SOLUTIONS

Methods of expressing concentration

1. **Mass Percent** (w/w) mass% of component = $\frac{\text{mass of that component}}{\text{Total mass of solution}} \times 100$

   eg: 23% (w/w) of H_2SO_4 means 23g of H_2SO_4 (solute) in 100 g solution

2. **Volume percent** (v/v) volume% of component = $\frac{\text{volume of that component}}{\text{Total volume of solution}} \times 100$

   eg: 23% w/v H_2SO_4 means 23 ml H_2SO_4 in 100 ml solution

3. **Mass volume percent** (w/v) = $\frac{\text{mass of given component}}{\text{total volume of solution}} \times 100$

   eg: 23% w/v H_2SO_4 means 23g H_2SO_4 in 100 ml solution

4. **Mole fraction** (X_i) = $\frac{\text{moles of given component}}{\text{Total moles}}$ | In binary solution with 2 components A & B $x_A = \frac{n_A}{n_A+n_B}$, $x_B = \frac{n_B}{n_A+n_B}$ ★ $\boxed{x_A + x_B = 1}$

5. **Molarity (M)** : number of moles of solute per litre of solution

   $M = \frac{n_B}{V}$ 'M' is an intensive quantity and changes with change in temprature

   M can also be calculated if % by mass is given as

   $M = \frac{10xd}{M_B}$ where x = % by mass, M_B = Molar mass of solute, d = density of solution in g/ml

   For every dilution problem

   $\boxed{M_{conc} V_{conc} = M_{dil} . V_{dil}}$ ★

6. **Molarity (m)** → number of moles of solute per kilogram of solvent

   $m = \frac{n_B}{w_A} \times 1000$ molality is intensive quality and is independent of temprature.

   M & m are related to each other by equation $\boxed{\frac{d}{M} = \frac{1}{m} + \frac{M_B}{1000}}$ ★

7. **Parts per million** (ppm)

   ppm = $\frac{\text{no. of parts of the component}}{\text{total no. of parts of all components of the solution}} \times 10^6$ = (% w/w) $\times 10^4$

Solid in Liquid type solution

- Solubility of solid increases with ↑ in temprature & is unaffected by changing pressure.
- Free energy change is given by

  $\boxed{\Delta G_{soln} = \Delta H_{soln} - T\Delta S_{solution}}$

- Change in entropy is +ve

Gas in Liquid type sol^n

- Solubility is affected by change in temprature and pressure
- Henry's Law

  $\boxed{P_i = K_H x_i}$ ★

  P_i = partial pressure of the gas

  x_i = mole fraction of gas

  K_H = Henry's law constant

  K_H depends on the nature of gas

  $K_H \propto \frac{1}{x_i} \propto$ Solubility of gas

  $x_i = \frac{n_i}{n_i + n_{H_2O}} = \frac{n_i}{n_{H_2O}} = \frac{m \times MW_{H_2O}}{1000}$

- Solubility of gas ∝ pressure ∝ 1/temprature ★
- Dissolution of gas is exothermic

Liquid in liquid type sol^n

- Vapour pressure ∝ temprature
- Raoult's Law - partial V.P of component ∝ mole fraction of component

  $P_i = P_i^\circ x_i$

  V.P of pure component

  $P_A = P_A^\circ x_A = P_A^\circ (1 - x_B)$

  $P_{total} = P_A + P_B$

  $= P_A^\circ (1 - x_B) + P_B^\circ x_B$

- In vapour phase, the component obey Dalton's Law

  $\frac{P_i}{P_T} = y_i$ → mole fraction in vapour phase

Colligative Properties

1. Relative lowering of V.P (RLVP)

$\frac{p^\circ - p}{p^\circ} = \chi_B$

p° → v.P of pure component

$M_B = \frac{W_B M_A}{W_A (RLVP)}$

$m = \frac{1000 (RLVP)}{M_A}$

2. Elevation in boiling pt.

$\Delta T_b = k_b m$

k_b: mole elevation const

$M_B = \frac{k_b W_B 1000}{(\Delta T_b) W_A}$

molar mass of solute

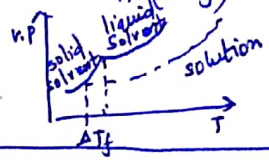
$m = \frac{\Delta T_b}{k_b}$ (molality of solution)

3. Depression in freezing pt

$\Delta T_f = k_f m$

$m = \Delta T_f / k_f$

$M_B = \frac{k_f W_B 1000}{W_A (\Delta T_f)}$



4. Osmotic Pressure (π)

$\pi = MRT$

$M_B = \frac{W_B RT}{\pi V}$

Electrolytic Solutions

Van't Hoff factor (i)

$i = \frac{\text{observed C.P}}{\text{calculated C.P}} = \frac{\text{normal molar mass}}{\text{abnormal molar mass}} = \frac{\text{Total no. of particles after diss}/\text{association}}{\text{Total no. of particles before diss}/\text{association}}$

$\alpha = \frac{1-i}{1-n}$ for dissociation

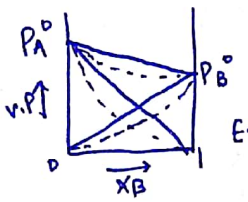
$\alpha = \frac{1-i}{1-1/n}$ for association

Modified –

$RLVP = i\chi_B$ $\quad \Delta T_f = i k_f m$

$\Delta T_b = i k_b m$ $\quad \pi = iCRT$

Non ideal with negative deviation



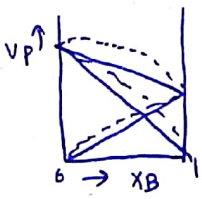
$p_i < p_i^\circ x_i$

A–B >> A–A or B–B

Ex: $CH_3OCH_3 + CHCl_3$

$CH_3COCH_3 + CHCl_3$

+ve deviation



$p_i > p_i^\circ x_i$

A–B << A–A or B–B

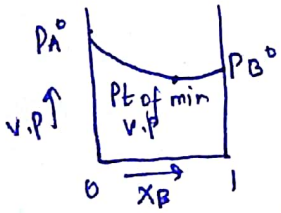
Ex: $C_2H_5OH + CH_3COCH_3$

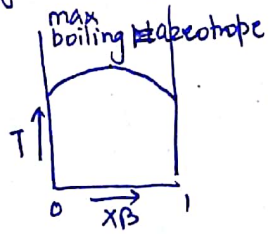
$H_2O + C_2H_5OH$

Azeotropes

↳ Negative deviation from Raoult's law

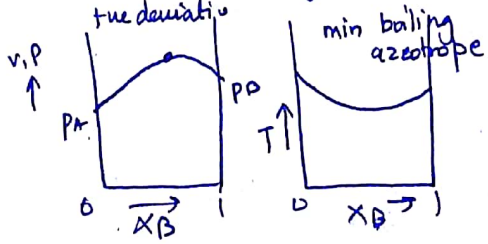
↳ Maximum boiling azeotropes



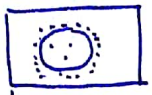


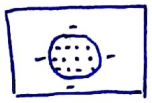
↳ Positive deviation from Raoult law

↳ Minimum boiling azeotropes



Surface Chemistry


adsorption

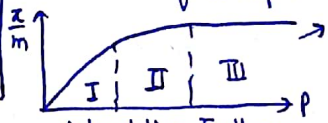

absorption


-ve adsorption

Physical Adsorption	Chemical Adsorp.
• Weak vander waal's forces present	• Strong chemical bonds
• enthalphy is low	• enthalphy is high
• Reversible	• Irreversible
• Multilayer adsorption	• Monolayer adsorption
• Non specific	• Specific - only some gases capable

Factors affecting rate of adsorption

1. Nature of solid
2. Nature of gas
3. Effect of pressure on extent of adsorption



Adsorption Isotherm

Region I : $\frac{x}{m} = kp$

Region III : $\frac{x}{m} = kp^0$ or $\frac{x}{m} = k$

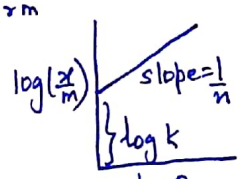
Region II : $\frac{x}{m} = kp^{1/n}$

↳ Freundlich adsorption theorem

$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log p$ at $p = 1$ atm

4. Effect of temp

Adsorption Isobar for physisorption



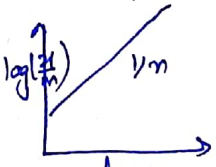
Adsorption Isobar for chemisorption

Adsorption in solutions

$x/m = k c^{1/n}$

$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log c$

x : amt of adsorbate
m : amt of adsorbent
c : conc of solutia



Solution

- < 1nm — Colloids — size 1 to 1000nm
- Suspension — > 1000 nm
- Precipitate — > 1000 nm

• The medium in which colloidal particles are suspended / dispersed / distributed is called Dispersion Medium. (D.M)

• Colloid particle themselves are called Dispersed phase (D.P)

Lyophyllic	Lyophobhic
- easier to prepare	- difficult
- stable & unaffected by impurity	- unstable but require some stablising agent (Ex: soap & detergent stablises oil-H_2O mixture)
- reversible	- irreversible
- starch solution	- blood, ferric hydroxide

Classification of Colloids -

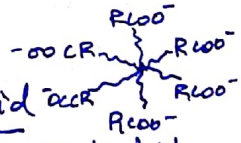
D.P	solid	solid	solid	liquid	liquid	liquid	gas	gas
D.M	solid	Liquid	gas	solid	Liquid	gas	solid	liquid
	Alloys	Charcoal in H_2O conc NaCl soln	smoke	water in silica gel	milk	fog mist	H_2/pt	soap bubbles in H_2O

On basis of single / aggregate

1. Multimolecular colloid
   individual size < 1nm
   aggregate size 1-1000
   Ex: Amm pretal & non metal soln, Au soln, Sulphur soln

2. Macromolecular
   One single large sized molecule is present.
   Ex: Polymer

3. Associated Colloid



↳ Kraft temp : the temp at which they are formed

↳ Critical micelles concentration

Ex: soap & detergents

Preparation of Colloid

A) **Lyophilic solution** → easy to prepare, mix the dispersed phase with the dispersion medium with constant stirring in order to prevent coagulation.

B) **Lyophobic solution** → difficult to prepare, various methods.

1. **Condensation**: [true solution is converted to colloid by increasing size of particle]

   - **Oxidation**
     - Hydrolysis to prepare $Fe(OH)_3$ sol.
       $FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$ (wine red color)
     - Reduction to prepare metal solution
       $2AuCl_3 + 3SnCl_2 \rightarrow 2Au + 3SnCl_4$ (gold solution)
   - **Double displacement reaction**
     $As_2O_3 + 3H_2S \rightarrow As_2S_3 + 3H_2O$ (yellow)

2. **Dispersion**: we reduce size of particle to the range of $1-10^3$ nm

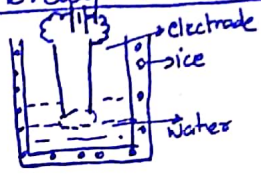
   2.1 **Peptisation**: to convert precipitate into particles of colloidal size

   $FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$ (reddish brown ppt)

   This precipitate adsorbs Fe^{+3} ions on the surface. Like charges repel each other & ppt becomes unstable and breaks down into colloid size particles

   Here Fe^{+3} → peptising agent (the substance which helps in breaking ppt)

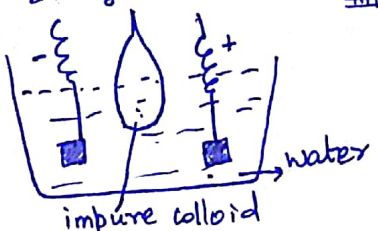
   2.2 **Bredig's Arc Method**: metal solution preperation like Au, Ag, Pt, Tungsten

   produces spark → disintegrated metal into small particle
   due to ice ← which evaporate
   they condense into ~~small particles~~ the medium ~~which evaporate~~ to give soln

Purification of Colloid

most impurities are electrolytic in nature → **Dialysis**



we take a semipermeable bag. When suspended in water, impurities pass out when electric field is used dialysis speeds up.

impurities have a size less than 1nm → **Ultrafilteration** → ultrafilter

↳ Coagulation power increases with increase in temprature.

