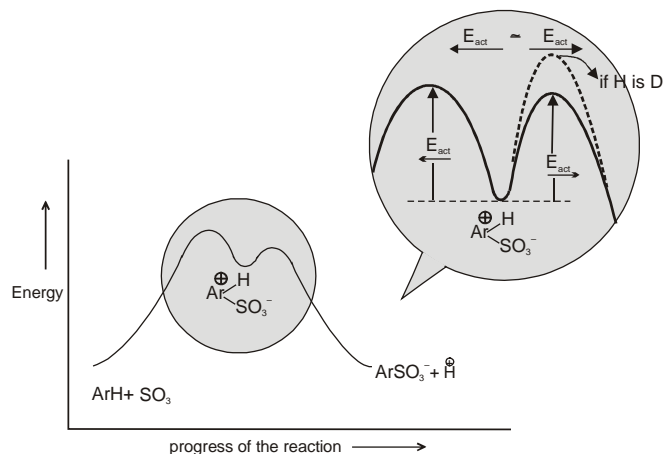
- **Mechanism**

$$H\ddot{O} - NO_2 \underset{}{\overset{H_2SO_4}{\rightleftharpoons}} H_2\overset{\oplus}{O} - NO_2 \underset{}{\overset{H_2SO_4}{\rightleftharpoons}} H_3O^\oplus + HSO_4^\ominus + {}^\oplus NO_2$$

$$HNO_3 + 2H_2SO_4 \rightleftharpoons \underbrace{{}^\oplus NO_2 + H_3O^\oplus + 2HSO_4^\ominus}$$

(π-complex)

(σ - complex)

$H^+ +$ Nitrobenzene
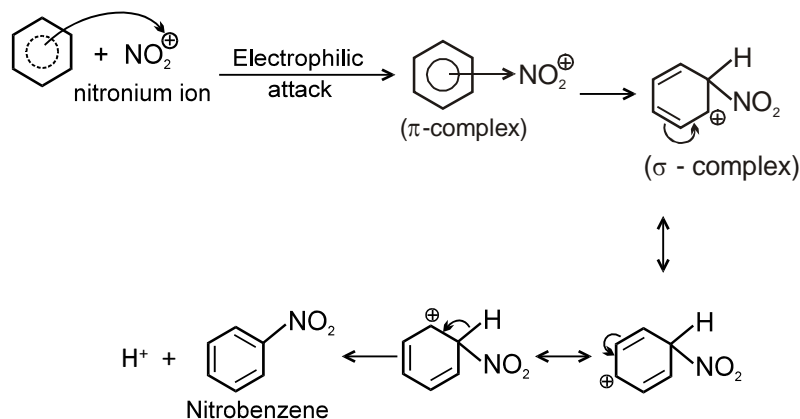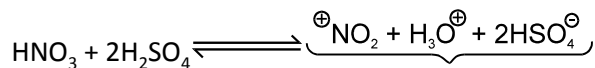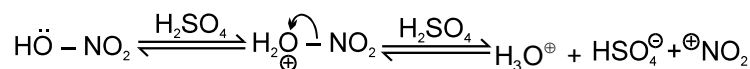
2.6. Sulphonation

Sulphur trioxide in sulphuric acid is used as the sulphonation agent.

$$2H_2SO_4 \rightleftharpoons SO_3 + H_3O^\oplus + HSO_4^\ominus$$

i.

ii.
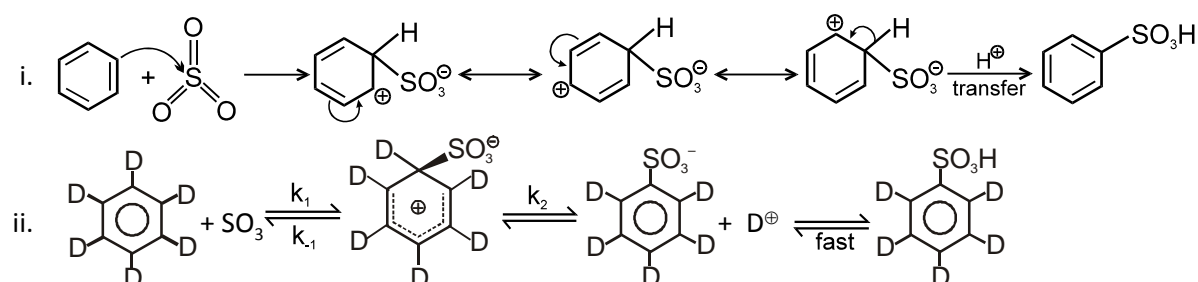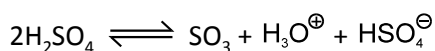
Sulphonation, is **reversible** and takes place in concentrated sulphuric acid. $(K_{-1}K_2)$

Energy Diagram

Aromatic Compounds

Some $Ar\overset{\oplus}{\underset{SO_3^-}{\diagdown}}^H$ or $Ar\overset{\oplus}{\underset{SO_3^-}{\diagdown}}^D$ go on to product, some revert to the starting material and decrease the rate of reaction. This effect is known as isotope effect.
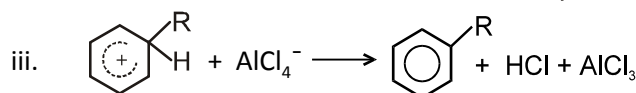
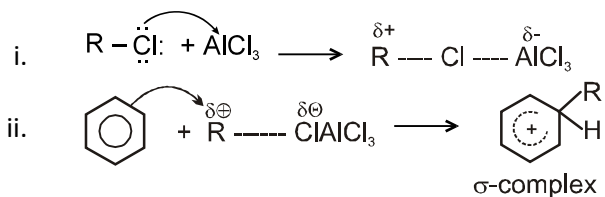## 2.7. Friedel Craft reaction

2.7.1 Alkylation :

- Electrophile is carbocation.
- Alkylating agents are : RX + AlX$_3$ (lewis acid), Alkene in acidic medium and alcohol in acidic medium.
- The order of effectiveness of Lewis acid catalyst has been shown to be

 $AlCl_3$ > $FeCl_3$ > BF_3 > $TiCl_3$ > $ZnCl_2$ > $SnCl_4$
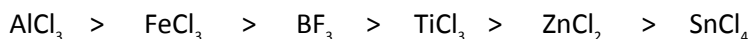
- Mechanism

- Rate law $\rightarrow$ rate = k. [Ar - H]. [R – X]. [MX$_3$]
- Me$_3$CCH$_2$Cl /FeCl$_3$ on benzene gives wholly the unrearranged product PhCH$_2$CMe$_3$
- On heating p-xylene or o-xylene with AlCl$_3$/HCl results in the conversion of the majority of it into the more stable meta-xylene.
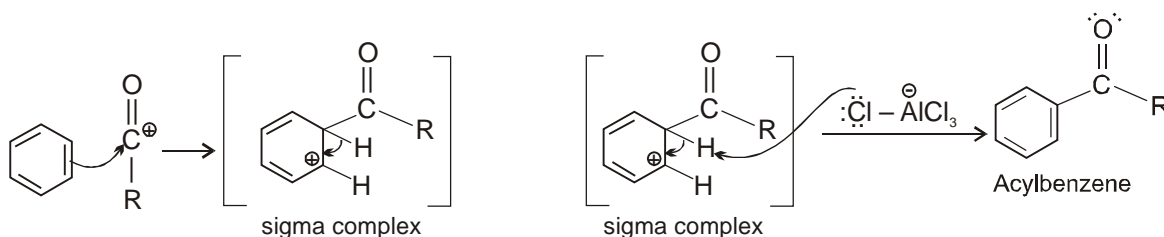
2.8. Acylation :

- Electrophile is acylium ion.
- Acylation of benzene may be brought about with acid, acid chlorides or anhydrides in presence of Lewis acids.
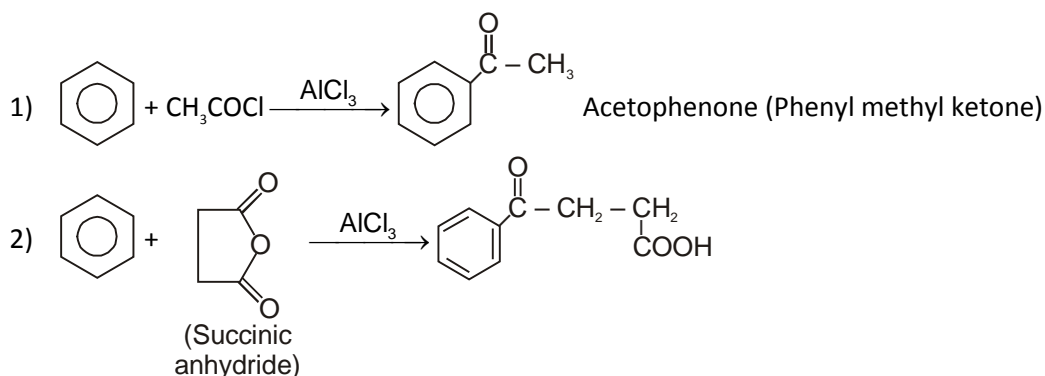- Mechanism

Step 1 : Formation of an acylium ion.
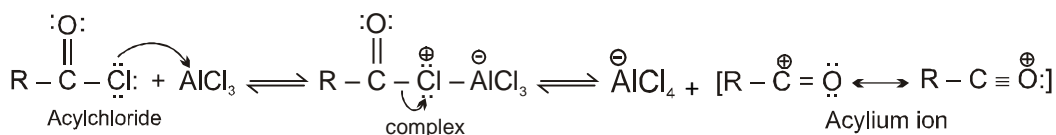
Step 2 : Electrophilic attack.   **Step 3 :** Loss of a proton.

- Friedel-Crafts acylations are generally free from rearrangements and multiple substitution. (but decarbonylation can take place)

Ex.

1) + CH_3COCl $\xrightarrow{AlCl_3}$ Acetophenone (Phenyl methyl ketone)

2) + $\xrightarrow{AlCl_3}$

(Succinic anhydride)

One significant difference of acytation from alkylation is that in former rather more than one mole of lewis acid is required.

2.9. Limitation of Friedel Craft Reaction :

1) **Re-arrangement :** In Friedel craft alkylation carbonium ion can rearrange but in Friedel craft acylation acylium ion can not rearrange.

2) **Polyalkylation** takes place because alylated benzene is more activited than benzene but **polyacylation** does not take place because acyl benzene is more deactivated.

3) **Friedel craft reaction is not possible in presence of following functional groups:-**

a. If –m groups are attahced to benzene ring.

b. If strong +m groups are attahced to benzene ring.

Ex. (1) (2)
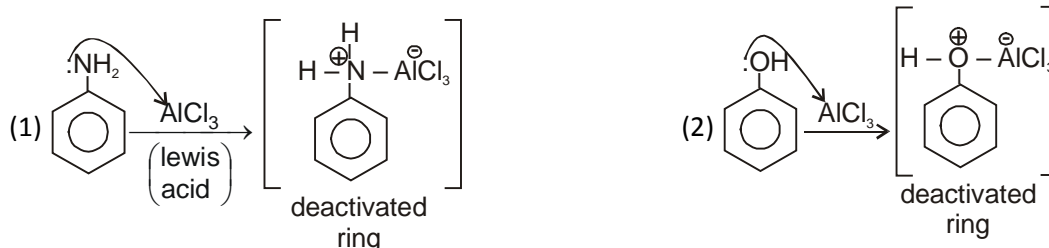
In presence of OH/NH_2 groups Friedel craft reaction is not possible because these groups make coordinate bond with Lewis acid (AlX_3) and the aromatic ring becomes deactivated.

