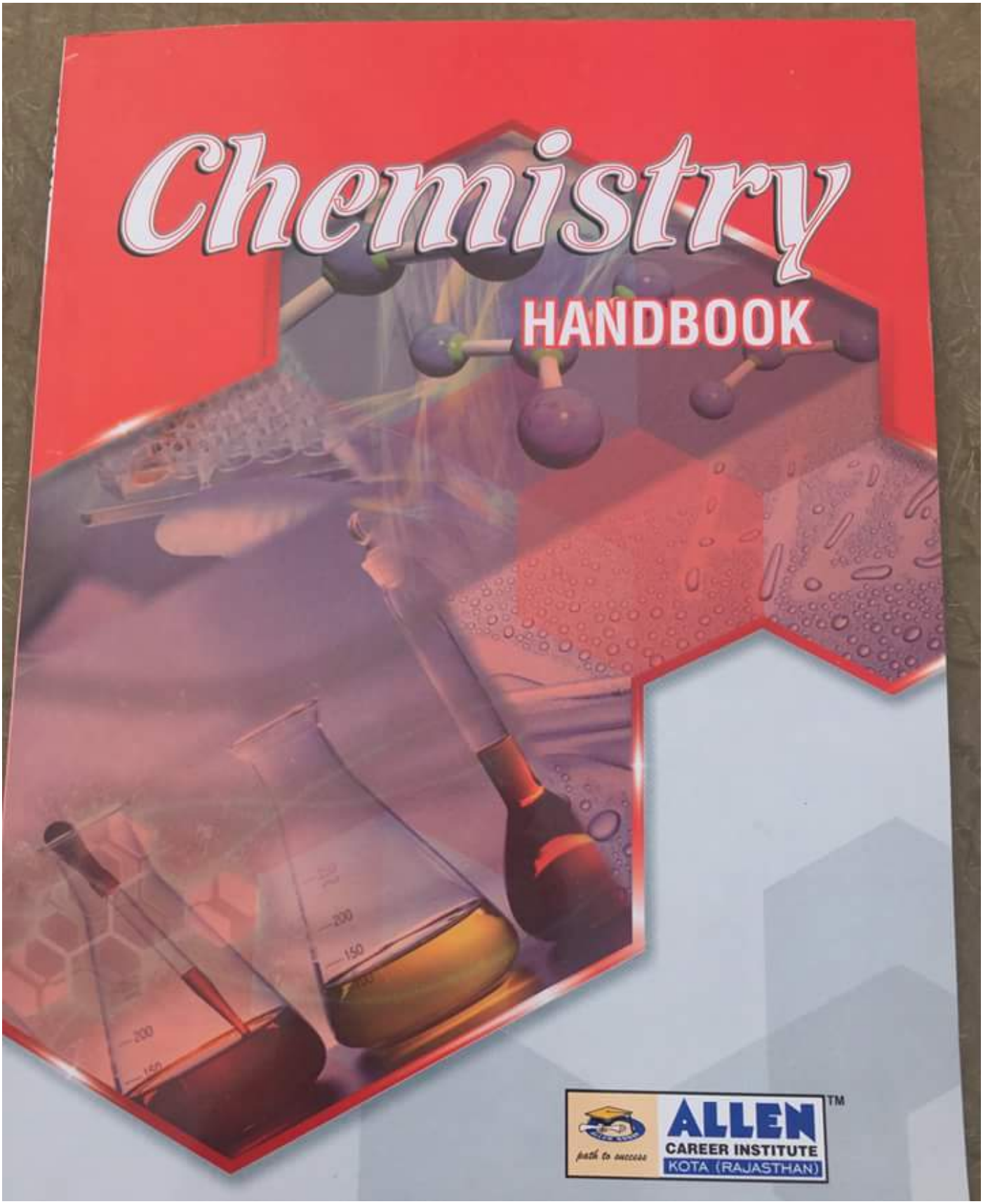
Chemistry

HANDBOOK



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ORGANIC CHEMISTRY

TABLE FOR IUPAC NOMENCLATURE

The order of priority of functional groups used in IUPAC nomenclature of organic compounds.

Functional group	Structure	Prefix	Suffix
Carboxylic acid		Carboxy	- oic acid
Sulphonic acid	$-SO_3H$	Sulpho	sulphonic acid
Anhydride		×	oic-anhydride
Ester		Alkoxy carbonyl or Carbalkoxy	alkyl....oate
Acid chloride		Chloroformyl or Chlorocarbonyl	- oyl chloride
Acid amide		Carbamoyl/ Amido	- amide
Carbonitrile/Cyanide	$-C \equiv N$	Cyano	nitrile
Aldehyde		Formyl or Oxo	- al
Ketone		Keto or oxo	- one
Alcohol	$-OH$	Hydroxy	- ol
Thio alcohol	$-SH$	Mercapto	thiol
Amine	$-NH_2$	Amino	amine
Ether	$-O-R$	Alkoxy	–
Oxirane		Epoxy	–
Nitro derivative	$-NO_2$	Nitro	–
Nitroso derivative	$-NO$	Nitroso	–
Halide	$-X$	Halo	–
Double bond	$C = C$	–	ene
Triple bond	$C \equiv C$	–	yne

CHAPTER 2

ISOMERISM

DEFINITION

Compounds having same molecular formula but differ in atleast one physical or chemical or biological properties are called isomers and this phenomena is known as isomerism.