↳ The min amount of electrolyte reqd to start coagulation is called **coagulation value**.

Ex: Blood, delta formation, Cottrel Precipitator (notes)

↳ **Gold Number**: min amount of protective colloid required to prevent coagulation of 10ml of red gold sol on addition of 1ml of 1% NaCl solution. Protective power of gold number are inversely related.

Properties of Colloid

1. **Brownian Movement**
2. **Electrical properties**

   The movt of colloid particles is called electrophoresis or cataphoresis

   eg: $AgNO_3 + KI \rightarrow AgI + KNO_3$ (yellow)

3. **Coagulation**: means precipitation of colloidal particles

   ↓

   ★Hardy-Schulze's rule: Ion carrying charge opposite to that of sol is more effective in coagulation

4. **Optical Properties** → Tyndal effect

   - size of particle should be comparable with wavelength of light used.
   - the difference in refractive indices of the DM & DP should be large.

Emulsions: a) oil in water type eg: milk, vanishing cream

b) Water in oil type eg: moisturising cream, cold cream

Catalysis

1. **Homogeneous Catalysis**

(i) $CH_3COOH_{(l)} + C_2H_5OH_{(l)} \xrightarrow{H^+} CH_3COOC_2H_5(l) + H_2O(l)$

(ii) $2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$ // Lead Chamber process

2. **Heterogeneous Catalysis** : diff physical states

$3H_2(g) + N_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$ (Habers process)

$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5(s)} 2SO_3(g)$ (Contact Process)

$C_2H_4(g) + H_2(g) \xrightarrow{Ni(s)} C_2H_6(g)$

Selectivity of a Catalyst

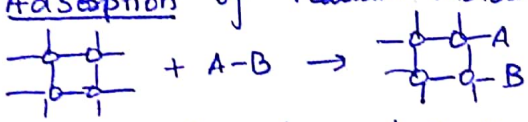
$CO + H_2$ —(ZnO + Cr_2O_3)→ CH_3OH

$CO + H_2$ —(Cu/Ag)→ HCHO

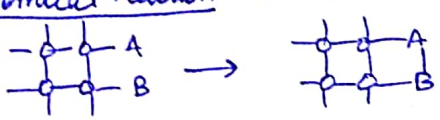
Mechanism of Heterogeneous Catalysis

a) **Diffusion** of reactant molecule into catalyst surface

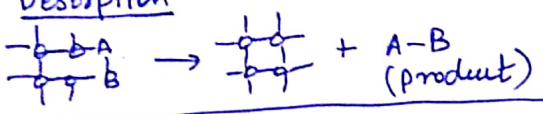
b) **Adsorption** of reactant molecule



c) **Chemical reaction** b/w reactant to form product



d) **Desorption**



Shape Selective Catalyst

Zeolite → 3 dimensional sodium aluminium silicates

C_6H_{14} (n-hexane) —(ZSM-5 Catalyst cracking)→ C_4H_{10} (butane) + C_2H_4 (ethene)

ZSM-5 → converts alchohol directly into gasoline

Promoters: $N_{2(g)} + 3H_2(g) \xrightarrow{Fe(s)|Mo(s)} 2NH_3(g)$

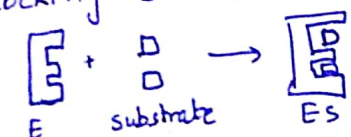
Inhibitors : when added reduces the activity of catalyst.

Poisons : Heavy metal ions like Ag^+ or Hg^{+2} Completely destroy activity of catalyst.

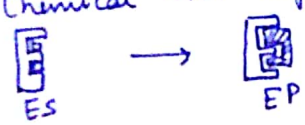
In Habers process if CO is present as an impurity, acts as a poison.

Mechanism of Enzyme Catalysis

1. Locking substrate into active sites



2. Chemical rxn regulate formⁿ of product



3. Unlocking

Enzyme Catalysis

- Enzymes are biological catalysts
- They are protein in nature
- Very specific in nature. Every rxn has its own enzyme.

$C_{12}H_{22}O_{11} + H_2O \xrightarrow{Invertase}$ $C_6H_{12}O_6 + C_6H_{12}O_6$

cane sugar — glucose + fructose

- Are active at body temprature (37°C) and pH of 5 to 7

$C_6H_{12}O_6 \xrightarrow{Zymase} 2C_2H_5OH + 2CO_2$

glucose

NOMENCLATURE (नाम-करण) :P

I) HALOALKANES $C_nH_{2n+1}X$

- In haloalkanes, each C atom is sp^3 hybridised
- If halogen is bonded directly to sp^2 carbon, then the class of compound is called vinylic halide. $-\overset{|}{C}=\overset{|}{C}-X$ eg: $CH_2=CH-Cl$ vinyl chloride *
- If the β carbon is sp^2 hybridised, then the class of compound is called allylic halide $-\underset{|}{C}=\overset{|}{C}-\underset{|}{C}-X$ eg: $CH_2=CH-CH_2Cl$ allyl chloride *

i) $CH_3-CH_2-CH_2-Cl$

n-propyl chloride (common)

1-chloro propane

ii) $CH_3-\underset{CH_3}{CH}-CH_2-Br$

Isobutyl bromide (common)

1-Bromo-2-methyl propane

iii) $CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{C}}}-Br$

test-butly bromide (common)

2-Bromo-2-methyl propane

iv) $CH_3-CH_2-\underset{CH_3}{CH}-Br$

sec-butyl bromide (common)

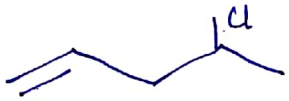
2-Bromobutane

v) $CH_2=CH-CH_2-Cl$

Allyl chloride (common)

3-chloroprop-1-ene

vi)

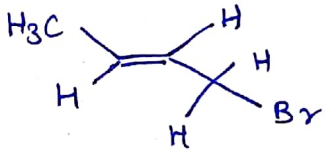


4-Chloropent-1-ene

vii)

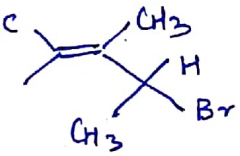
1-chloro-4ethylcyclohexane

viii)



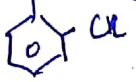
1-Bromobut-2-ene

ix)



4-Bromo-3-methylpent-2-ene

x) $I-CH_2-CH-(CH_2)_5-CH_3$



2-(2'-chlorphenyl)-1-iodooctane

xi) $CH_3CH=CH\,C-(CH_3)_2$

Br

4Bromo-4-methylpent-2-ene

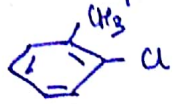
* xii) $(CH_3)_2\,CHCH\,(Cl)CH_3$

2-Chloro-3-methyl butane

II) HALOARENES

In haloarenes, the hydrogen atom is directly attached to an aromatic ring carbon. eg:  ,  also called aryl hallides

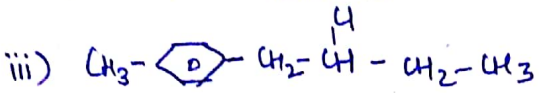
In nomenclature, the halogen comes as a prefix called 'halo' to the parent compound. Some examples are given below:

i) 

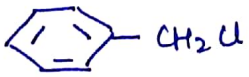
1-Chloro-2methyl benzene
o-chlorotoulene (common)

ii) 

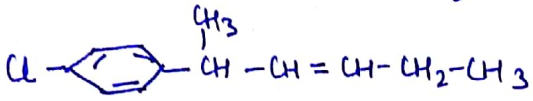
1-Bromo-2, 4dinitrobenzene

iii) 

2-chloro-1-(4'methylphenyl) butane

iv) 

Chlorophenylmethane
Benzyl chloride (common)

v) 

2-(4'-chlorophenyl)hex-3-ene

AMINES

Common name : alkyl amine
IUPAC : replace -e of the parent compound by amine

A) Primary 1° Amines $R-NH_2$

$CH_3CH_2CH_2NH_2$
n-propyl amine
(Propanamine)

$CH_3CH_2CH(Br)-NH_2$
sec-butyl amine
(Butan-2-amine)

$CH_3-C(CH_3)_2-NH_2$
t-butyl amine
(2-methyl propan-2-amine)

B) Secondary 2° Amine

Common name : dialkylamine
IUPAC : N-alkylalkanamine

$CH_3CH_2NHCH_2CH_3$
Diethylamine
(N-ethyl ethanamine)

$CH_3NHCH(CH_3)_2$
Isopropyl methylamine
N-methyl propan-2-amine

$CH_3CH_2-CH_2-NH-CH_3$
Methyl propylamine
(N-methyl propanamine)

$CH_3-C(CH_3)_2-NH-C_2H_5$
Ethyl t-butyl amine
(N-ethyl-2-methyl propan-2-amine)

C) Tertiary 3° Amine

$CH_3-N(CH_3)-CH_3$
Tri-methyl amine
(N,N-Dimethyl methanamine)

$C_2H_5-N(C_2H_5)-(CH_2)_3-CH_3$
N,N-Diethyl butylamine
(N,N-Diethyl butylamine)

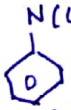
$(CH_3CH_2)_2NCH_3$
N,N-diethyl methylamine
(N-ethyl-N-methyl ethanamine)

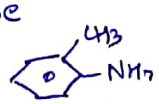
* In case, more than one NH_2 group present then letter E of the parent H-carbon HC is retained and NH_2 then comes as suffix amine

eg: $H_2N-CH_2-CH_2-NH_2$ ethane-1,2-diamine

d) Aryl Amines


aniline
(benzenamine)


N,N-Dimethylaniline
(N,N-Dimethylbenzenamine)


o-toluidine
(2-amino-toulene)


p-bromoaniline
(4-Bromobenzenamine)

More eg:

$CH_2=CH-CH_2-NH_2$
Prop-2-en-1-amine

$CH_3-CH(NH_2)-CH(CH_3)-OH$ (3-aminobutan-2ol)

e) Quaternary Ammonium Salts ($R_4N^+X^-$)