4) **Friedel craft reaction is Possible in following compounds :**
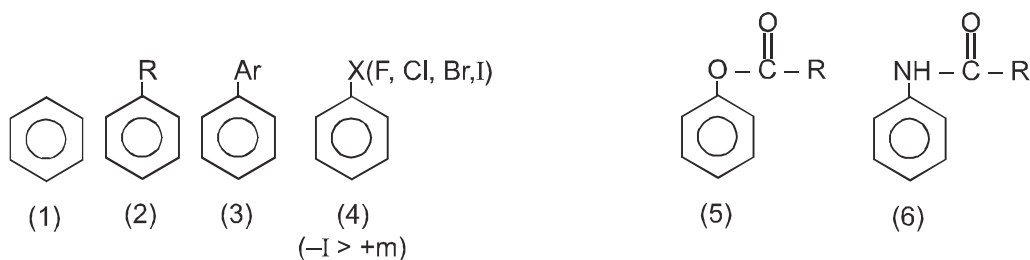
- In acylation rearrangement of R does not takes place, but decarbonylation can take place so the end result is then alkylation.

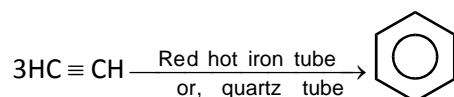**Example 1.** How will you get propylbenzene from benzene ?

Ans.
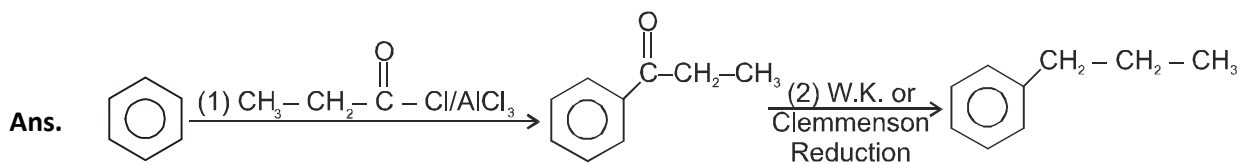
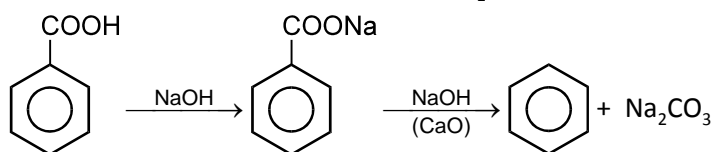- Vinyl halide and arylhalides can not be used in Friedel craft reaction.
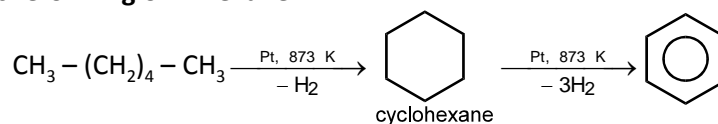
3. BENZENE :

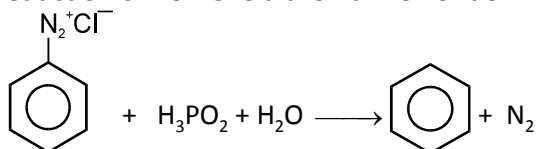## 3.1. Preparation of Benzene

1) **By polymerisation of Acetylene :**

$$3HC \equiv CH \xrightarrow[\text{or, quartz tube}]{\text{Red hot iron tube}}$$

2) **By decarboxylation of Benzoic acid : (mechanism S_E1)**

3) **By catalytic reforming of n-Hexane :**

$$CH_3 - (CH_2)_4 - CH_3 \xrightarrow[-H_2]{Pt, \ 873 \ K} \underset{\text{cyclohexane}}{\bigcirc} \xrightarrow[-3H_2]{Pt, \ 873 \ K} \bigcirc$$
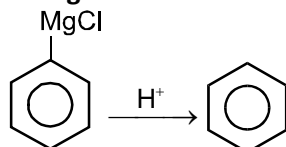
4) **By reduction of Benzene diazonium Chloride :**

5) **By reduction of Phenol :**
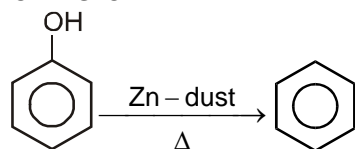
6) **From Grignard reagent :**

3.2. Preparation of Toluene :

1) By Friedel-craft's reaction :

Toluene
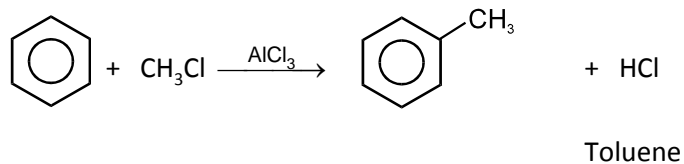
2) By Wurtz fitting reaction :

Bromobenzene   Toluene
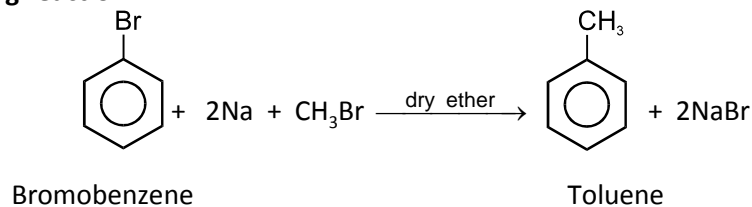
3) From Grignard reagents :
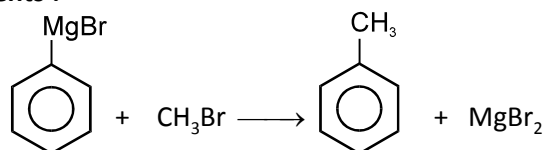
4) By catalytic reforming of n-Heptane :

Methylcyclohexane   Toluene
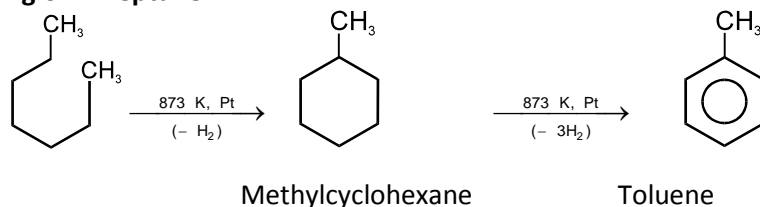
3.3. Preparation of Xylene :

Toluene   o-Xylene
                                              p-Xylene
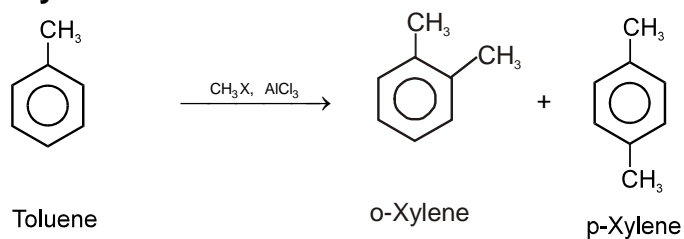
3.4. Chemical Reactions of Benzene :

Diketone also undergoes the friedel craft reaction with benzene.

3.5. Other Chemical Reactions of Benzene :

$$\xrightarrow[\text{Zn/H}_2\text{O}/\Delta]{3\text{O}_3} 3 \begin{array}{c} \text{CH=O} \\ | \\ \text{CH=O} \\ \text{Glyoxal} \end{array} + 3\text{H}_2\text{O} + 3\text{ZnO}$$