Types of Isomerism : (A) Structural isomerism (B) Stereo isomerism

(A) STRUCTURAL ISOMERISM

Structural isomerism is a form of isomerism in which molecules with the same molecular formula have atoms bonded together in different orders.

TYPES OF STRUCTURAL ISOMERISM

CHAIN ISOMERISM

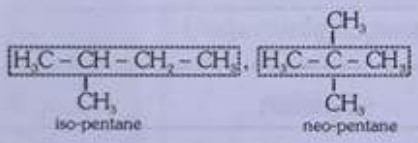
This type of isomerism is due to difference in the arrangement of carbon atoms constituting the chain.

Key points :

Parent carbon chain or side chain should be different.

e.g. C_5H_{12} : $CH_3-CH_2-CH_2-CH_2-CH_3$

n-pentane



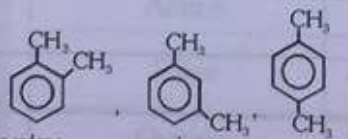
iso-pentane neo-pentane

POSITIONAL ISOMERISM

It occurs when functional groups or multiple bonds or substituents are in different positions on the same carbon chain.

Key point : Parent carbon chain remain same and substituent, multiple bond and functional group changes its position.

e.g. $C_6H_4(CH_3)_2$:



o-xylene m-xylene p-xylene

FUNCTIONAL ISOMERISM

It occurs when compounds have the same molecular formula but different functional groups.

e.g. C_3H_9N : $CH_3-CH_2-CH_2-NH_2$,

1-propanamine

$CH_3-CH_2-NH-CH_3$,

N-methylethanamine

$CH_3-N(CH_3)-CH_3$,

N, N-dimethylmethanamine

METAMERISM

This type of isomerism occurs when the isomers differ with respect to the nature of alkyl groups around the same polyvalent functional group.

e.g. $C_4H_{10}O$:

$CH_3-O-CH_2-CH_2-CH_3$

n-propyl methylether

$CH_3-CH_2-O-CH_2-CH_3$

diethyl ether

RING-CHAIN ISOMERISM

In this type of isomerism, one isomer is open chain but another is cyclic.

e.g. C_3H_6 : $CH_3-CH=CH_2$ (propene) $H_2C(CH_2)CH_2$ (cyclopropane)

- For chain, positional and metamerism, functional group must be same.
- Metamerism may also show chain and position isomerism but priority is given to metamerism.

TAUTOMERISM

This type of isomerism is due to spontaneous interconversion of two isomeric forms into each other with different functional groups in dynamic equilibrium.

Conditions :

(i) Presence of $-\overset{O}{\overset{\|}{C}}-$ or $-\overset{O}{\overset{\|}{N}}\rightarrow O$

(ii) Presence of at least one α-H atom which is attached to a saturated C-atom.

e.g. Acetoacetic ester.

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2COOC_2H_5 \rightleftharpoons CH_3-\overset{OH}{\overset{|}{C}}=CHCOOC_2H_5$

keto form enol form

ENOL CONTENT ENHANCE BY:

- Acidity of α-H of keto form
- Intra molecular H-Bonding in enol form
- Resonance in enol form
- Aromatisation in enol form

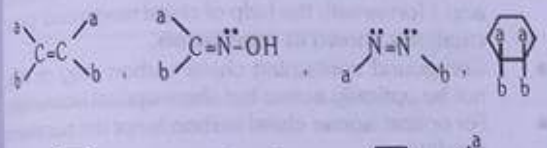
(B) STEREOISOMERISM

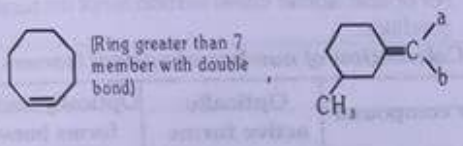
Compounds with the same molecular formula and structural formula but having difference in the spatial arrangement of atoms or groups in 3D space are called stereoisomers and the phenomenon is called stereoisomerism.

TYPES OF STEREOISOMERISM

GEOMETRICAL ISOMERISM

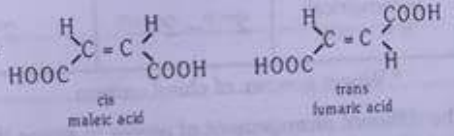
It is due to restricted rotation and is observed in following systems





- **Cis-trans isomerism :** The cis compound is the one with the same groups on the same side of the bond, and the trans has the same groups on the opposite sides. Both isomers have different physical and chemical properties.

e.g.



- General physical properties of geometrical isomer of but-2-ene

(i) Stability	*trans* > *cis*
(ii) Dipole moment	*cis* > *trans*
(iii) Boiling point	*cis* > *trans*
(iv) Melting point	*trans* > *cis*

Calculation of number of geometrical isomer

Unsymmetrical	2^n
Symmetrical	$2^{n-1} + 2^{m-1}$ $m = \frac{n}{2}$ (If n is even) $m = \frac{n+1}{2}$ (If n is odd)

• Where n = number of sites where GI is possible.