$(CH_3)_4N^+Br^-$
Tetramethyl ammonium bromide

$(CH_3CH_2)_3N^+(C_6H_5)Cl^-$
Triethylphenyl ammonium chloride

ALCHOHOLS

1) monohydric alchohol $C_nH_{2n}O$ eg: CH_3CH_2OH ethyl alchohol

2) Dihydric alchohol eg: $CH_2(OH)-CH_2(OH)$ ethylene glycol

$CH_2(OH)-CH(OH)-CH_2(OH)$ Glycerol ← Trihydric Alchohol

Examples

i) $CH_3CH_2CH_2CH_2OH$
n-butyl alchohol
(Butanol)

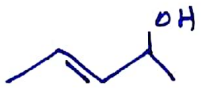
ii) $CH_3-CH(OH)-CH_3$
isopropyl alchohol
(propan-2-ol)

iii) $CH_3-CH_2-CH(OH)-CH_3$
sec-butyl-alchohol
(butan-2-ol)

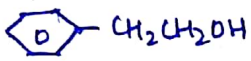
iv) $CH_3-CH(CH_3)-CH_2OH$
isobutylalchohol

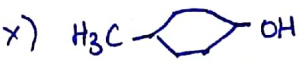
v) $CH_3-C(CH_3)_2-OH$
tert butyl alchohol
(2-methyl propan-2-ol)

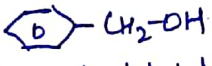
vi) $CH_3-C(CH_3)_2-CH_2OH$
neopentylalchohol
(2,2-dimethyl propanol)

(vii) 
pent-3-en-2ol

(viii) $(CH_3)_2-CH(OH)-CH(Cl)-CH_3$
1-chloro-3methylbutan 2-ol

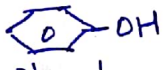
ix) 
2 phenyl ethanol

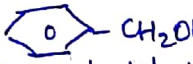
x) 
4-methyl cyclohexanol

xi) 
benzyl alchohol (common)
phenyl methanol

(xii) 
6-methyl hept-4-en2ol

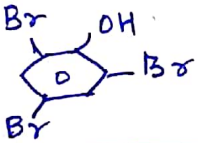
PHENOLS


Phenol

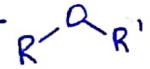

Benzyl alchohol (common)
Phenyl methanol (IUPAC)


p-cresol
4-methyl phenol (IUPAC)


2,4-dinitrophenol


2,4,6 tri bromophenol

ETHERS



if R = R' common name : dialkyl ether
if R ≠ R' arrange R group alphabetically, then write a suffix ether
↳ in IUPAC alkoxy comes as a suffix to parent alkane

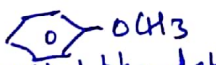
CH_3-O-CH_3
dimethyl ether
(methoxymethane)

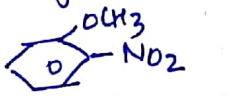
$(CH_3CH_2)_2O$
diethyl ether
(ethoxy ethane)

$CH_3OCH_2CH_2CH_3$
methyl propyl ether
(methoxy propane)

$CH_3CH_2-O-CH(CH_3)-CH_3$
ethyl isopropyl ether
(2 ethoxy propane)

$CH_3OC(CH_3)_3$
methyl t-butyl ether


methyl phenyl ether
(anisole)
Methoxybenzene (IUPAC)


o-nitroanisole
(1-methoxy 2nitro benzene)

$CH_3-O-CH_2-CH_2OCH_3$
1,2-dimethoxy ethane

$CH_3OCH(CH_3)-CH_2-CH(OH)-CH_3$
4 methoxypentan-2-ol

Preparation of Alchohols

A) From RX using aq alkali / aq KOH, aq NaOH or aq Na_2CO_3 or moist Ag_2O

$$RX + \underset{(aq)}{OH^-} \rightarrow ROH + X^-$$

eg: $CH_3CH_2CH_2Cl \xrightarrow{aq\ KOH} CH_3CH_2CH_2OH$

Q) $(CH_3)_2CHCH=CH_2 \xrightarrow{A} (CH_3)_2CHCH_2Br \xrightarrow{aq\ NaOH} B$

A → HBr/org peroxide B → $(CH_3)_2CHCH_2CH_2OH$

B) From alkene (Hydration of alkenes)

1) Acid catalysed hydration using H_2O/H_2SO_4

$$CH_3CH=CH_2 \xrightarrow{H^+} \underset{\text{Markovnikov's rule}}{CH_3-\overset{+}{C}H-CH_3} \xrightarrow[-H^+]{H_2O} CH_3-\underset{OH}{CH}-CH_3$$

Markovnikov's rule but rearrangement of R^+ can take place

eg: $CH_3-\underset{CH_3}{CH}-CH=CH_2 \xrightarrow{H^+} CH_3-\underset{CH_3}{\overset{H}{C}}-\overset{+}{C}H-CH_3 \xrightarrow[\text{shift}]{H} CH_3-\underset{CH_3}{\overset{+}{C}}-CH_2CH_3 \xrightarrow[-H^+]{H_2O} (CH_3)_2\overset{OH}{C}CH_2CH_3$

(2°) (3°)

2) Hydroboration using B_2H_6/H_2O_2 OH^-

$$CH_3CH=CH_2 \xrightarrow[ii)\ H_2O_2/OH^-]{i)\ B_2H_6} CH_3CH_2CH_2OH$$

Mechanism $CH_3CH=CH_2 + \overset{\delta-}{H}-\overset{\delta+}{B}H_2 \rightarrow CH_3CH_2CH_2BH_2 \xrightarrow{CH_3CH=CH_2} (CH_3CH_2CH_2)_2BH$

$$H_3BO_3 + 3CH_3CH_2CH_2OH \xleftarrow[OH^-]{H_2O_2} \underset{\text{Trialkyl borane}}{\underset{CH_3CH_2CH_2}{\overset{CH_3CH_2CH_2}{CH_3CH_2CH_2}}B} \xleftarrow{CH_3CH=CH_2}$$

3) Reduction (gain of H or loss of O) only to prepare 1° or 2° alchohol

$$R/H-\overset{O}{\overset{\|}{C}}-H/R \xrightarrow[\text{or } NaBH_4]{LiAlH_4} R/H-\underset{OH}{CH}-H/R$$

ald or ketone (1° or 2°)

$R-CHO \xrightarrow{LiAlH_4} R-CH_2-OH$ aldehyde gives 1° alchohol

$R-COR' \xrightarrow{LiAlH_4} R-\underset{OH}{CH}-R'$ ketone gives 2° alchohol.

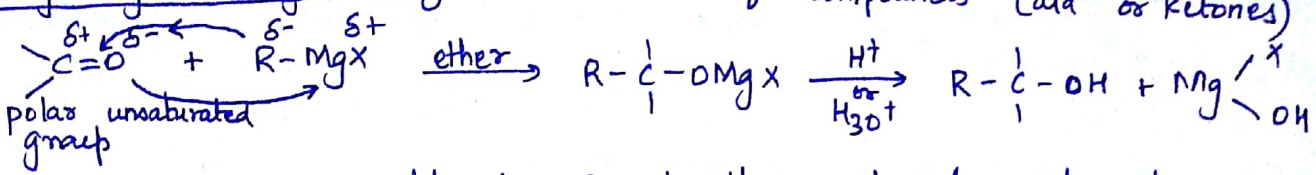
or $R-COOH$, $R-COCl$ $\xrightarrow{LiAlH_4} R-CH_2OH$ (1°)

Note: $LiAlH_4$ is a supplier of H^-

Q) $CH_3CH_2COCH_3 \xrightarrow{LiAlH_4} A \xrightarrow{SOCl_2} B \xrightarrow{Mg/ether} C$

A → $CH_3CH_2-\underset{OH}{CH}-CH_3$ B → $CH_3CH_2-\underset{Cl}{CH}-CH_3$ C → $CH_3CH_2\underset{MgCl}{CH}-CH_3$

D) Using Grignard Reagent (RMgX) with carbonyl compounds (ald or ketones)



R group of RMgX adds to C of the carbonyl group and O of carbonyl group changes to finally OH

$HCHO + RMgX \xrightarrow[ii)\ H_3O^+]{i)\ ether} R-CH_2-OH$ 1°

$R-CHO + R'MgX \longrightarrow R-CH(OH)-R'$ 2°

any ald. any G.R

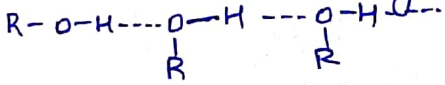
$R-CO-R' + R''MgX \xrightarrow[ii)\ H_3O^+]{i)\ ether} R-C(OH)(R')-R''$ 3°

any ketone

E) Oxo Process : is a method to increase number of C atom

$CH_2=CH_2 + H_2 + CO \xrightarrow{Co_2(CO)_8} CH_3CH_2CHO \xrightarrow[or\ LiAlH_4]{H_2/Ni} CH_3CH_2CH_2OH$

Properties of Alchohol (i) Boiling points ROH have higher b.p than RX because of OH group present, ROH are associated via intermolecular H bonding.



B.P of ~~alchols~~ alcohols increases down homogeneous series

MW ↑
SA
VWF

Hence bp increases

For the same alchohol, as branching ↑, surface area ↓, VW forces ↓, BP ↓

$CH_3-C(OH)(CH_3)-CH_3$ is of lower bp than $CH_3CH_2CH_2CH_2OH$

For the same number of C atom as the number of OH group ↑, extent of H bonding ↑, bp increases.

CH_3-CH_2 (OH, OH) has higher bp than CH_3CH_2OH

Q. Arrange in order of ↑ bp

CH_3CH_2Cl (1)

$CH_3CH(CH_3)OH$ (2)

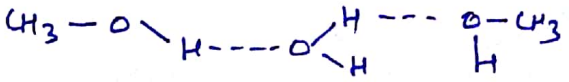
$CH_3-CH(OH)-CH_2OH$ (3)

CH_3CH_2OH (4)

Ans (1) < (4) < (2) < (3)

---

2) **Solubility** : Lower alchohols are completely miscible in water, due to their ability to form H-bonds with H_2O. CH_3OH & CH_3CH_2OH are completely miscible in H_2O.



- As size of R group ↑, solubility ↓
- As branching ↑, surface area ↓, solubility in H_2O ↑
  ↳ ∵ R group becomes more compact with branching and easier to dissolve as OH group becomes more exposed to form H bond.

∴ t-butanol is more miscible while n-butanol is immisible.

3) **Acidic Strength of Alchohols**

Alchohols are derivatives of water 

↳ Alchohols are weaker acids than water bcz R group is EDG, increases the e^- density around H atom. It becomes difficult to remove H as H^+ ion. Hence, alchohols are weaker acid & are insoluble in NaOH.

$$\text{Acidic strength} \propto \frac{1}{\text{E density around H}} \propto ka \propto \frac{1}{pka} \qquad pka = -\log ka$$

↑ acidic strength $3^\circ < 2^\circ < 1^\circ$

Reason: As number of R grp of α-Carbon ↑, the e^- density around H increases. ∴ difficult to remove H as H^+

↑ O-H bond strength order is

1° R-O-H < 2° R-O-H < 3° R-O-H

↑ C-O bond strength order is

3° R-OH < 2° R-OH < 1° R-OH

Chemical Reactions of Alchohols.