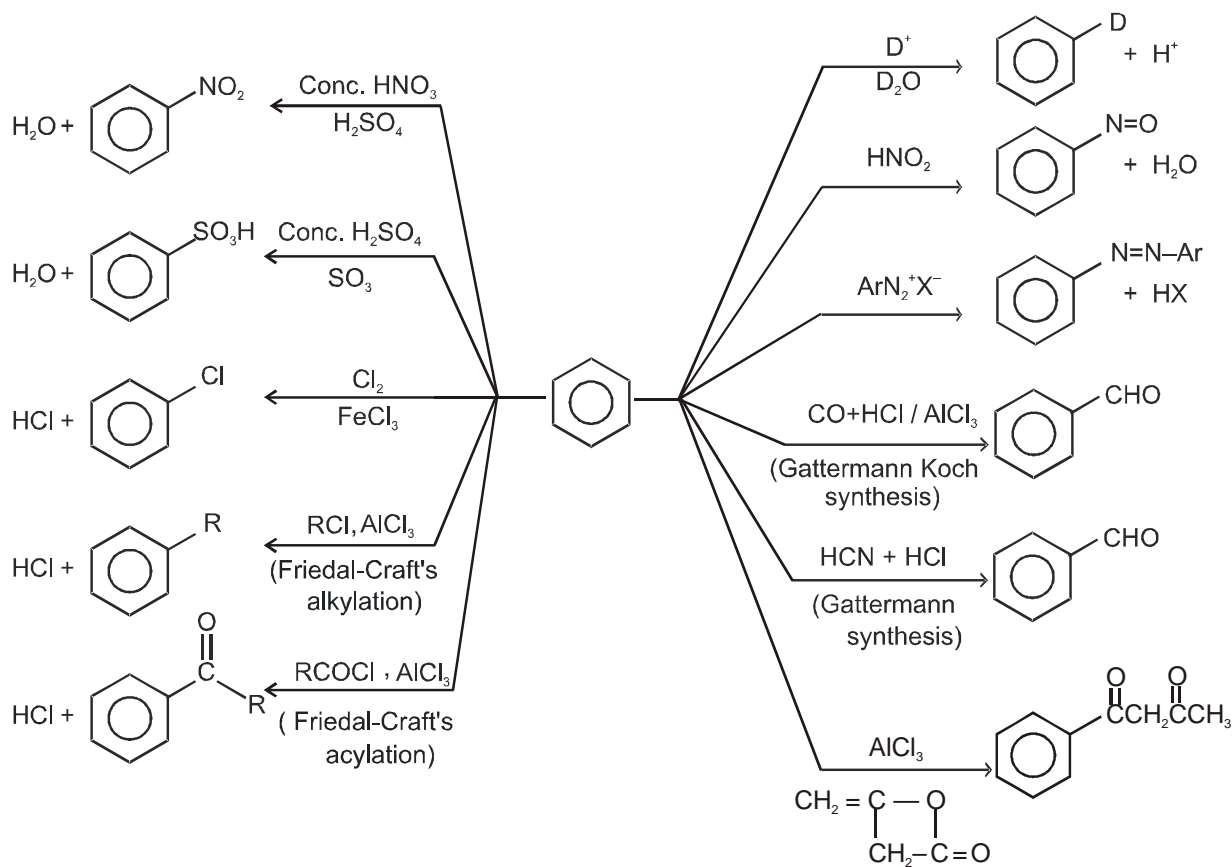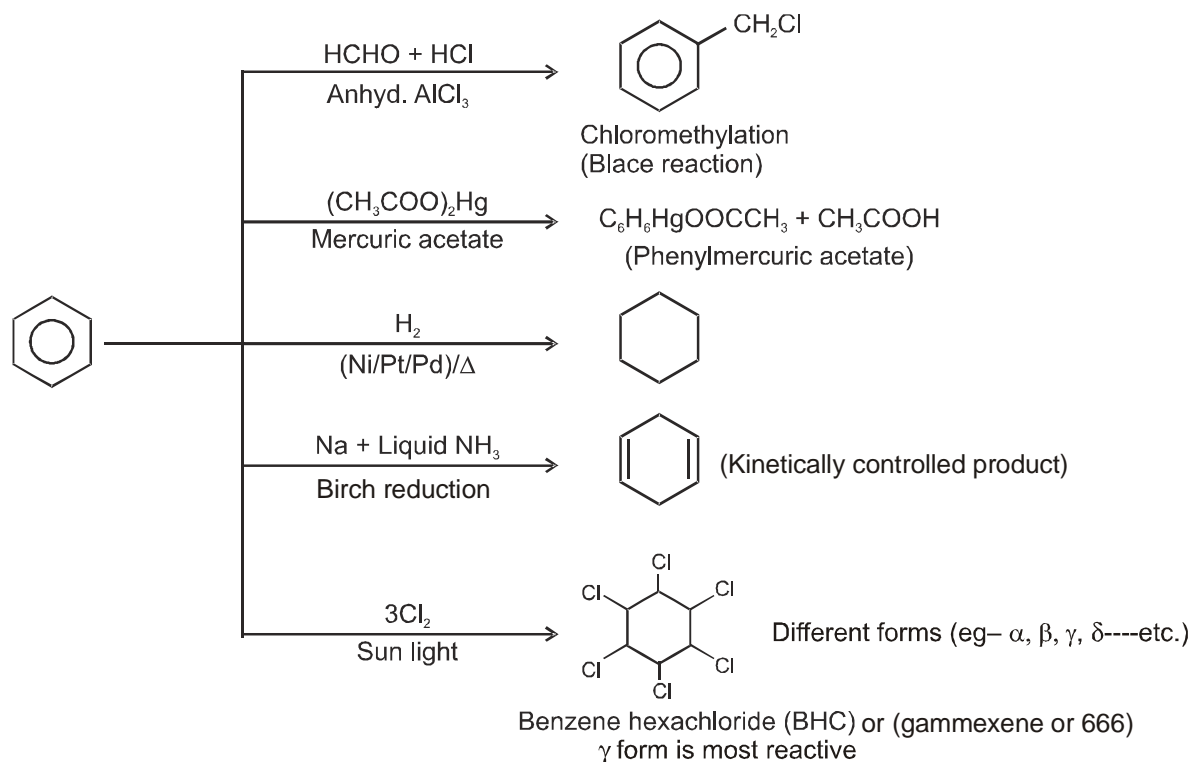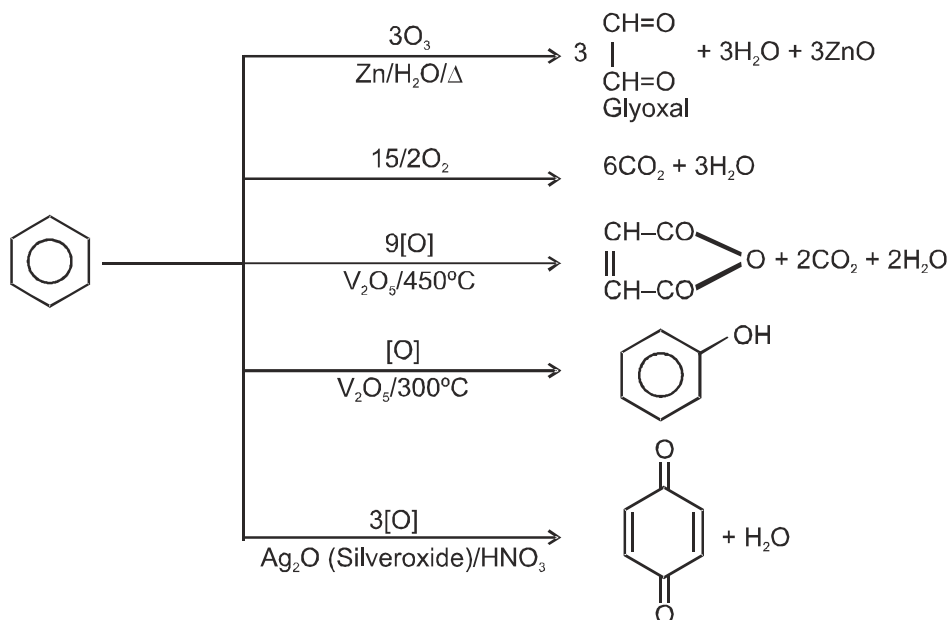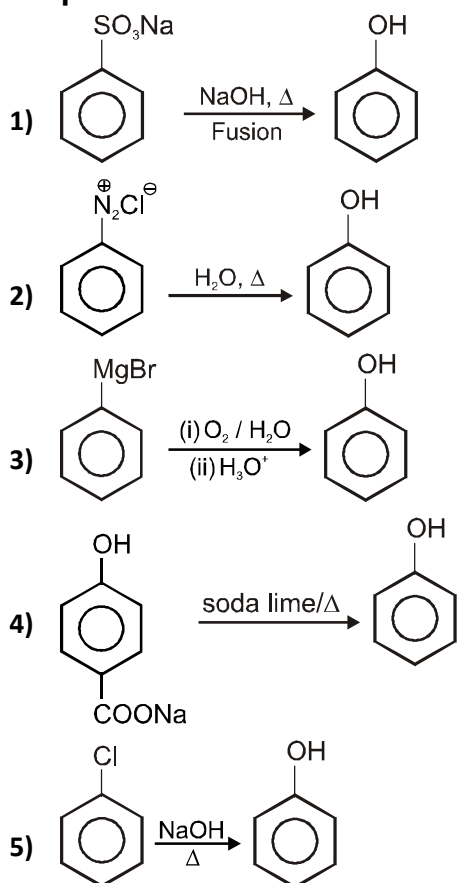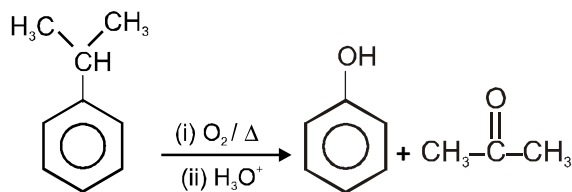$$\xrightarrow{15/2\text{O}_2} 6\text{CO}_2 + 3\text{H}_2\text{O}$$

$$\xrightarrow[\text{V}_2\text{O}_5/450^\circ\text{C}]{9[\text{O}]} \begin{array}{c} \text{CH–CO} \\ \parallel \quad\quad \text{O} + 2\text{CO}_2 + 2\text{H}_2\text{O} \\ \text{CH–CO} \end{array}$$

$$\xrightarrow[\text{V}_2\text{O}_5/300^\circ\text{C}]{[\text{O}]} \text{(phenol, OH)}$$

$$\xrightarrow[\text{Ag}_2\text{O (Silveroxide)/HNO}_3]{3[\text{O}]} \text{(benzoquinone)} + \text{H}_2\text{O}$$

4. PHENOLS (ArOH) :

4.1. Preparation of Phenol

1) $\text{(C}_6\text{H}_5\text{SO}_3\text{Na)} \xrightarrow[\text{Fusion}]{\text{NaOH, }\Delta} \text{(C}_6\text{H}_5\text{OH)}$

2) $\text{(C}_6\text{H}_5\overset{\oplus}{\text{N}}_2\text{Cl}^{\ominus}) \xrightarrow{\text{H}_2\text{O, }\Delta} \text{(C}_6\text{H}_5\text{OH)}$

3) $\text{(C}_6\text{H}_5\text{MgBr)} \xrightarrow[\text{(ii) H}_3\text{O}^+]{\text{(i) O}_2 / \text{H}_2\text{O}} \text{(C}_6\text{H}_5\text{OH)}$

4) $\text{(p-HO-C}_6\text{H}_4\text{-COONa)} \xrightarrow{\text{soda lime/}\Delta} \text{(C}_6\text{H}_5\text{OH)}$

5) $\text{(C}_6\text{H}_5\text{Cl)} \xrightarrow[\Delta]{\text{NaOH}} \text{(C}_6\text{H}_5\text{OH)}$

6) Cumene hydroperoxide method :

$$\underset{\text{(Cumene)}}{C_6H_5CH(CH_3)_2} \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } O_2 / \Delta} \text{C}_6\text{H}_5\text{OH} + CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

Mechanism :

(Migratory aptitude Ph > me)

$$Ph-OH + CH_3-\overset{O}{\underset{\|}{C}}-CH_3 \xleftarrow{H^+} Ph-\overset{\oplus}{O}-\overset{CH_3}{\underset{\underset{OH}{|}}{\overset{|}{\underset{H}{C}}}}-CH_3$$

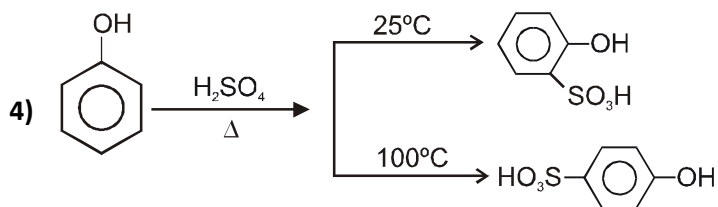Hemiketal
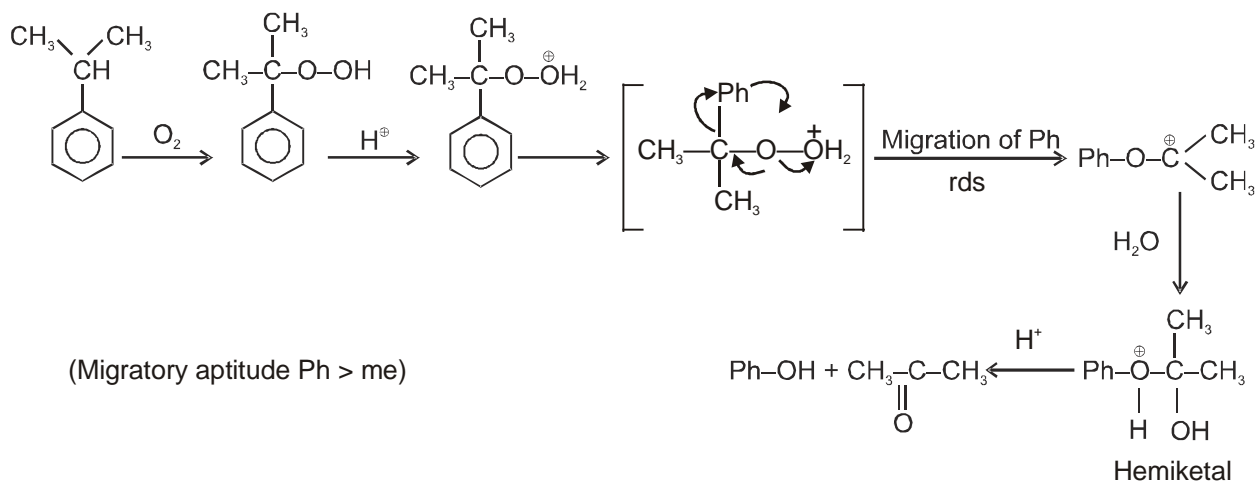
4.2. Properties of phenol

Phenol is a colourless crystalline solid, m.p. 43°, b.p. 182°C, which turns pink on exposure to air and light.

Phenol is used as an antiseptic and disinfectant and in the preparation of dyes, drugs, bakelite, etc.
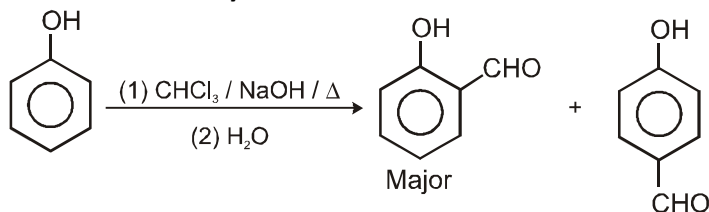
4.3. Chemical Reactions of Phenols :

Phenol generally gives electrophilic substitution with electrophilic reagent.

1) Phenol $\xrightarrow{Br_2, \text{ water}}$ 2,4,6-tribromophenol

2) Phenol $\xrightarrow{\text{dil. } HNO_3}$ 4-nitrophenol + 2-nitrophenol

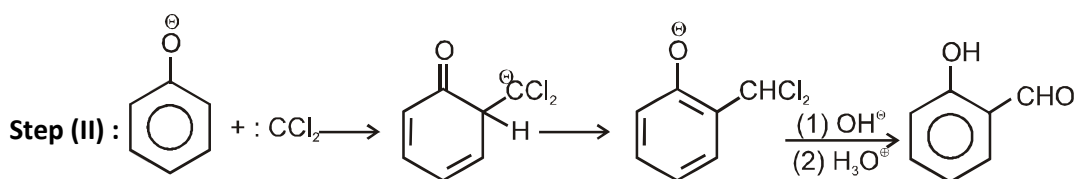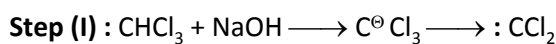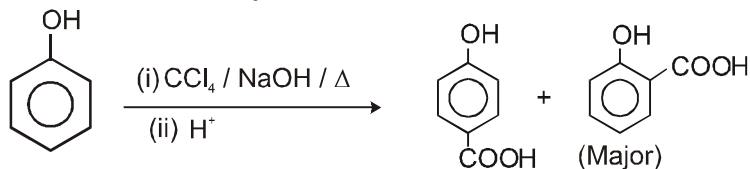**3)** Phenol $\xrightarrow{HNO_3 / H_2SO_4}$ (Major is oxidative cleavage of ring) + Picric acid (small amount)

4)
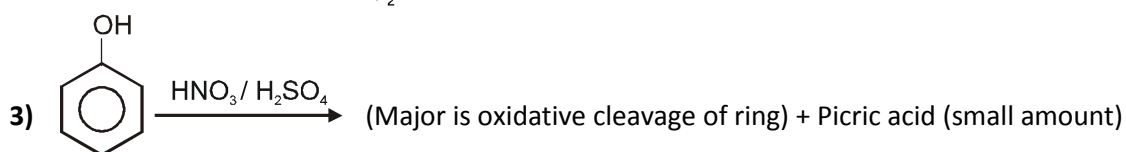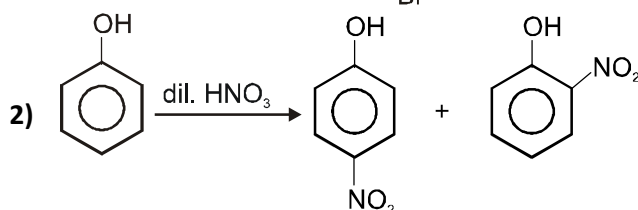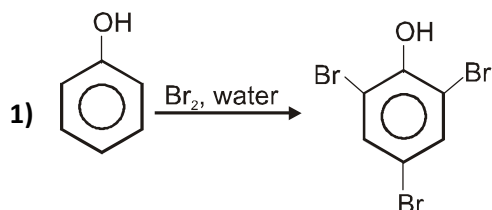
5) **Reimer-Tiemann formylation reaction :**

Major

Mechanism :

Step (I) : $CHCl_3 + NaOH \longrightarrow C^{\ominus}Cl_3 \longrightarrow \; : CCl_2$

Step (II) :

6) **Reimer-Tiemann carboxylation reaction :**

(Major)

7) **Kolbe reaction :**

8)

9)

10)

11)

12)
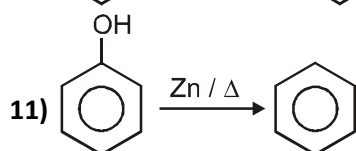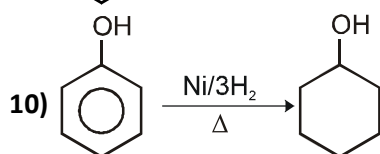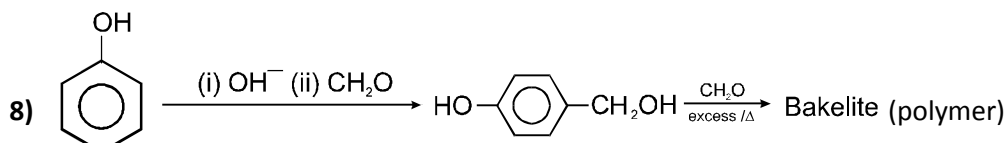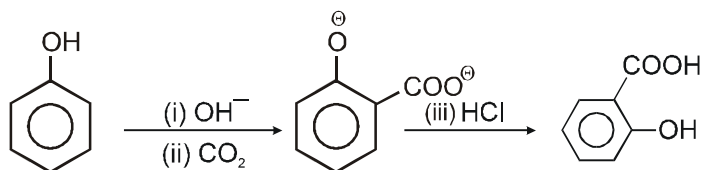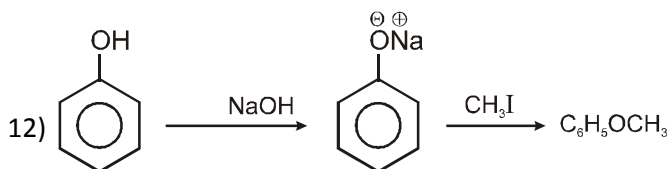
13) **Schotten-Bauman reaction.**
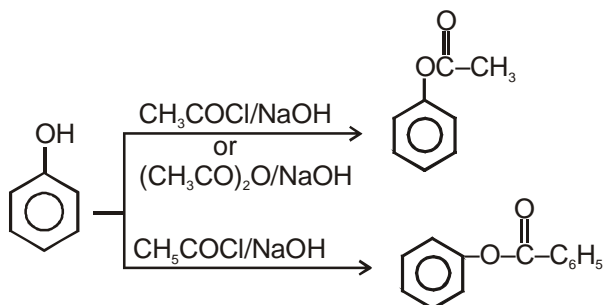
14) **Fries Rearrangement :**
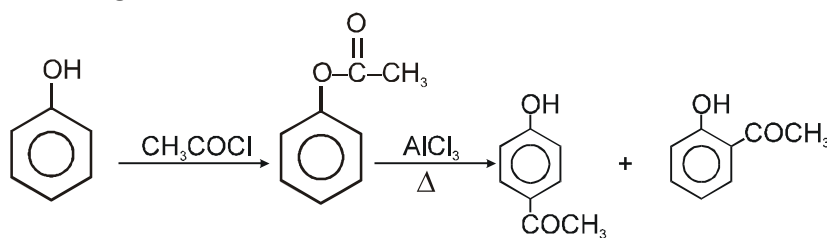
4.4. Test of Phenol

(i)　　Phenol turns blue litmus red. Phenols behave as acids because of the presence of polar O–H group in them. They ionise in aqueous solutions to give H^+ ions.
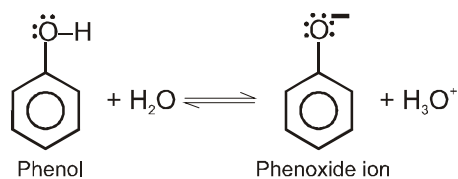
(ii)　　**Reaction with Ferric Chloride**

Phenol gives a violet-coloured water soluble complex with ferric chloride.

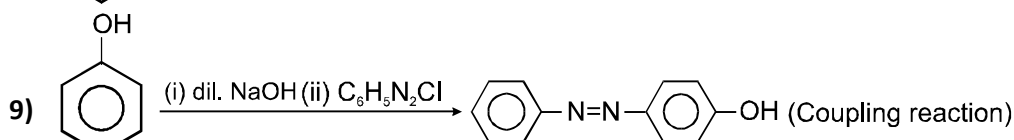$$6C_6H_5OH + FeCl_3 \longrightarrow [Fe(OC_6H_5)_6]^{-3} + 3H^+ + HCl$$
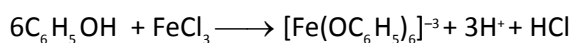
Violet complex

(iii)　　**Libermann's test**

When sodium nitrite $(NaNO_2)$ is added to phenol and dissoved in conc. sulphuric acid, red or brown colouration is produced. The colour changes to blue by the addition of a strong alkali. This test can be used to distinguish phenols from alcohols.

$$2NaNO_2 + H_2SO_4 \longrightarrow 2HNO_2 + Na_2SO_4$$
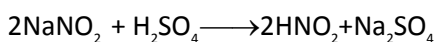
Sodium nitrite　　　　Nitrous acid

Indophenol (red)   Indophenolate (blue)
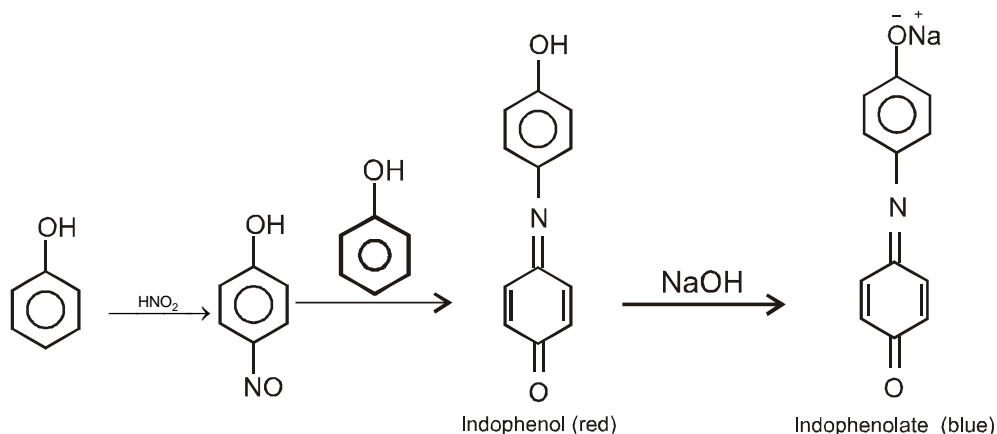
5. NITROBENZENE :

5.1. General properties of nitrobenzene

(i)   Yellow liquid

(ii)   Denser than water. Insoluble in water but soluble in organic solvents

(iii)   b.p. = 211°C

(iv)   steam – volatile

5.2. Chemical Reactions of Nitrobenzene

1) Nitrobenzene $\xrightarrow[\text{(Weakly acidic medium)}]{\text{H}_2/\text{Ni or Ni / Pd}}$ Aniline (Catalytic reduction)

2) Nitrobenzene $\xrightarrow[\text{Fe and HCl}]{\text{Sn and HCl}}$ Aniline

3) Nitrobenzene $\xrightarrow[\text{+ 4H}]{\text{glucose/NaOH or Na}_2\text{AsO}_3\text{/ NaOH}}$ $C_6H_5-N=N-C_6H_5+3H_2O$ Azoxybenzene

4) Nitrobenzene $\xrightarrow[\text{or alkaline sod. stannite (+8H)}]{\text{Zn, alcoholic NaOH or LiAlH}_4}$ $C_6H_5N=NC_6H_5+4H_2O$ Azobenzene

5) Nitrobenzene $\xrightarrow[\text{+10[H]}]{\text{Zn, aqueous NaOH}}$ $C_6H_5-NH-NH-C_6H_5+4H_2O$ Hydrazobenzene $\xrightarrow[\text{Benzidine rearrangement}]{\text{H}^+}$ $H_2N-\bigcirc-\bigcirc-NH_2$ Benzidine (70%)

+

$H_2N-\bigcirc-\bigcirc-NH_2$ (30%)

6) Electrolytic reduction (Weakly acidic medium) → Aniline (NH_2)

7) Electrolytic reduction (Strongly acidic medium) → Phenyl hydroxylamine (NHOH) → Rearrangement → p-Aminophenol (NH_2, OH)

8) HNO_3/363 K → m-Dinitrobenzene

9) Br_2/Fe → m-Bromonitrobenzene

10) Conc. H_2SO_4 → m-Nitrosulphonic acid m-nitrobenzene sulphonic acid (SO_3H)

11) Selective reduction

(a) Zenin reaction : $\overline{Na_2S}$ or $\overline{NH_4HS}$ → (NO_2, NH_2)

(b) $CH = CH_2$, $FeSO_4/\overline{OH}$ → (NH_2, $CH=CH_2$)

5.3. Test of Nitro Benzene : (Mulliken- Barker's Test)

 + Zn + NH_4Cl → (NH–OH) $\xrightarrow{AgNO_3 + NH_4OH}$ (N=O) + H_2O + Ag ↓ black ppt
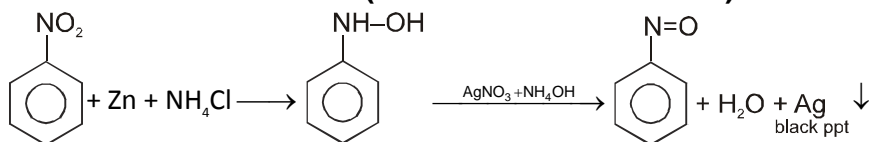
6. ANILINE :