A) Reaction involving cleavage of O-H bond

Reactivity order of alcohol is $3^\circ < 2^\circ < 1^\circ$

1) with reactive metals (Na or K), liberate H_2 gas

$$ROH + Na \longrightarrow RO^-Na^+ + \tfrac{1}{2} H_2$$

Q) $CH_3CH_2OH \xrightarrow{Na} A \xrightarrow{CH_3CH_2I} B$ A : $CH_3CH_2O^-Na^+$ (Sodium ethoxide) B : $CH_3CH_2OCH_2CH_3$ (diethyl ether)

2) With RMgX (only given by 1° alchohol)

$$R-O-H + R'MgX \longrightarrow R'H + ROMgX$$

Ex: $CH_3CH_2OH + CH_3MgBr \longrightarrow CH_4 + CH_3CH_2OMgBr$

ily

3) with acetic anhydride (replacement of H of O-H by CH_3CO group is called acetylation)

$$R-O-H + (CH_3CO)_2O \longrightarrow R-O-C(=O)-CH_3 + CH_3COOH$$

ester

(acetic anhydride)

B) Reactions involving cleavage of C-O bond ($1^\circ < 2^\circ < 3^\circ$ alcohol)

$R-OH \xrightarrow{PCl_5} RCl + POCl_3 + HCl$

$\xrightarrow[Pyridine]{SOCl_2} RCl + SO_2 + HCl$

$\xrightarrow{PX_3} R-X + H_3PO_3$

$\xrightarrow{KX/H_3PO_4} R-X$ ($X = Br, I$)

Reaction with Lucas Reagent : Lucas Reagent is HCl / anhydr $ZnCl_2$

$$R-OH + HCl \xrightarrow[anhydr\ ZnCl_2]{} R-Cl + H_2O$$

As RCl is immiscible in H_2O, the cloudiness or milkiness or turbidity appears in solution. As reactivity order is $1^\circ < 2^\circ < 3^\circ$

3° gives cloudiness with Lucas Reagent immidiately

2° gives " after 5-10min ; 1° → no cloudiness

This is called Lucas Reagent Test to distinguish $1^\circ, 2^\circ, 3^\circ$ alcohol.

Oxidation of Alcohols : For oxidation to take place, atleast one H at α-C is must. Therefore 3° alcohols are most resistant to oxidation.

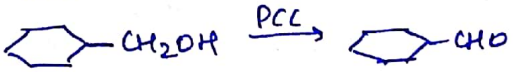
Oxidation depends upon → i) Oxidising Agent ii) Structure of alcohol $1^\circ, 2^\circ, 3^\circ$

1° $R-CH_2OH \xrightarrow[(O)]{PCC} R-CHO + H_2O$

2° $R-CH(OH)-R' \xrightarrow[(O)]{PCC} R-CO-R' + H_2O$

Mild Oxidation with PCC

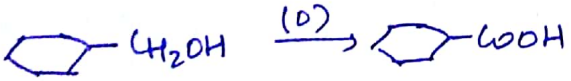
3° alcohol + PCC → no rxn



Strong Oxidation with hot alk $KMnO_4$ (or $K_2Cr_2O_7/H_2SO_4$)

$R-CH_2OH \xrightarrow{(O)} R-CHO \xrightarrow{[O]} R-COOH$

same no. of c as parent alcohol



* 1° alcohol changes the color of $KMnO_4$ from pink to black ppt of MnO_2 readily

2° alcohol gives ketone with same number of c-atom

2° alcohol on further oxidation give carboxylic acids with less no. of C atoms.

$R-\underset{OH}{\underset{|}{CH}}-R \xrightarrow{[O]} R-\overset{O}{\overset{\|}{C}}-R' \xrightarrow{[O]}$ RCOOH + R'COOH each acid containing less no. of C-atom.

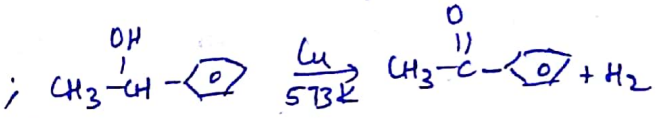
3° alc. with alk. $KMnO_4$ → no rxn

3° alc. with acidic $KMnO_4$ → ketone with less no of carbon

$(CH_3)_3COH \xrightarrow{[O]} (CH_3)_2=CH_2 \xrightarrow{[O]} (CH_3)_2CO$

Dehydrogenation with Cu / 573 K

1° alc. $R-CH_2OH \xrightarrow[573K]{Cu} RCHO + H_2O$

2° alc $R-\underset{OH}{\underset{|}{CH}}-R' \xrightarrow{Cu} R-\overset{O}{\overset{\|}{C}}-R' + H_2$; 

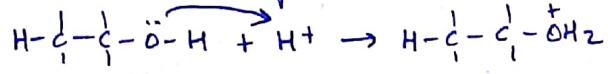
3° alc $(CH_3)_3C-OH \xrightarrow[573K]{Cu} CH_3-\underset{CH_3}{\underset{|}{C}}=CH_2$

Dehydration of alcohols

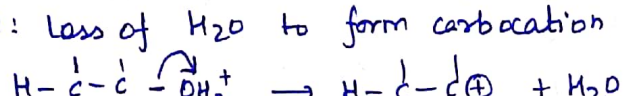
$C_nH_{2n+1}-OH \xrightarrow[443K]{H_2SO_4} C_nH_{2n} + H_2O$

Mechanism $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$

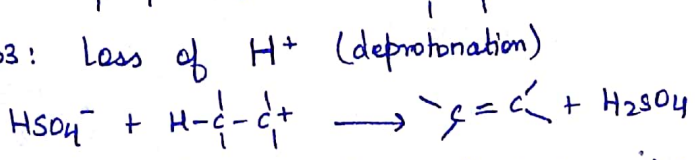
step1 : Protonation of alcohol



step2: Loss of H_2O to form carbocation



step3: Loss of H^+ (deprotonation)



In case of dehydration of alcohols follows the order $\boxed{1° < 2° < 3°}$

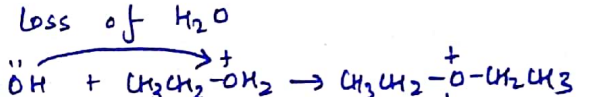
Ex : $CH_3-CH_2-OH \xrightarrow[\Delta\ 443K]{H_2SO_4} CH_3-CH=CH_2$

$CH_3-CH_2CH_2-OH \xrightarrow[443K]{H_2SO_4} CH_3CH=CH_2$

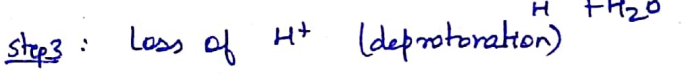
★ $CH_3-CH_2-CH_2-CH_2-OH \xrightarrow[443K]{H_2SO_4} CH_3-CH=CH-CH_3$ (because 2° carbon cation is more stable)

Dehydration of alc. to form ether

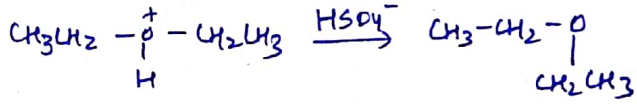
$C_nH_{2n+1}-OH \xrightarrow[413K]{H_2SO_4} C_nH_{2n+1}-O-C_nH_{2n+1}$

step1 : 

step2: loss of H_2O



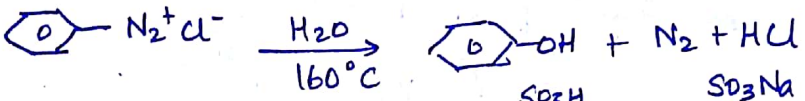
step3 : Loss of H^+ (deprotonation)



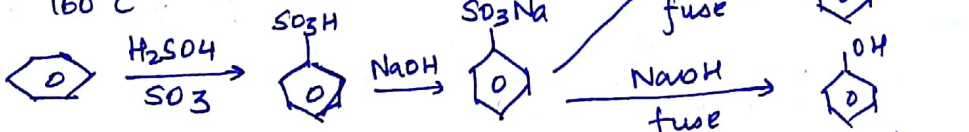
PHENOLS

Preperation (1) From chlorobenzene (S_N) **Dow's process**

(2) From benzene diazonium chloride

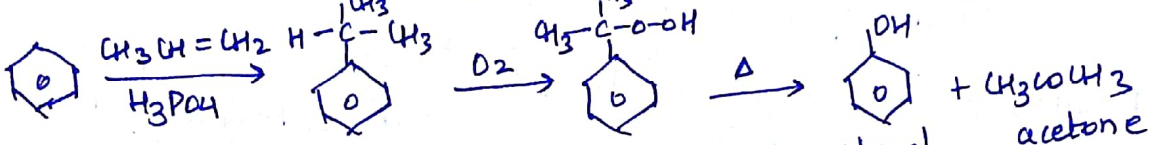


(3) From benzene



4) **Cumene - Phenol process**

commercial method to prepare phenol



Properties - 1) Phenol is specifically soluble in water

2) Phenol when pure is a colourless liquid with charateristic small but turns light pink on expose to air due to formation of p-benzoquinone or o-benzoquinone.

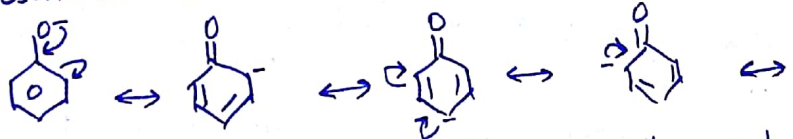
3) Higher bp than chlorobenzene due to the presence of intermolecular H-bonding.

Acidic Nature of Phenol : 1) Phenols are acidic in nature & give H^+ ion in H_2O.

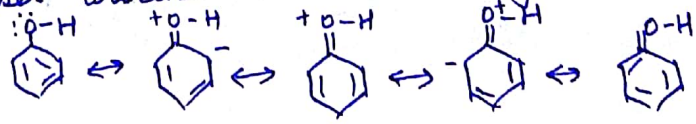
$$C_6H_5OH + H_2O \rightleftharpoons C_6H_5O^- + H_3O^+$$

$$K_a = \frac{[C_6H_5O^-][H^+]}{[C_6H_5OH]}$$

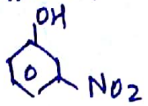
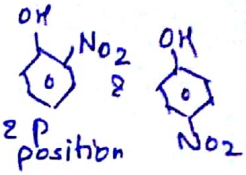
2) Phenols are stronger acid than alcohols as the peroxide ion is more resonance stabalised than alkoxide ion.



Imp ★ 3) The LP of electrons on oxygen participates into resonance with the benzene ring. The oxygen acquires a δ+ charge. The e⁻ density of OH then shift towards oxygen and decreases around H. H can easily be removed as H^+ ion. Hence phenol is acidic.

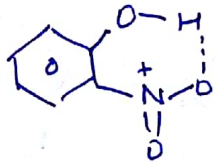


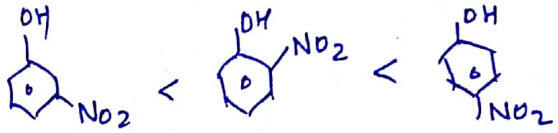
- Presence of EWG (NO_2) increases the acidic strength of phenol from all three position.


is a weaker acid than o & p nitrophenol 

∵ NO_2 exert -R effect only when present at o/p position

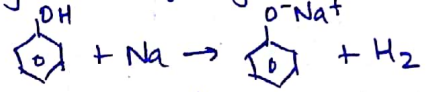
o-nitrophenol is a weaker acid than p-nitrophenol due to intramolecular H-bonding.