6.1. Prepartion of Aniline

1)

$\xrightarrow[+6H]{Sn/HCl}$

2)

$\xrightarrow{NH_3 + Cu_2O/\Delta}$
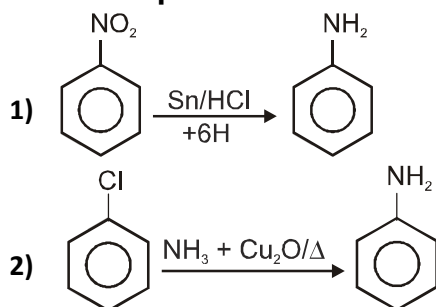
6.2. Chemical Reactions of Aniline

1)

$\xrightarrow[\text{Or } Br_2/CCl_4]{Br_2/H_2O}$

2)

$\xrightarrow{Br_2/CS_2}$

3)

$\xrightarrow[288 \text{ K}]{HNO_3 / H_2SO_4}$

+ many oxidation products

p-Nitro aniline (51%)   m-Nitro aniline (47%)   o-Nitro aniline (2%)
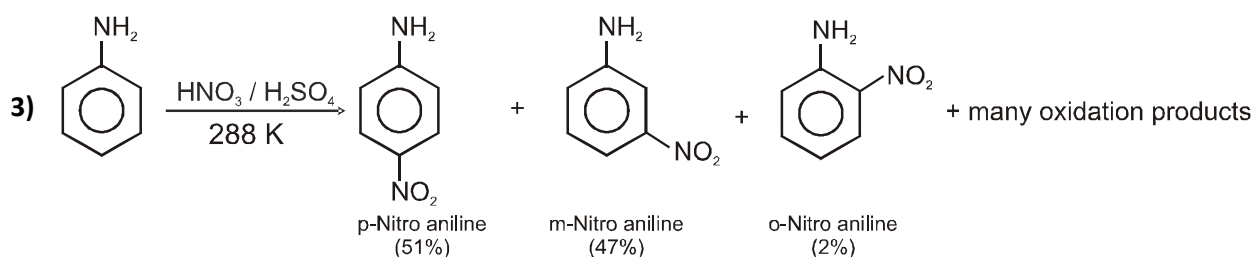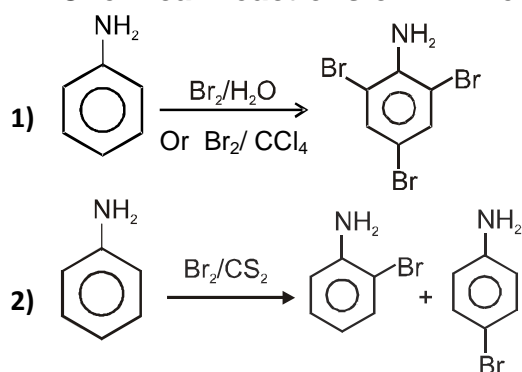
Direct nitration of aniline yields black tarry (coaltar type) oxidation products in addition to the nitro derivatives.

4)

$\xrightarrow{H_2SO_4} [C_6H_5\overset{\oplus}{N}H_3]_2SO_4{}^{2-}$
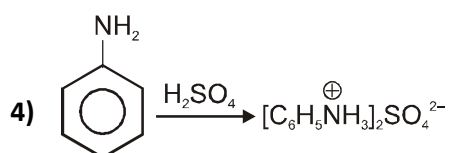
5) Protection of –NH$_2$ group

$\xrightarrow[\text{(ii) } HNO_3 / H_2SO_4 \text{ (iii) } H_3O^+]{\text{(i) } CH_3COCl}$

o -Nitro Aniline < p -Nitro Aniline

6)

$\xrightarrow[\text{(Hinsberg reagent)}]{C_6H_5SO_2Cl}$ $C_6H_5 - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}} - NH - C_6H_5 + HCl$

7)

$$C_6H_5 - NH - \underset{\underset{O}{\|}}{C} - NH - C_6H_5$$

8)

$\xrightarrow[-HI]{CH_3I}$ $C_6H_5NH(CH_3)$ $\xrightarrow[-HI]{CH_3I \text{ (excess)}}$ $C_6H_5\overset{+}{N}(CH_3)_3I$

9)

$\xrightarrow[H_2SO_4]{Na_2Cr_2O_7}$ $O=\!\!\!\!\bigcirc\!\!\!\!=O$ (Controlled oxidation)

10)

$\xrightarrow{Ni/H_2}$
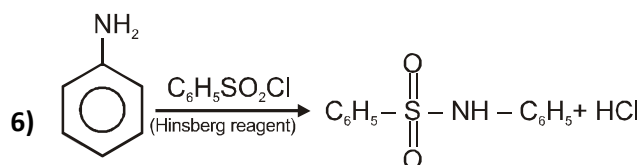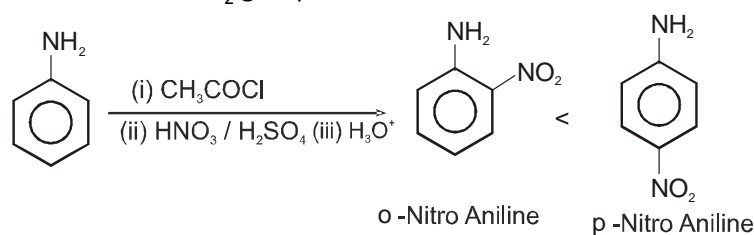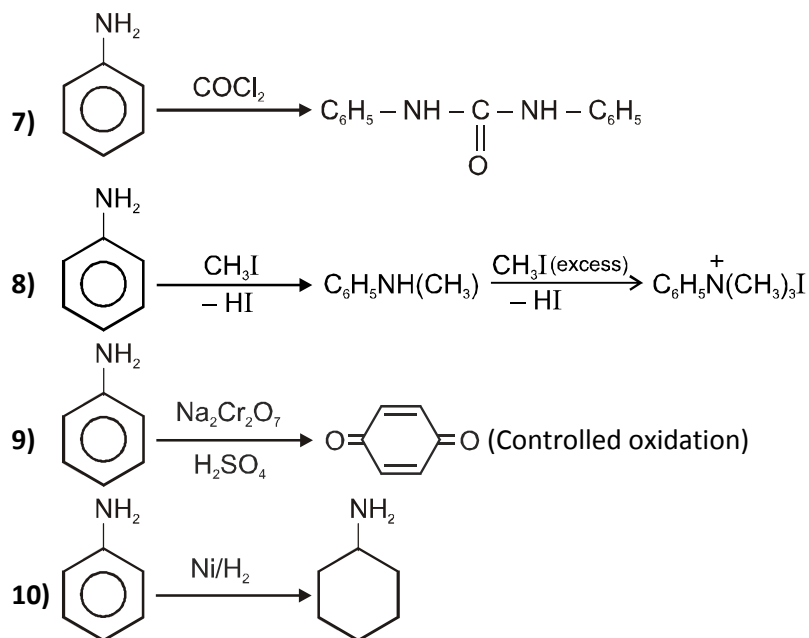
6.3. Test of Aniline and aliphatic amines :

6.3.1 Carbylamine Reaction (Test of 1⁰ aliphatic or aromatic amine)

Primary amines (alphatic as well as aromatic) react with chloroform ($CHCl_3$) on heating in the presence of ethanolic solution of KOH to form isocyanides (also called carbylamines) which are foul smelling substances. Secondary and tertiary amines do not undergo this reaction, therefore this reaction is used as a test for primary amino group ($-NH_2$).

Carbylamine reaction occurs through carbene (dichlorocarbene) intermediate which is obtained as

$$CHCl_3 \xrightarrow[-H_2O]{OH^{\ominus}} \overset{\ominus}{C}Cl_3 \xrightarrow{-Cl^{\ominus}} \quad : CCl_2 \text{ (Dichlorocarbene)}$$

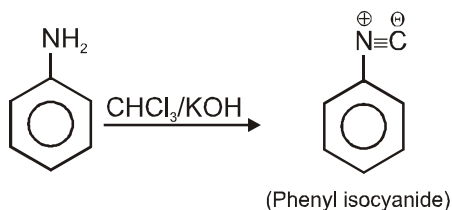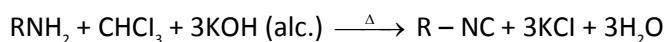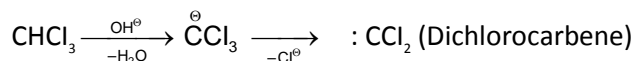$$RNH_2 + CHCl_3 + 3KOH \text{ (alc.)} \xrightarrow{\Delta} R-NC + 3KCl + 3H_2O$$

(Phenyl isocyanide)

6.3.2 Reaction with Nitrous Acid

• Amines of different classes react with nitrous acid (prepared by the reaction of sodium nitrite ($NaNO_2$) and dilute hydrochloric acid).

• Primary aromatic amines react with nitrous acid at low temperature (273-278 K) to give aromatic diazonium salts. This reaction is known as diazotisation.

• Three moles of acid is required for permole aniline to diazotized. Excess of nitrous acid is destroyed by urea.

Benzene
diazonium chloride
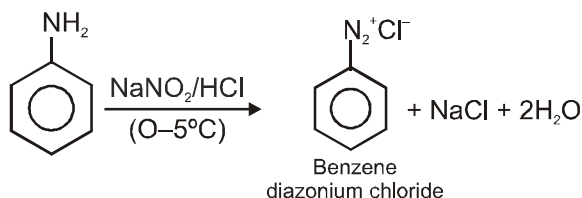
- Primary aliphatic amines react with nitrous acid to form diazonium salt, however, the aliphatic diazonium salts being unstable, decompose to yield mixture of alcohols, alkenes along with nitrogen gas.So this reaction is used to distinguished between aromatic and aliphatic 1º amine. Some times alkylhalide & cycloalkanes are also produced as side products. Methylamine is exception to this reaction.

$$C_2H_5NH_2 \xrightarrow{NaNO_2/HCl} [C_2H_6\overset{+}{N}_2\overset{-}{Cl}] \xrightarrow{H_2O} C_2H_5OH + CH_2 = CH_2 + N_2 + H_2O$$
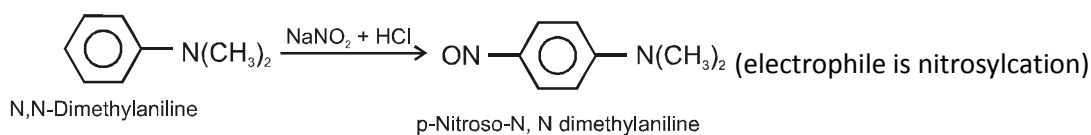(Unstable)
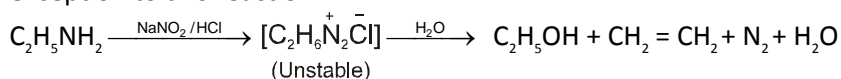
- Secondary aliphatic and aromatic amines react with nitrous acid to produce nitroso-amines that are insoluble in the aqueous solution and separate out as a yellow oily layer.

N-Methylaniline   N–Nitroso–N–methylaniline

$$(C_2H_5)_2 NH + HNO_2 \longrightarrow (C_2H_5)_2 NH — NO + H_2O$$
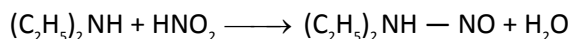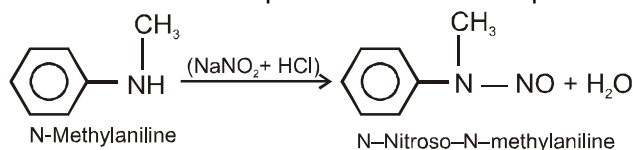
Diethyl amine   N-Nitrosodiethylamine

- Tertiary aliphatic amines on reaction with nitrous acid to form salts which decompse on warming to nitrosoamine and alcohol while tertiary aromatic amines undergo electrophilic substitution at the ring.

$$R_3N + HNO_2 \longrightarrow \underset{\text{Nitrite salt}}{R_3N.HNO_2} \xrightarrow{\Delta} \underset{\text{Nitrosoamine}}{R_2N–N=O} + ROH$$

N,N-Dimethylaniline   p-Nitroso-N, N dimethylaniline
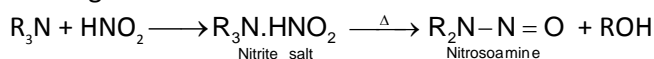
6.3.3   Hofmann mustard oil reaction

It is a test for 1º amine and aniline. Primary amine reacts with carbon disulphide to form dithioalkyl carbamic acids which decompose on heating with mercuric chloride ($HgCl_2$) to give alkyl isothiocyanates having mustard oil like smell.

Dithioethylcarbamic acid   Alkylisothiocyanate
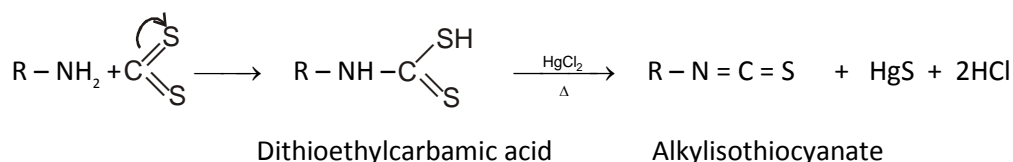
Similarly aniline gives phenlyisothiocyanate

$C_6H_5N=C=S$
Phenylisothiocyanate

Aromatic Compounds

Note : Aniline on heating with ethanolic CS_2 and solid KOH forms N, N-diphenylthiourea which on treating with conc. HCl gives phenylisothiocyanate as –

$$C_6H_5-NH-H \quad + \quad S=C=S \xrightarrow[\Delta]{2\ KOH} C_6H_5NH-\overset{\overset{\displaystyle S}{\|}}{C}-NH-C_6H_5 + H_2S + H_2O$$
$$C_6H_5-NH-H$$
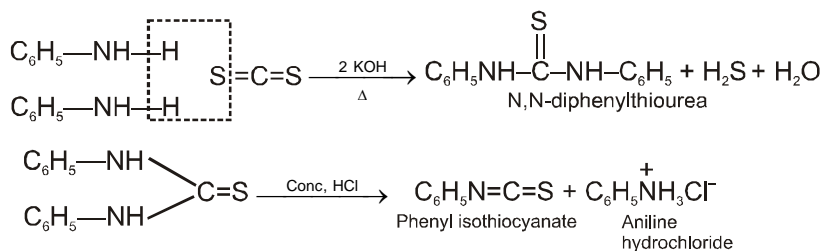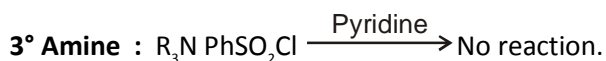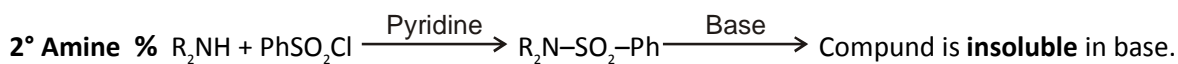N,N-diphenylthiourea

$$\begin{matrix} C_6H_5-NH \\ \\ C_6H_5-NH \end{matrix}\!\!\!\!\!\!\Big\rangle C=S \xrightarrow{\text{Conc, HCl}} C_6H_5N=C=S + C_6H_5\overset{+}{N}H_3Cl^-$$
Phenyl isothiocyanate   Aniline hydrochloride
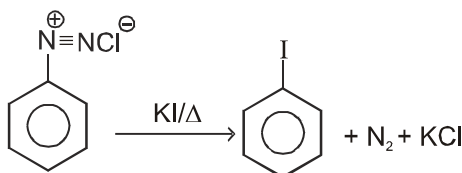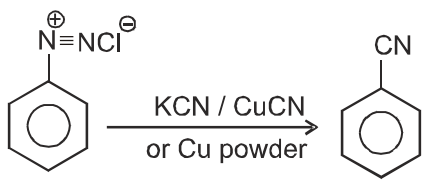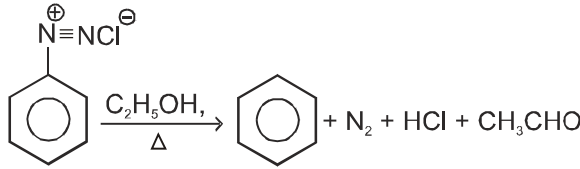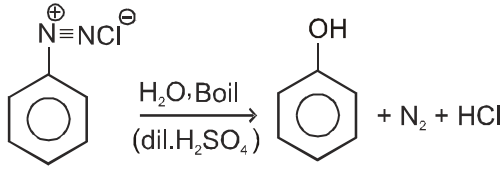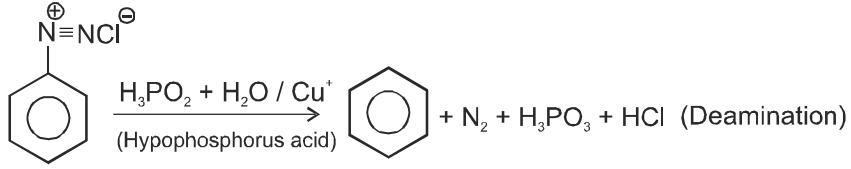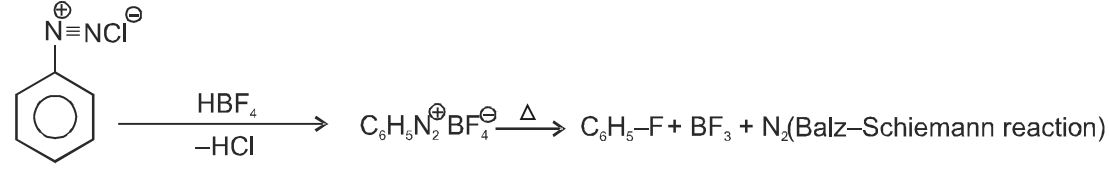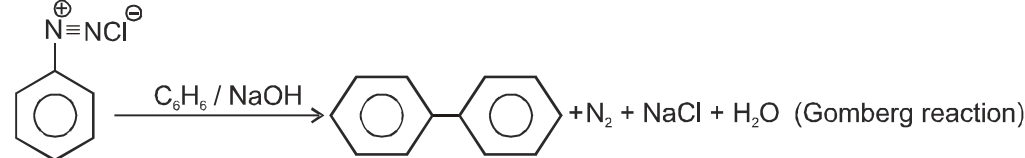
6.3.4   Hinseberg reaction :
It is used to distinguish between primary, secondary and tertiary amines.

Hinsberg reagent ($C_6H_5SO_2Cl$) :

1° Amine % $R-NH_2 + PhSO_2Cl \xrightarrow{\text{Pyridine}} R-NH-SO_2-Ph \xrightarrow{\text{Base}}$ Compund is **soluble** in base.

2° Amine % $R_2NH + PhSO_2Cl \xrightarrow{\text{Pyridine}} R_2N-SO_2-Ph \xrightarrow{\text{Base}}$ Compund is **insoluble** in base.

3° Amine : $R_3N\ PhSO_2Cl \xrightarrow{\text{Pyridine}}$ No reaction.
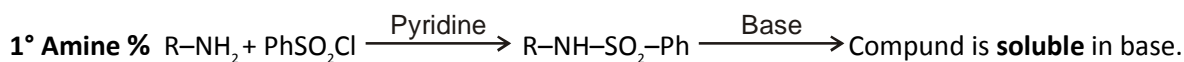
7. REACTION OF BENZENEDIAZONIUM SALT :
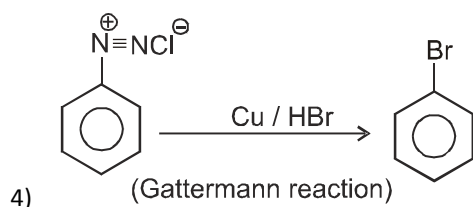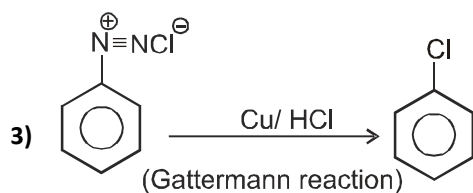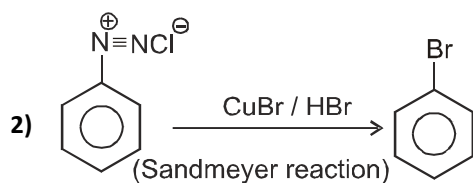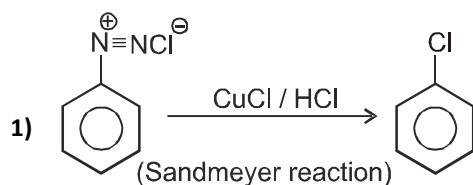
1)
(Sandmeyer reaction)

2)
(Sandmeyer reaction)

3)
(Gattermann reaction)

4)
(Gattermann reaction)

5) $\overset{\oplus}{N}\equiv N\overset{\ominus}{Cl}$ benzene $\xrightarrow{KI/\Delta}$ iodobenzene $+ N_2 + KCl$

6) $\overset{\oplus}{N}\equiv N\overset{\ominus}{Cl}$ benzene $\xrightarrow[\text{or Cu powder}]{KCN / CuCN}$ benzonitrile (CN)

7) $\overset{\oplus}{N}\equiv N\overset{\ominus}{Cl}$ benzene $\xrightarrow[\Delta]{C_2H_5OH,}$ benzene $+ N_2 + HCl + CH_3CHO$

8) $\overset{\oplus}{N}\equiv N\overset{\ominus}{Cl}$ benzene $\xrightarrow[(dil.H_2SO_4)]{H_2O, Boil}$ phenol (OH) $+ N_2 + HCl$

9) $\overset{\oplus}{N}\equiv N\overset{\ominus}{Cl}$ benzene $\xrightarrow[\text{(Hypophosphorus acid)}]{H_3PO_2 + H_2O / Cu^+}$ benzene $+ N_2 + H_3PO_3 + HCl$ (Deamination)

10) $\overset{\oplus}{N}\equiv N\overset{\ominus}{Cl}$ benzene $\xrightarrow[-HCl]{HBF_4}$ $C_6H_5\overset{\oplus}{N_2}\overset{\ominus}{BF_4} \xrightarrow{\Delta}$ $C_6H_5{-}F + BF_3 + N_2$ (Balz–Schiemann reaction)

11) $\overset{\oplus}{N}\equiv N\overset{\ominus}{Cl}$ benzene $\xrightarrow{C_6H_6 / NaOH}$ biphenyl $+ N_2 + NaCl + H_2O$ (Gomberg reaction)

Coupling reaction :

12)

p – Hydroxyazobenzene (Coupling Reaction)

13)

p–Aminoazobenzene
(yellow dye) (Coupling Reaction)
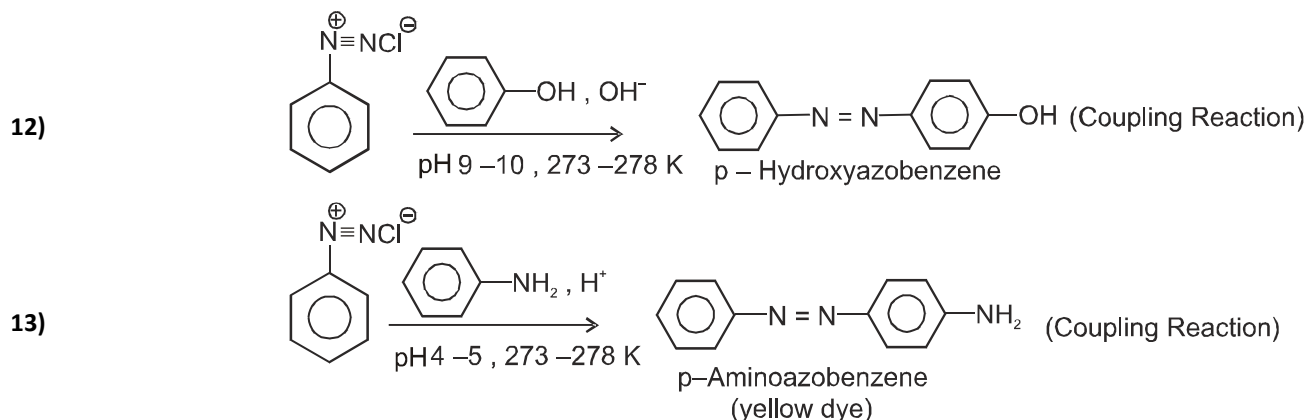
Electron withdrawing groups increases eletrophilicity of diazonium cation hence rate of coupling reaction also increases.