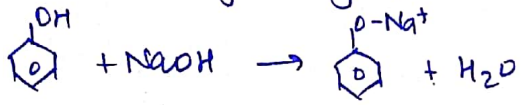
∴ 

- Presence of EDG (CH_3) decreases the acidic strength of phenol. Hence p-cresol is a weaker acid than phenol. Hence p-cresol < phenol.
- More EWG present, more acidic strength. Hence picric acid (2,4,6 trinitrophenol) is stronger than phenol & behaves like normal carboxylic acid.

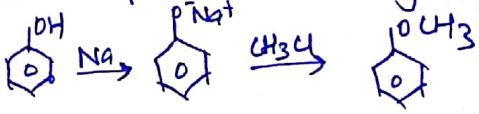
Reaction of Phenol A) involving cleavage of o-H bond

1) with reactive metals  (given by alcohol, phenol & acids)

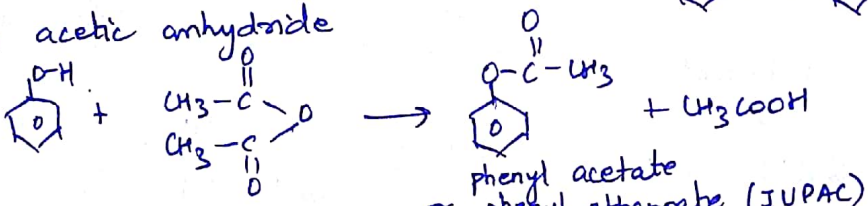
2) with NaOH (given by phenol & acids, not alcohols)



Q. Convert phenol to methoxy benzene

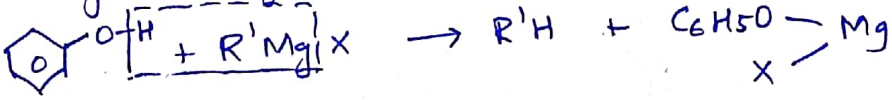


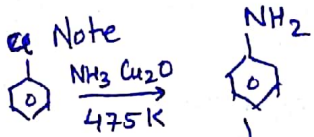
3) with acetic anhydride



phenyl acetate or phenyl ethanoate (IUPAC)

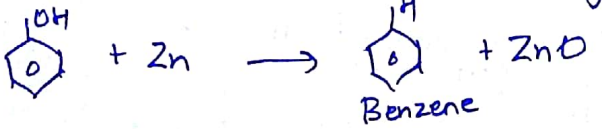
4) with Grignard reagent



Note 

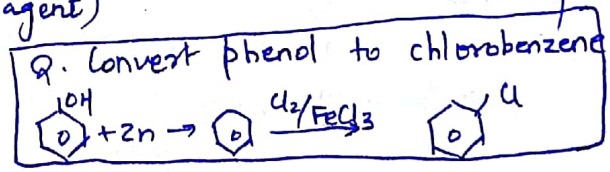
B) Involving cleavage of C-OH bond (removal of OH group)

1) with Zn dust (Zn is a reducing agent)

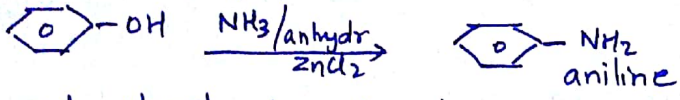


Benzene

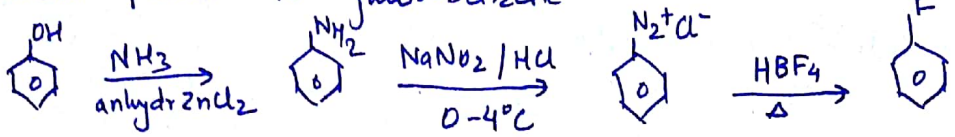
Q. Convert phenol to chlorobenzene



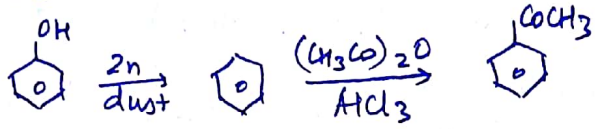
2) with NH_3 / anhydr $ZnCl_2$



Q. Convert phenol to fluorobenzene



Q. Phenol into acetophenone

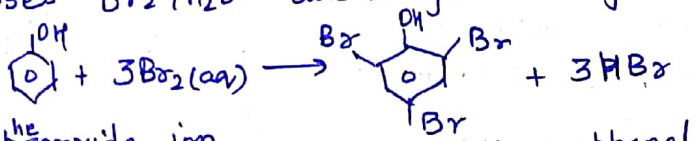


C) Reaction involving benzene ring

↳ also called electrophyllic substitution reactions

- Phend is more reactive than benzene towards electrophillic substitution. (S_E)
- Presence of OH group increases e^- density more at o- and p- position than m-position. Hence OH group is ortho, para director.

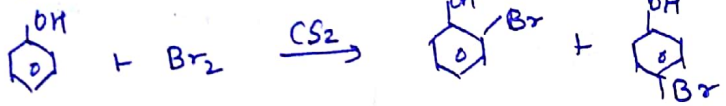
1) **Bromination**: Phend decolourises Br_2/H_2O due to formation of 2,4,6 tribromo phenol, a white ppt.



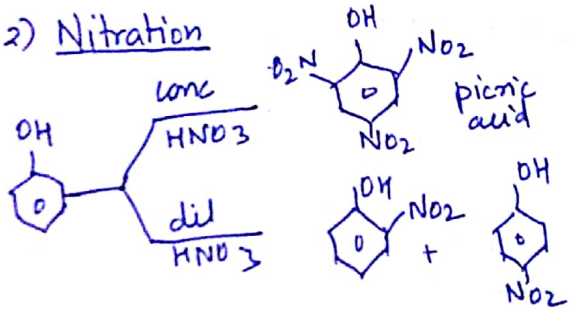
2,4,6 tribromophenol

In aqueous solution/medium, phend gets ionised to form phenoxide ion which is more e^- rich than phend itself. Hence tribromo product is formed.

In CS_2 medium, the phend gives only monobromo product

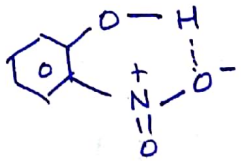


2) **Nitration**

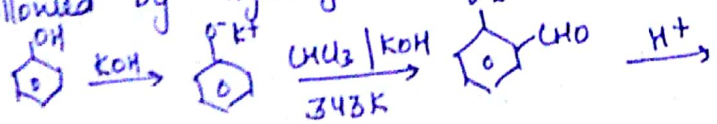


★ Due to presence of intramolecular H-bonding o-nitrophenol is

i) immisible in H_2O
ii) low bp than p nitro phenol
iii) steam volatile
iv) less acidic than p nitrophenol



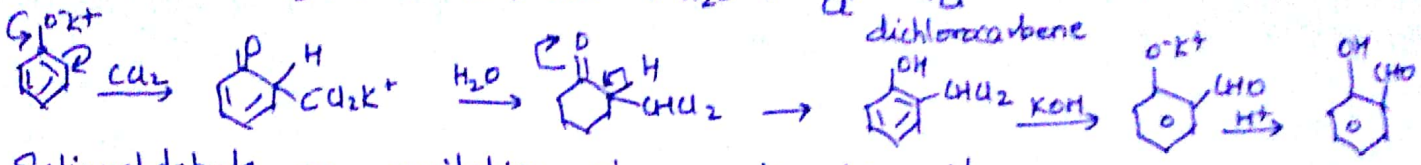
★ 3) **Reimer-Tiemann Reaction**: is a method to prepare phenolic aldehyde by reaction sod. or potassium phenoxide with $CHCl_3$/KOH or NaOH at 60°C followed by hydrolysis.



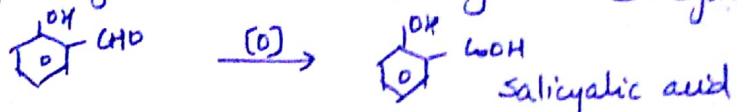
⊕ steam volatile due to intramolecular H bonding

2-hydroxy benzaldehyde (salicyaldehyde)

Mechanism $CHCl_3 + KOH \rightarrow KCl + H_2O +$ dichlorocarbene



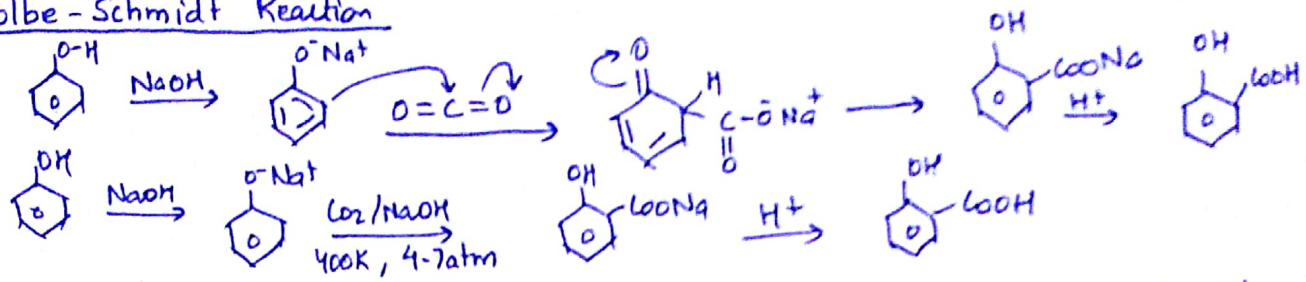
Salicyaldehyde on oxidation gives salicylic acid.



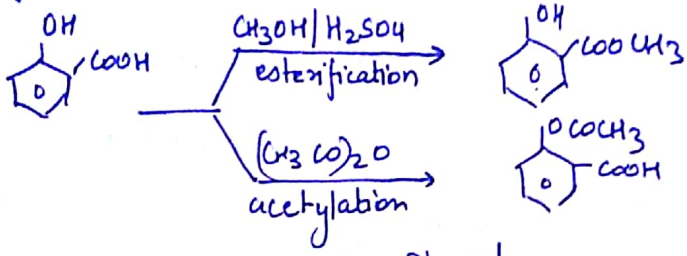
Salicylic acid

★ 4) Kolbe-Schmidt Reaction

Mechanism



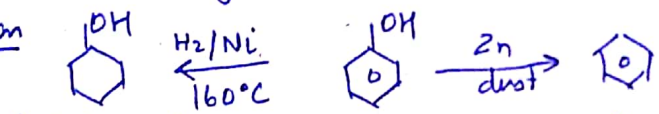
Salicylic is used to prepare methyl salicylate (called oil with wintergreen)



Test for Phenol
i) Litmus test
ii) Br_2/H_2O → phenol gives white ppt of 2,4,6 tribromophenol
iii) Neutral $FeCl_3$ → phenol gives a violet color with neutral $FeCl_3$
iv) Dye test → phenol gives a yellow dye on coupling with benzene diazonium chloride.