Indicator methyl orange is also prepared by this reaction.

14) $C_6H_5N_2Cl \xrightarrow{Sn/HCl} [C_6H_5NHNH_2]$

15) $C_6H_5\overset{\oplus}{N}\equiv \overset{\ominus}{N}Cl \xrightarrow{Zn/HCl} [C_6H_5NHNH_2] \xrightarrow{Zn/HCl} C_6H_5NH_2 + NH_3$

16) $C_6H_5\overset{+}{N_2}\overset{-}{Cl} \xrightarrow{C_6H_5-CH=CH-COOH} C_6H_5-CH=CH-C_6H_5 + N_2 + HCl + CO_2$
                                                                        Stilbene
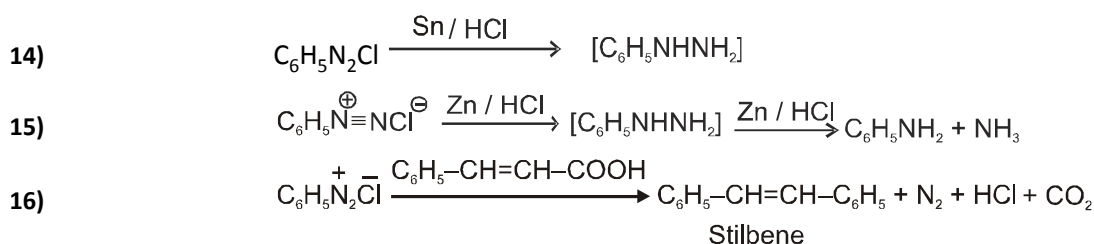
8. ALIPHATIC AMINES :

8.1. Introduction :

Amines are alkyl derivatives of ammonia having general formula $C_nH_{2n+3}N$. These are of three types depending upon no. of alkyl group present in ammonia.This can be represented as -
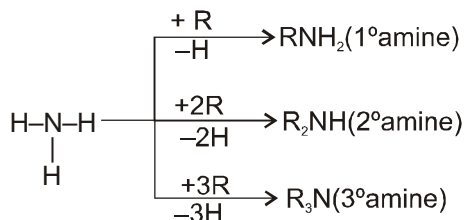
Note : (1) 2º and 3º amine show metamerism (having same functional group but different alkyl part attached to functional group).

(2) In case of alkyl amine N-atom is in sp^3 hybridised state as in ammonia because these are ammonia derivatives.

(3) If H-atoms of ammonia are replaced by aryl groups then these are said to be arylamines. N atom of aryl amines is sp^2 hybridised.

(4) In 2º and 3º amines if alkyl parts are different then N-atom is chiral but compound will be optically inactive due to rapid interconversion of their enantiomers. This amine inversion operates through sp^2 hybridized intermediate state.

(5) In cyclic 2º, 3º amines with N in cycle, the compound is optically active. because umbrella inversion is not possible.

8.2. Gabriel phthalimide synthesis of aliphatic primary amines :

It is used for preparation of 1º aliphatic amine and α-amino acid.
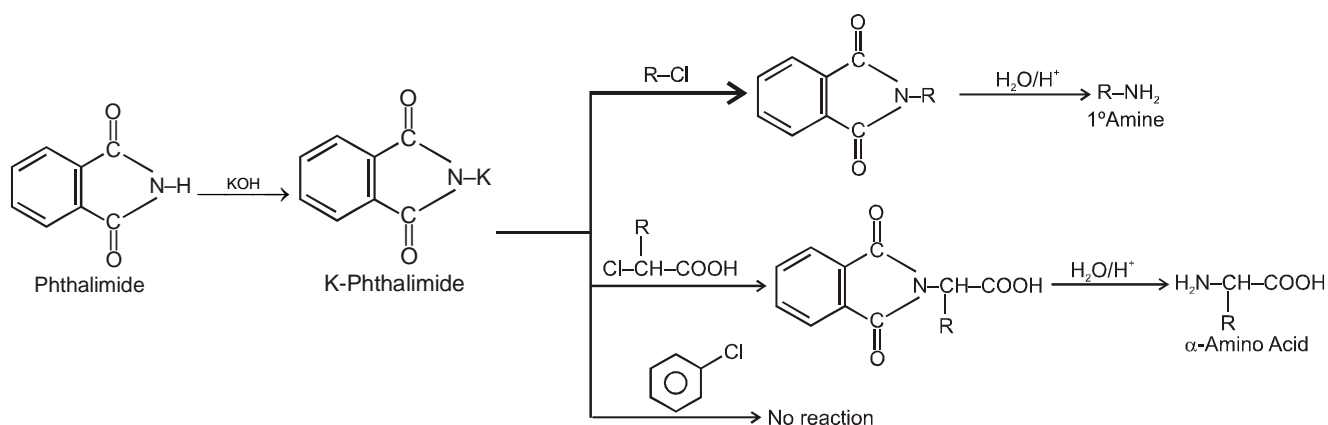

8.3. Physical Properties :

1) lower members are gases at ordinary temperature and have smell like ammonia. Higher members are liquid with fishy smell

2) lower members are water soluble because of hydrogen bonding but higher members are water insoluble.

3) On increasing the size of alkyl part in amine water solubility decreases due to increase in the hydrocarbon part.

4) Amines have higher boiling points than comparable molecular mass hydrocarbon due to H–bonding. This hydrogen bonding is weaker than H–bonding of alcohol.

9. NITROALKANE :
9.1. Preparation :

1. $RX + AgNO_2 \text{ (alc.)} \xrightarrow{\Delta} R-NO_2 + AgX$
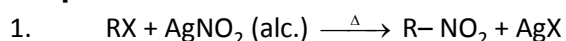
   During the reaction some quantity of alkylnitrite is also formed which is removed by fractional distillation as alkylnitrite have much lower boiling point than nitroalkane

2. Nitration of alkane

   $RH + HNO_3 \text{ (fuming)} \xrightarrow{400ºC} RNO_2 + H_2O$
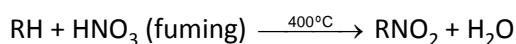
   This reaction takes place in vapour phase and results into mixture of nitro products due to cracking of hydrocarbon at high temperature.

9.2.   Properties :

Nitroalkanes are colourless pleasent smelling liquid having higher boiling point than isomeric alkylnitrite.

They are less soluble in water but readily soluble in organic solvent.

$R - CH_2 - NO_2$
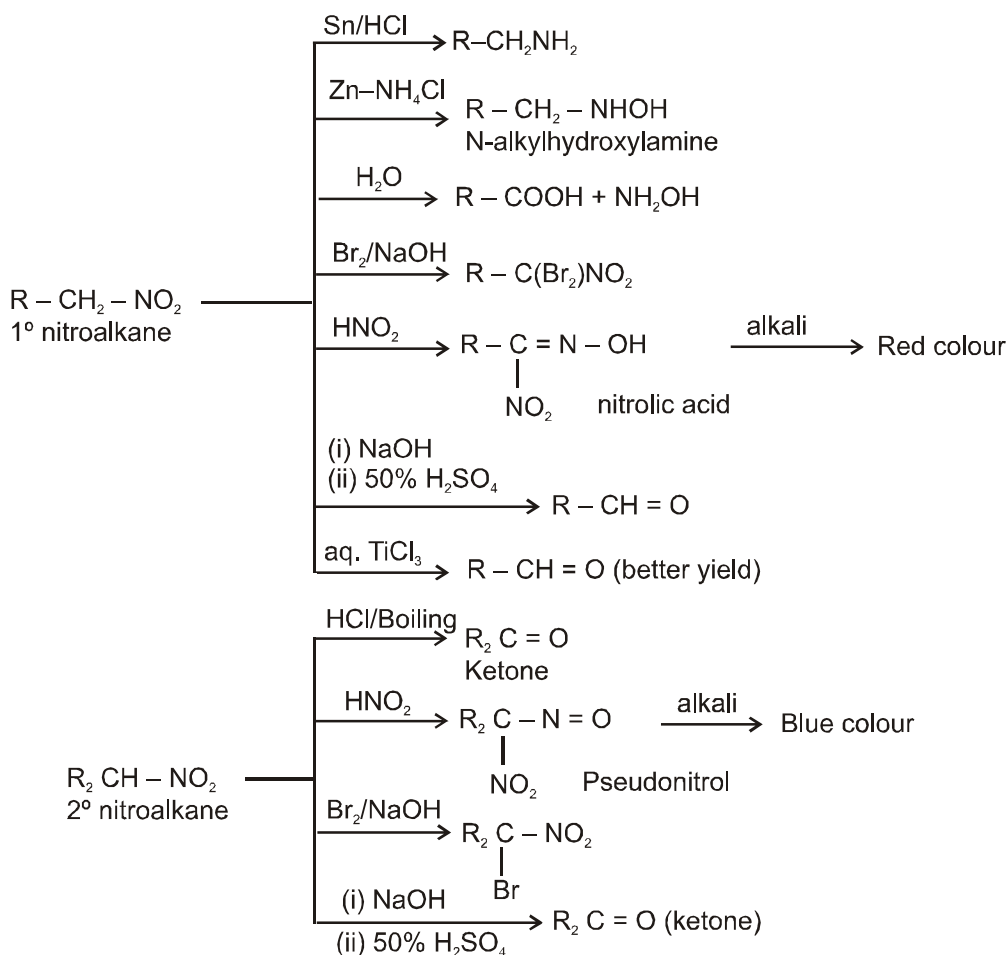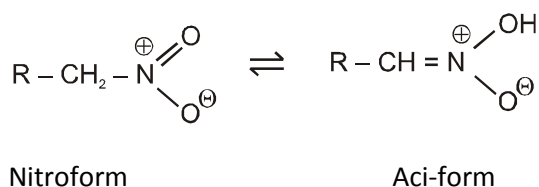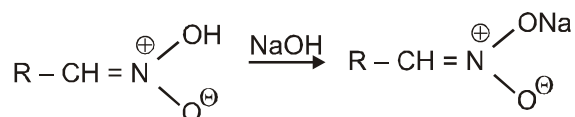1° nitroalkane

- $\xrightarrow{Sn/HCl}$ $R-CH_2NH_2$
- $\xrightarrow{Zn-NH_4Cl}$ $R - CH_2 - NHOH$
  N-alkylhydroxylamine
- $\xrightarrow{H_2O}$ $R - COOH + NH_2OH$
- $\xrightarrow{Br_2/NaOH}$ $R - C(Br_2)NO_2$
- $\xrightarrow{HNO_2}$ $R - C = N - OH$ $\overset{|}{NO_2}$ $\xrightarrow{alkali}$ Red colour
  nitrolic acid
- $\xrightarrow[(ii)\ 50\%\ H_2SO_4]{(i)\ NaOH}$ $R - CH = O$
- $\xrightarrow{aq.\ TiCl_3}$ $R - CH = O$ (better yield)