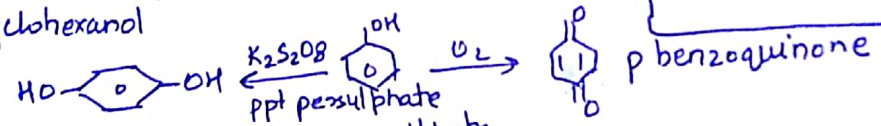
D) Miscellaneous Rxn of Phenol

1) Reduction



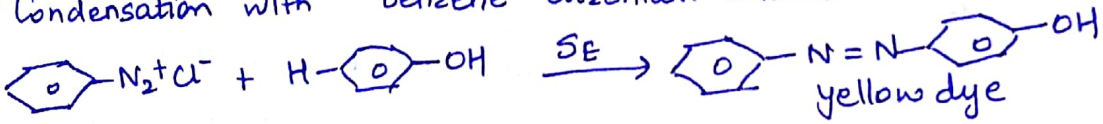
Cyclohexanol

2. Oxidation



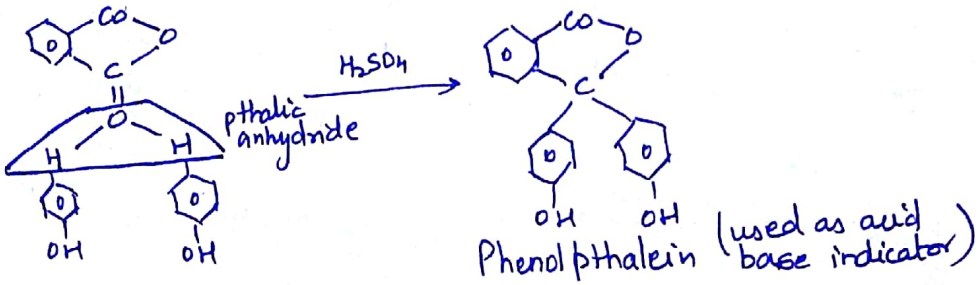
p benzoquinone

3) Condensation with benzene diazonium chloride.



yellow dye

4)



Phenolphthalein (used as acid base indicator)

ETHERS

Preperation (1) From alcohol using H_2SO_4 at 140°C

This rxn is given by 1° Alcohol. 2°,3° alc. tend to give alkene.

$$R\text{-}OH + H\text{-}OR \xrightarrow[140°C]{H_2SO_4} R\text{-}O\text{-}R + H_2O$$

R. $CH_3Br \xrightarrow[\text{Dry ether}]{Mg} A \xrightarrow[ii)\ H^+]{i)\ HCHO} B \xrightarrow[413K]{H_2SO_4} C$

A → CH_3MgBr B → CH_3CH_2OH C → $CH_3CH_2OCH_2CH_3$

2) From RX using sodium alkoxides (Williamson's synthesis)
Best method to prepare ether. Example of S_N2 rxn, given by 1° RX.

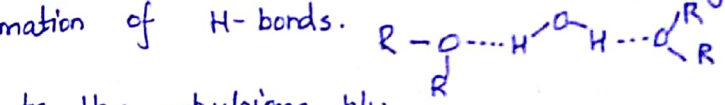
$$RX + Na^+O^-R' \longrightarrow R\text{-}O\text{-}R'$$

Ex: $CH_3CH_2Br + Na^+O^-$(C6H5) → CH_3CH_2-O-(C6H5) phenetole

* R should be less bulkier than R'

Properties - (1) **Boiling point** : Ethers have a lower bp than isomeric alcohols. This is due to their inability to associate via H-bonding. Thats why ethers are highly volatile.
However, ethers have a higher b.p than RX. This is due to strong dipole-dipole interaction in R_2O.

(2) **Solubility** : Lower ethers dimethyl ether or diethyl ether are completely miscible with H_2O due to formation of H-bonds.



(3) sp^3 hybradised but >109° due to the repulsions b/w the bulky large size R groups

4) Ethers have a net dipole mout even if the R grp are similar. This is due to their bent structure.

5) Due to presence of two EDG (R group), e^- density on O_2 is very high Therefore ethers have a tendancy to accept H^+ ions. Ethers are strong Bronsted bases. $R_2O + HCl \rightarrow R_2OH^+Cl^-$

$$(CH_3CH_2)_2O + HCl \longrightarrow (CH_3CH_2)OH^+Cl^-$$

Reaction of Ethers: (1) with HX

The reactivity of HX towards ether HCl < HBr < HI
C-O bond cleavage in ethers take place with HI. (not HCl & HBr)

$$R\text{-}O\text{-}R + HI \rightarrow ROH + RI.$$

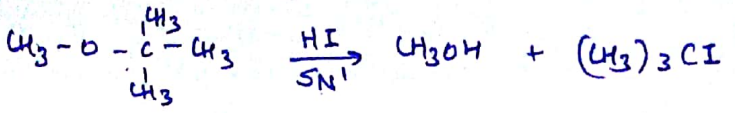
eg: $CH_3CH_2OCH_3 \xrightarrow{HI} CH_3I + CH_3CH_2OH$

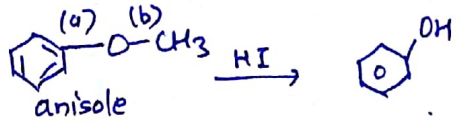
Reaction follows SN1 mechanism

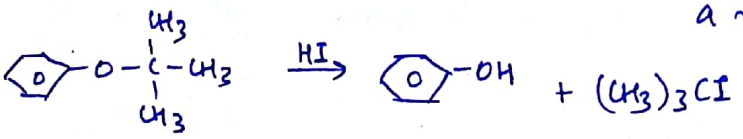
$$R\text{-}O\text{-}R \xrightarrow{H^+} R\text{-}\overset{+}{O}H \xrightarrow[S_N2]{I^-} R\text{-}I + R\text{-}OH$$

$$R\text{-}\overset{+}{O}H \xrightarrow[S_N1]{} R\text{-}OH + R' \xrightarrow{I^-} RI.$$

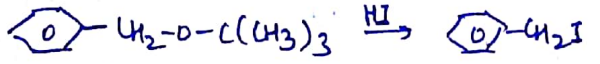
eg: $CH_3CH_2O\underset{\underset{CH_3}{|}}{CH}\text{-}CH_3 \xrightarrow{HI} CH_3CH_2I + (CH_3)_2CHOH$

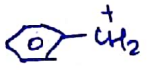


In  bcz it is easier to break bond (b) than bond (a). Bond (a) has partial double bond character. Also, breaking bond (b) gives a resonance stabalized phenoxide ion.



Aromatic ether always give phenol as one of the product.

eg: 

 is more stable carbocation than $(CH_3)_3C^+$

2) <u>with PCl_5</u> $R_2O + PCl_5 \longrightarrow RCl + POCl_3$

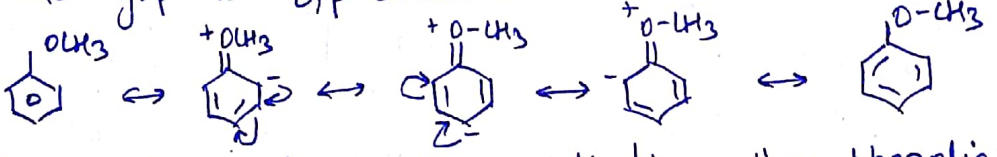
Q. Convert diethyl ether into propanoic acid

$(CH_3CH_2)_2O \xrightarrow{PCl_5} CH_3CH_2Cl \xrightarrow[ii)\ H^+]{i)\ alc\ KCN} CH_3CH_2COOH$

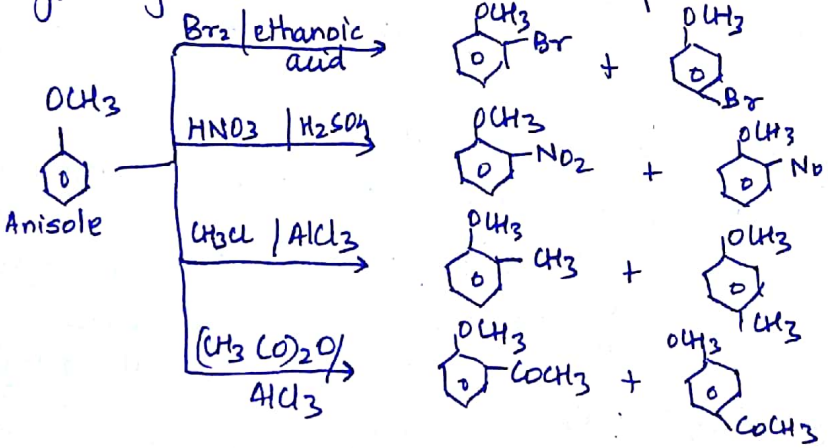
Reaction of Aromatic Ethers

i) RO group is an activating group (i.e increases the e^- density on benzene ring) & ↑ reactivity towards S_E reaction.

ii) RO grp is o,p directive



But –OR group is less activating than phenolic grp bcz phenol easily gets ionized to form phenoxide which is more e^- rich. This type of ionisation is not possible in aromatic ethers.



<u>Oxidation of Ethers</u>

Ethers get oxidised by air to form $R_2O + \frac{1}{2}O_2 \longrightarrow R-O-O-R$

Presence of peroxide can be detected by adding Fe^{+2} Peroxide if present oxidises $Fe^{+2} \rightarrow Fe^{+3}$ which gives a blood red color with KCNS. $O_2^{2-} + 2Fe^{+2} + 4H^+ \rightarrow 2Fe^{+3} + 2H_2O$

$Fe^{+3} + 6KCNS \rightarrow K_3[Fe(CNS)_6] + 3K^+$ (blood red color)

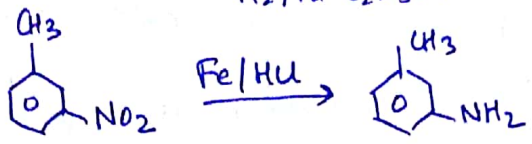
AMINES ☺

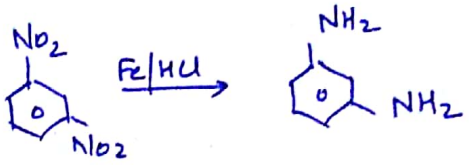
Preperation of Amines

A) Reduction (1) Reduction of nitro compounds

$Ar/R-NO_2 \xrightarrow[Fe/HCl \text{ or } H_2/Pd-C_2H_5OH]{Sn/HCl \text{ or}} Ar/R-NH_2$

$FeCl_2$ formed gets hydrolysed to release HCl during the rxn. Thus, only a small amount of HCl is reqd to initiate the reaction





(2) Reduction of nitriles ($RX \xrightarrow{alc.\ KCN} RCN$)

$R-C\equiv N \xrightarrow[Na/C_2H_5OH]{LiAlH_4 \text{ or } H_2/Ni} RCH_2NH_2$ (Mendius rxn)

whereas R-NC with H_2/Pt gives 2° amine.