$R_2 CH - NO_2$
2° nitroalkane

- $\xrightarrow{HCl/Boiling}$ $R_2 C = O$
  Ketone
- $\xrightarrow{HNO_2}$ $R_2 C - N = O$ $\overset{|}{NO_2}$ $\xrightarrow{alkali}$ Blue colour
  Pseudonitrol
- $\xrightarrow{Br_2/NaOH}$ $R_2 C - NO_2$ $\overset{|}{Br}$
- $\xrightarrow[(ii)\ 50\%\ H_2SO_4]{(i)\ NaOH}$ $R_2 C = O$ (ketone)

Note : 1. The α-hydrogen atoms in aliphatic primary and secondary nitroalkanes becomes acidic due to electron withdrawing nature of nitro group. The acidic character can be explained on the basis of tautomerism

$$R - CH_2 - \overset{\oplus}{N}\overset{O}{\underset{O^{\ominus}}{}} \rightleftharpoons R - CH = \overset{\oplus}{N}\overset{OH}{\underset{O^{\ominus}}{}}$$

Nitroform   Aci-form

(they are Neutral to litmus, consequently are called pseudo acids)

The aci form is weak acid and can form salt with strong alkali.

$$R - CH = \overset{\oplus}{N}\overset{OH}{\underset{O^{\ominus}}{}} \xrightarrow{NaOH} R - CH = \overset{\oplus}{N}\overset{ONa}{\underset{O^{\ominus}}{}}$$

2. 3º nitroalkanes do not have α-hydrogen atom and therefore do not exhibit tautomerism

3. Nitroalkanes are used as solvent for polar substance such as cellulose acetate, synthetic rubber etc. and also used as explosives.
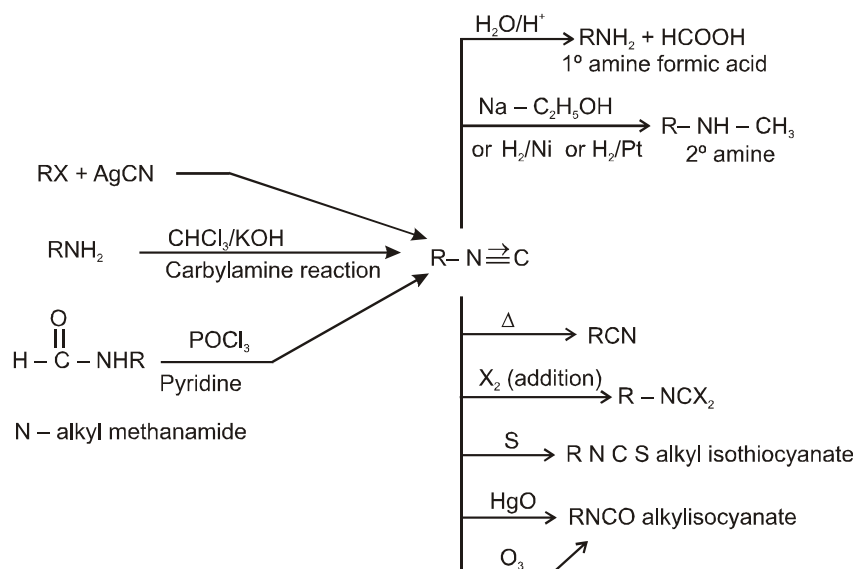
10. CYANIDES & ISOCYANIDES :

Flow chart for preparation and properties of Alkyl cyanides
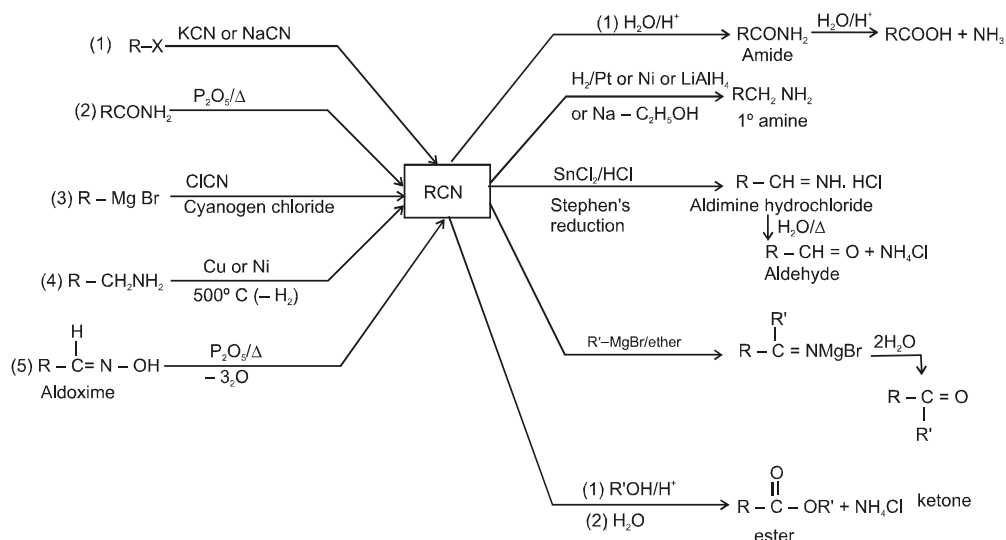
Note : 1. Alkyl cyanides are neutral and have odour like oil of bitter almond. It is soluble in organic solvent and water, also it is poisonous compound.

2. It is used in textile industry in manufacturing nitrile rubber and as a solvent in perfume industry.

3. Alkyl cyanide is hydrolysed by acid as well as alkali.

**Flow chart for the preparation and properties of alkyl isocyanides.**

Note :

1. Isocyanides are colourless, unpleasent water insoluble but soluble in organic solvent. These are more poisonous than isomeric cyanides.

2. In alkyl isocyanide ($R - \overset{+}{N} \equiv \overset{-}{C}$) carbon atom initially attracts electrophile (H^+) in acidic media but repel nucleophile (OH^- ion) hence it is hydrolysed only by acids not by alkalies.

3. Alkyl isocyanide gives addition reactions due to presence of unshared electron pairs on carbon atom $[R - \overset{+}{N} \equiv \overset{-}{C}]$
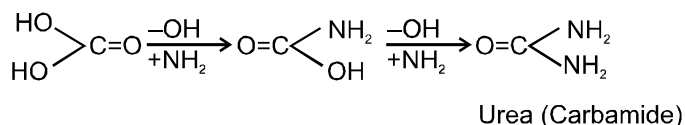
    both electrophile and nucleophile add to the same carbon.

4. Bhopal tragedy in December 1984 was caused by MIC (methylisocyanate) which is industrially prepared by the action of methylamine and phosgene -

    $$CH_3NH_2 + COCl_2 \xrightarrow[-HCl]{} [CH_3NHCOCl] \xrightarrow[-HCl]{\Delta} CH_3 - N = C = O \text{ methylisocyanate}$$
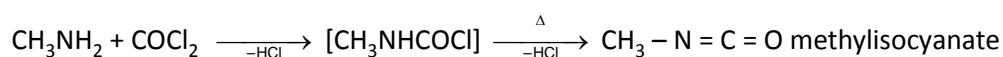
11. UREA :

It was the first organic compound synthesised by Wohler in lab by heating a mixture of ammonium sulphate and potassium cyanate. It is the decomposition product of protein's metabolism present in man and mammals that is excreted along with urine. Adult excrete 30g urea per day in urine. As it was first isolated from urine hence named as urea.
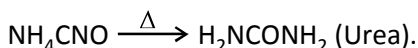
Urea is considered as diamide of carbonic acid (H_2CO_3) as –

$$\underset{HO}{\overset{HO}{{>}}}C=O \xrightarrow[+NH_2]{-OH} O=C\underset{OH}{\overset{NH_2}{{<}}} \xrightarrow[+NH_2]{-OH} O=C\underset{NH_2}{\overset{NH_2}{{<}}}$$

Urea (Carbamide)

11.1. Preparation :

1) **Lab method :** Ammonium cyanate obtained from potassium cyanate and ammonium sulphate on heating form urea.

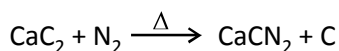 $$2KCNO + (NH_4)_2SO_4 \xrightarrow{\Delta} 2NH_4CNO + K_2SO_4$$
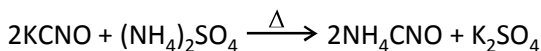
    Ammonium cyanate

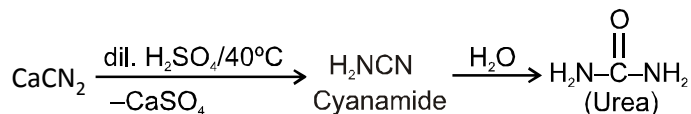 $$NH_4CNO \xrightarrow{\Delta} H_2NCONH_2 \text{ (Urea)}.$$

Note: Urea and ammonium cyanate are isomers.

**2)** By partial hydrolysis of calcium cyanamide which is obtained by passing N_2 over CaC_2 at 800ºC.

$$CaC_2 + N_2 \xrightarrow{\Delta} CaCN_2 + C$$

Calcium cyanamide

$$CaCN_2 \xrightarrow[-CaSO_4]{dil.\ H_2SO_4/40ºC} H_2NCN \xrightarrow{H_2O} H_2N\overset{\overset{O}{\|}}{-C}-NH_2$$

Cyanamide   (Urea)

Note: Cyanamide on hydrolysis in acidic media gives urea.

11.2. Physical properties :

Urea is colourless, odourless water soluble crystalline solid (mp = 132ºC). By resonating structure it is clear that both C-N bonds are of same bond length.
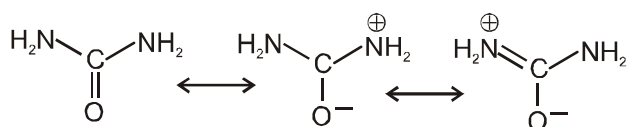

11.3. Chemical properties :

Aqueous solution of urea is neutral in nature but it behaves as a weak monoacidic base as it forms salt with strong acid.

Note: **1.** Urea is stronger base than ordinary amides due to resonance stabilization of cation.

(a) Urea melts at 132º which on gentle heating at slightly higher temperature, evolves ammonia and leaves a solid residue (Biuret)

$$H_2NCONH_2 + HNHCONH_2 \xrightarrow{\Delta} H_2N-CONHCONH_2 + NH_3$$
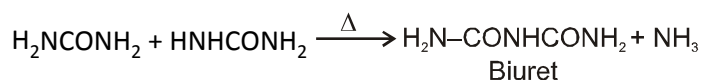
Biuret

Biuret is dissolved in water and make it alkaline by using few drops of NaOH. Then by adding $CuSO_4$ solution it give violet colour (Biuret test).

Biuret test is charasteristics of proteins (peptides) and all other compounds having –CONH– group.

(b) Urea on heating rapidly at 170ºC decomposes to NH_3 and cyanic acid.

2. Urea reacts with malonic ester and oxalic ester in the presence of sodium ethoxide or PCl_5 to give cyclic ureides.

Barbituric acid (Malonyl urea)

Aromatic Compounds
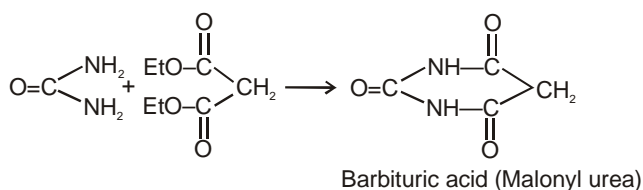
Note :

1. Urea is oxidised to N_2 when heated with excess of alkaline NaOCl or NaOBr.

2. Used as nitrogen fertilizer.

3. Used as stabilizer for nitrocellulose explosive.

4. Ureides are useful drugs e.g. Bromural.

5. Barbituric acid are used in medicine as hypnotic and sedative.