$R-NC \xrightarrow{H_2/Pt} R\,NHCH_3$

eg: $CH_3-CH=CH_2 \xrightarrow{HBr} A \xrightarrow{alc\ KCN} B \xrightarrow{H_2/Ni} D$

$A \xrightarrow{alc\ AgCN} C \xrightarrow{H_2/Pt} E$

Ans: A → $CH_3-\underset{CH_3}{\overset{CH_3}{CH}}-Br$

B → $CH_3-\underset{CH_3}{CH}-CN$

C → $CH_3-\underset{CH_3}{CH}-NC$

D → $CH_3-\underset{CH_3}{CH}-CH_2NH_2$

E → $CH_3-\underset{CH_3}{CH}-CH_2NHCH_3$

3) Reduction of Amides

$R-\overset{O}{\overset{\|}{C}}-N< \xrightarrow[ii)\ H_2O]{i)\ LiAlH_4} R-CH_2-N<$

eg: $CH_3CONH_2 \xrightarrow[H_2O]{LiAlH_4} CH_3CH_2NH_2$

B) Ammonolysis of Alkyl halides (SN rxn)

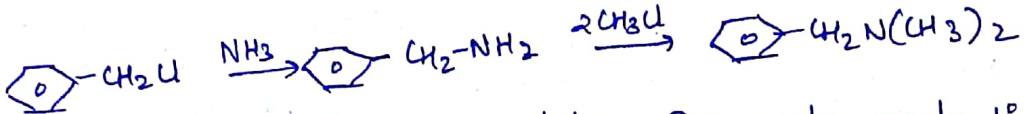
Reactivity of RX is RI > R-Br > R-Cl

$R-X + :NH_3 \longrightarrow \underset{(1°)}{RNH_2} \xrightarrow{RX} \underset{(2°)}{R_2NH} \xrightarrow{RX} \underset{(3°)}{R_3N} \xrightarrow{RX} R_4N^+X^-$

The free amines can be obtained by treating quaternary salt with a strong base. $R_4N^+X^- + NaOH \rightarrow NaX + R_3N + ROH$

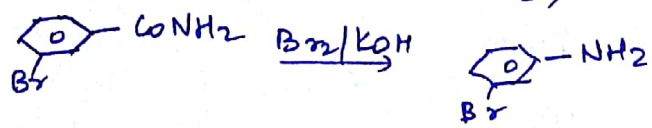
$R-X + NH_3 (excess) \longrightarrow RNH_2$ (1°) major

$4R-X\ (excess) + NH_3 \longrightarrow R_4N^+X^-$ major

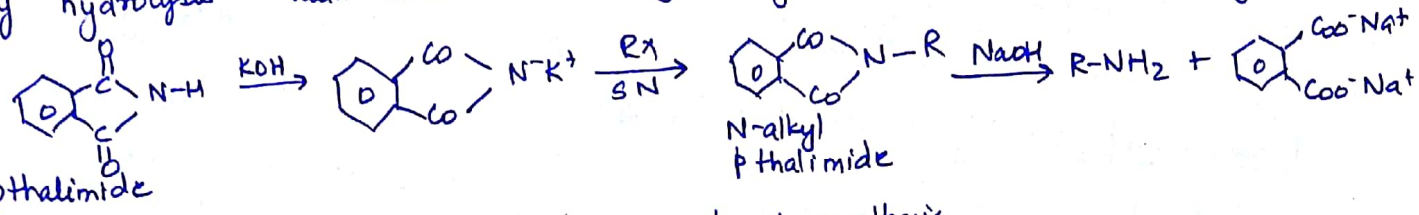
eg: 

C) Hofmann Bromoamide Degradation Rxn : to create 1° amine from amide containing α-C by treating the amide with $Br_2/alc\ KOH$ or NaOH. Amine formed contain 1 carbon less.

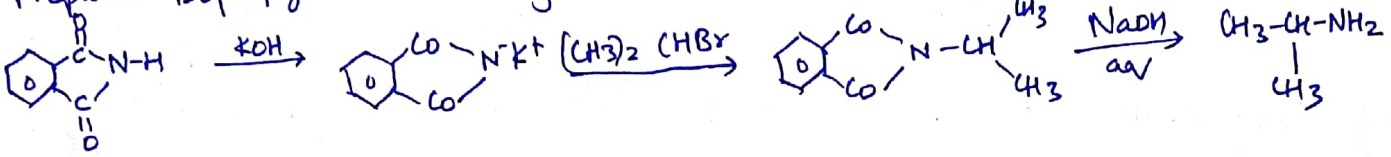
$$R-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 + 4KOH \longrightarrow \underset{(1^\circ)}{R-NH_2} + 2KBr + 2H_2O + K_2CO_3$$

eg: 

Gabriel Phthalimide Synthesis : used exclusively for preperation of primary amines. by treating phthalimide with (i) KOH (ii) RX followed by hydrolysis with alkali. Not for arylhalides, aromatic primary amines.



Q. Prepare isopropyl amine by Gabriel pth. synthesis



Physical properties of Amines

1. **Boiling point**: Amines have higher bp than R-X or R-H. This is due to ability to associate via intermolecular H bonding.
   - But lower bp than alcohols. This is due to less electronegativity and large size of N that the extent of H-bonding is less as compared to alcohol.
   - As the number of H available on N for H-bonding decreases, the boiling point decreases. $RNH_2 > R_2NH > R_3N$
2. **Solubility**: Lower amines completely miscible $\downarrow_{in\ H_2O}$ due to their ability to form intermolecular H-bonding with H_2O.
   - Solubility of amines ↓ down the homologous series.
   - For isomeric amines, the solubility order is $RNH_2 > R_2NH > R_3N$
   - Aniline is immiscible in water due to the presence of bulky benzene ring.
3. **Basicity of Amines**: $\boxed{\text{Basicity} \propto K_b \propto pK_a \propto \frac{1}{pK_b}}$

$$K_b = \frac{[RNH_3^+][OH^-]}{[RNH_2]}$$

$$RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^-$$

- Aliphatic amines are stronger bases than NH_3

Basicity is decided by
   i) +I effect of R group
   ii) Stability (or Hydration) of conjugate acid
   iii) Steric effect

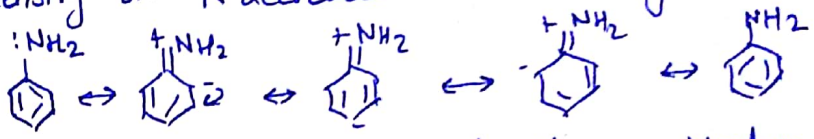
★ $(CH_3)_2NH$ > CH_3NH_2 > $(CH_3)_3N$ > NH_3

- +I effect of two groups increases the e^- density on N atom, increases basicity
- Also the conjugate acid is stabalised via H-bonding with water.

- +I effect of one Me grp
- Stability of conjugate acid $CH_3NH_3^+$ via H-bonding with H_2O

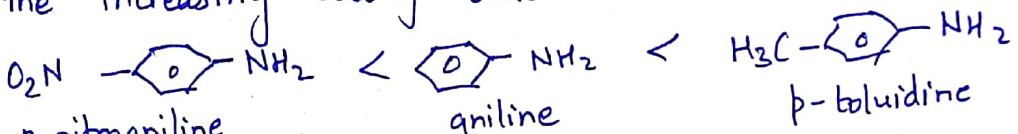
- ↑ At +I effect of CH_3 grp increases the e^- density on N but due to crowding, difficult for N atom to accept H^+ ion.
- Conjugate acid is also less stabalised via H-bonding with water.

- Aniline is weaker base than NH_3 : because the lone pair of e^- on N participates into resonance with the benzene ring. As a result, N acquires a partial +ve charge. The e^- density on N decreases. The tendency to accept H^+ ion decrease, basicity ↓.



⇒ Presence of e^- donating grp increases the e^- density on N-atom hence, increases the bascity of aniline.

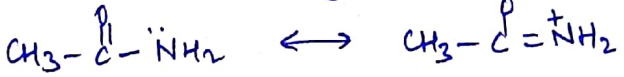
So, the increasing bascity order is



p-nitroaniline aniline p-toluidine

(a) Ethanamide is a weaker base than ethanamine. Explain.

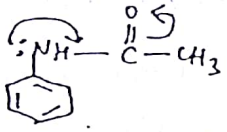
→ In ethanamide, lone pair of N is delocalised with the carbonyl group. Therefore the e^- density on N decreases. The tendency to accept H^+ ions decreases, bascity decreases.



In ethanamine, C_2H_5 is EDG, increases the e^- density on N atom. The tendency to accept H^+ ion ↑, bascity ↑

Q. Why is acetanilide a weaker base than p-nitroaniline?

Ans.



Acetanilide

p-nitroaniline

In acetanilide, the C=O (EWG) is present directly at the N-atom whereas in p-nitroaniline, the EWG (NO_2) is present at p- position. Therefore, the decrease in e^- density on N atom in acetanilide is more than in p-nitroaniline. Hence, the tendency to accept H^+ ion is less in acetanilide, acetanilide is a weaker base than p-nitroaniline.

Reactions of Amines

With nitrous acid ($NaNO_2 + HCl$)

1° amine: 1° RNH_2 forms alcohol with the liberation of colourless, odourless N_2 gas. whereas 1°  forms diazonium salt with no effervescence.

$$R-\underset{1^\circ}{NH_2} + NaNO_2 + HCl \longrightarrow \underset{1^\circ}{R-OH} + NaCl + H_2O + N_2\uparrow$$

$$C_6H_5-NH_2 + NaNO_2 + 2HCl \longrightarrow C_6H_5-N_2^+Cl^- + NaCl + 2H_2O$$

Note: This reaction is used to distinguish 1° aliphatic amines and 1° aromatic amines.

2° amines: both aliphatic and aromatic amines forms nitroso amines

$$Ar/R-\underset{R}{NH} + \underset{\text{nitrous acid}}{HO-NO} \longrightarrow Ar/R-\underset{R}{N}-NO + H_2O$$

e.g.

$$(CH_3)_2NH + HNO_2 \longrightarrow \underset{\text{nitrosoamines}}{(CH_3)_2NNO} + H_2O$$

3° amines: 3° aliphatic amines forms nitrites with HNO_2

$$R_3N: + HONO \longrightarrow \underset{\text{Trialkylammonium nitrite}}{R_3NH^+\,ONO^-}$$

$$(CH_3)_3N + HNO_2 \longrightarrow (CH_3)_3NH^+\,\bar{O}NO \quad (\text{Trimethylammonium nitrite})$$

3° aromatic amines undergo S_E reaction with HNO_2 at para position.

$$C_6H_5-N(CH_3)_2 \xrightarrow{HONO} ON-C_6H_4-N(CH_3)_2$$

N,N-dimethyl-4-nitrosobenzenamine

With Chloroform and Caustic potash, primary amines (only) forms a product called carbylamine which has a very unpleasant smell. The reaction is known as Carbylamine reaction. The reaction is used to distinguish 1° amine from 2° and 3° amine but cannot distinguish 1° aliphatic and 1° aromatic amine. This is called Isocyanide Test.

$$Ar/R-NH_2 + CHCl_3 + 3KOH \xrightarrow{\text{warm}} Ar/R-NC + 3KCl + 3H_2O$$

$$C_6H_5-NH_2 + CHCl_3 + 3KOH \xrightarrow{\text{warm}} C_6H_5-NC + 3KCl + 3H_2O$$

phenylcarbylamine

$$(CH_3)_2NH + CHCl_3 + KOH \longrightarrow \text{No reaction}$$

$$CH_3-\underset{CH_3}{CH}-NH_2 \xrightarrow[\text{Warm}]{CHCl_3/KOH} CH_3-\underset{CH_3}{CH}-NC + KCl + H_2O$$

Q. Give a chemical test to distinguish between
(i) ethylamine and dimethyl amine
(ii) cyclohexylamine and aniline

A.

(i)

Test	$CH_3CH_2NH_2$ (1°)	$(CH_3)_2NH$ 2°
Isocyanide test $CHCl_3$ + KOH + warm	unpleasant smell	No reaction

(ii)

Test		
HNO_2 ($NaNO_2$ + HCl)	gives brisk effervescence due to liberation of N_2	No nitrogen gas evolved

3. Acetylation of amines Replacement of H of amines by RCO group using RCOCl or $(RCO)_2O$ to prepare amides.

$$RNH_2 + R'COCl \longrightarrow RNH-\overset{O}{\overset{\|}{C}}-R' + HCl$$

$$R_2NH + R'COCl \longrightarrow R_2N-\overset{O}{\overset{\|}{C}}-R' + HCl$$

C.f $CH_3COCl + C_2H_5NH_2 \longrightarrow CH_3CONHC_2H_5 + HCl$

4. Reactions with metal ions (Lewis acid - base reactions)

$$Cu^{2+} + 4\,CH_3NH_2 \longrightarrow [Cu(CH_3NH_2)_4]^{2+}$$

blue colour

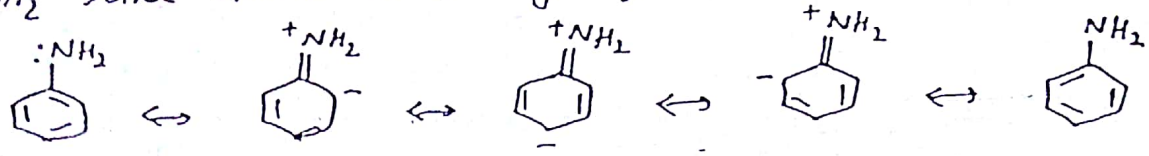
$$AgCl + 2\,CH_3NH_2 \longrightarrow [Ag(CH_3NH_2)_2]^+Cl^-$$

white ppt. soluble

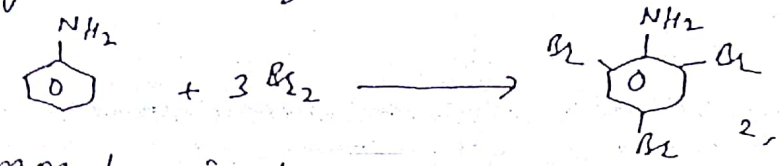
Reactions of Aniline

$-NH_2$ group is strongly activating group and increases the reactivity of the benzene towards electrophilic substitution reactions. $-NH_2$ group is more activating than OH group due to comparable size of C and N that the lone pair of N is more easily delocalized with the benzene ring than the lone pair of e^- on oxygen.

NH_2 like other activating groups is o- & p- directing

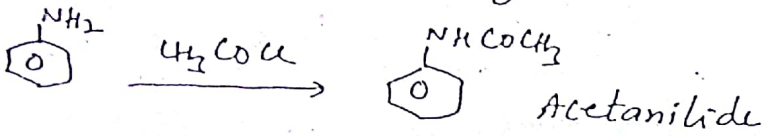


1. **Bromination** Aniline decolourise bromine water due to the formation of 2,4,6-tribromoaniline (white ppt.)

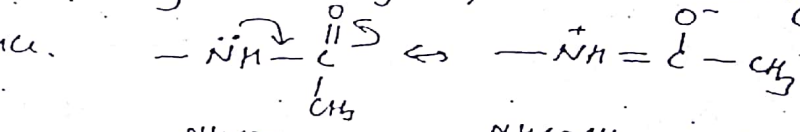


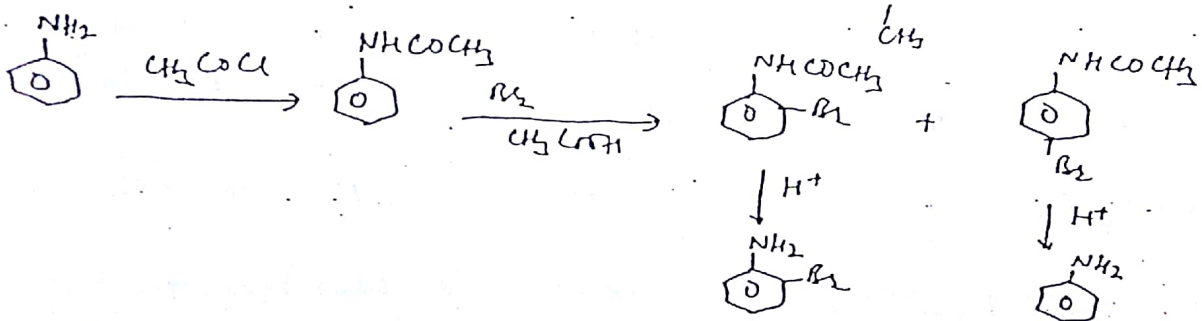
2,4,6-tribromoaniline

For monobromination, we first convert the aniline into acetanilide (anilide → N-phenyl derivative of amide
Acetanilide → N-phenyl derivative of acetamide (CH_3CONH_2)

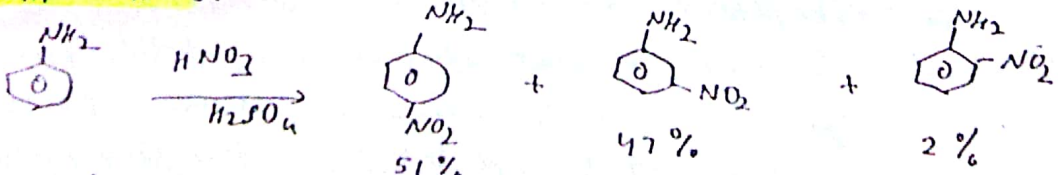


Acetanilide

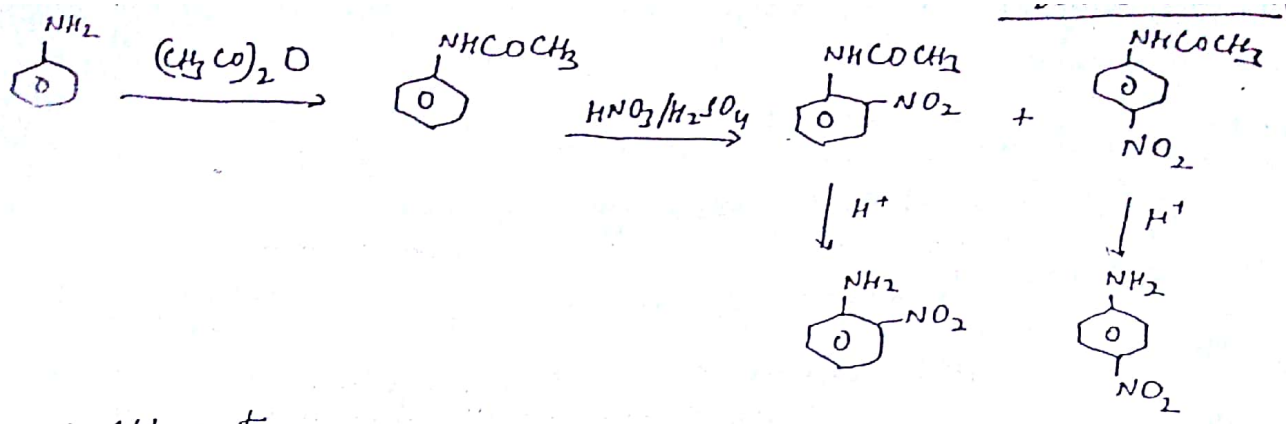
- $NHCOCH_3$ group is o,p-directing but slightly less activating than NH_2. due to resonance. 



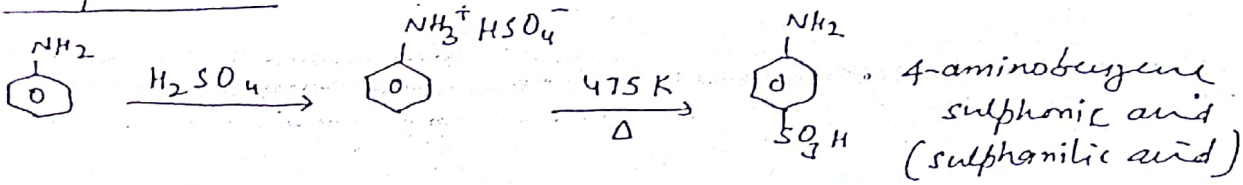
2. **Nitration** Direct nitration of aniline does not take place
Reason: As NH_2 group is strongly activating, the benzene ring gets oxidised by HNO_3/H_2SO_4 mixture to form black tar like material. Also, in strongly acidic condition, aniline forms anilinium ion which is EWG and gives m-nitroaniline



So, to perform nitration, we first acetylate aniline to form acetanilide. This slightly deactivate ring and prevents oxidation.

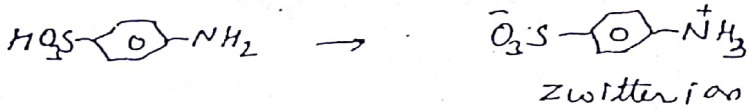


3. Sulphonation



4-aminobenzene sulphonic acid (sulphanilic acid)

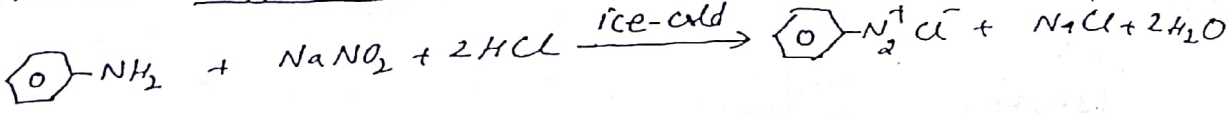
sulphanilic acid contains both acidic functional group (SO_3H, H^+ ion donor) and basic functional group (NH_2, H^+ ion acceptor) hence, NH_2 and SO_3H both neutralise each other and results in the formation of a salt. The salt formed as a result of H^+ ion transfer within a molecule is called ZWITTER ION or dipolar ion.

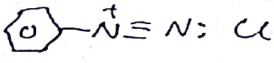


zwitterion

Diazonium salt

Benzene diazonium Chloride (BDC) is formed when a compound with $-NH_2$ group directly bonded to benzene is being treated with $NaNO_2$ and HCl in ice-cold solution. The reaction is known as diazotisation.



The structure of the diazonium salt is 

As N directly bonded to benzene is +ve charge, N_2^+ is a very good leaving group and can be lost as N_2 gas. There are two types of reactions given by benzene diazonium Chloride:

(A) Reactions involving replacement of N_2^+ group (substitution reaction, N_2^+ is lost as N_2 gas)

(B) Reactions involving retention of diazonium group (these reactions are called coupling reactions)

substitution reactions of benzene diazonium Chloride (BDC)

Reactions of BDC means the reactions of aniline because in one step aniline can be changed into BDC.

$-N_2^+Cl^-$ group can be changed into any functional group