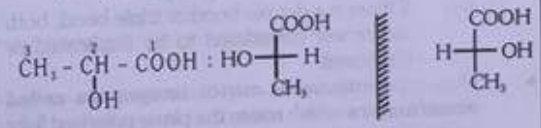
OPTICAL ISOMERISM

Compounds having similar molecular and structural formula but differing in the stereo chemical formula and behaviour towards plane polarised light are called optical isomers and this phenomenon is called optical isomersim.

- ***Types of optical isomers***
  (1) Optically active
  • dextrorotatory (d)
  • laevorotatory (ℓ)
  (2) Optically inactive
  • meso
- ***Condition :***
  Molecule should be asymmetric or chiral i.e. symmetry element (POS & COS) should be absent.
- The carbon atom linked to four different groups is called ***chiral carbon.***
- ***Fischer projection :*** An optical isomer can be represented by Fischer projection which is planar representation of three dimensional structure.

Fischer projection representation of lactic acid

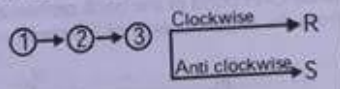
(2-hydroxypropanoic acid)



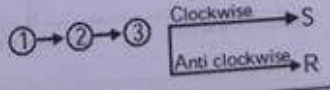
- ***Configuration of optical isomer :***
  (a) Absolute configuration (R/S system)
  (b) Relative configuration (D/L system)
- ***Determination of R/S configuration :***

Rule-1 Assign the priority to the four groups attached to the chiral carbon according to priority rule.

Rule-2 If lowest priority ④ is bonded to vertical line then moving



Rule-3 If lowest priority ④ is bonded to horizontal line then moving

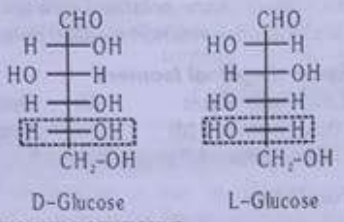


DETERMINATION OF D/L SYSTEM :

- Reference molecule glyceraldehyde
- It is used to assign configuration in carbohydrate, amino acid and similar compounds

Rule: Arrange parent carbon chain on the vertical line

- Placed most oxidised carbon on the top or nearest to top.
- On highest IUPAC numbered chiral carbon
  If OH group on RHS → D
  If OH group on LHS → L



D-Glucose L-Glucose

- ***CIP SEQUENCE RULE :***
  The following rules are followed for deciding the precedence order of the atoms or groups :-
  (i) Highest priority is assigned to the atoms of higher atomic number attached to asymmetric carbon atom.
  (ii) In case of isotopes, isotopes having higher atomic mass is given priority.
  (iii) If the first atom of a group attached to asymmetric carbon atom is same then we consider the atomic number of 2nd atom or subsequent atoms in group.
  (iv) If there is a double bond or triple bond, both atoms are considered to be duplicated or triplicated.
- Non-superimposable mirror images are called ***enantiomers*** which rotate the plane polarised light up to same extent but in opposite direction.
- ***Diastereomers*** are stereoisomers which are not mirror images of each other. They have different physical and chemical properties.
- ***Meso compounds*** are those compounds whose molecules are superimposable on their mirror images inspite of the presence of asymmetric carbon atom.
- An equimolar mixture of the enantiomers (d & ℓ) is called ***racemic mixture.*** The process of converting d- or ℓ- form of an optically active compound into racemic form is called ***racemisation.***
- The process by which dℓ mixture is separated into d and ℓ forms with the help of chiral reagents or chiral catalyst is known as ***resolution.***
- Compound containing chiral carbon may or may not be optically active but show optical isomerism.
- For optical isomer chiral carbon is not the necessery condition.

Calculation of number of optical isomers

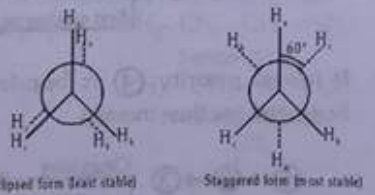
The compound	Optically active forms	Optically inactive forms (meso)
Unsymmetrical	2^n	Zero
Symmetrical If n = even	$2^{(n-1)}$	$2^{\frac{n}{2}-1}$
Symmetrical If n = odd	$2^{(n-1)} - 2^{(n-1)/2}$	$2^{(n-1)/2}$

* Where n = no. of chiral carbon

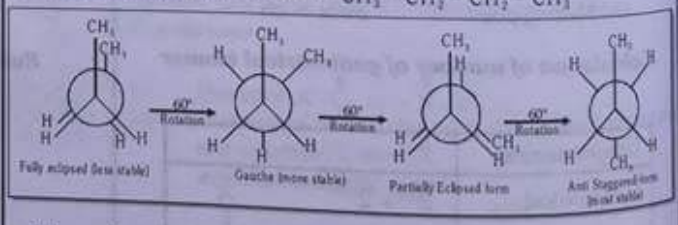
The different arrangement of atoms in space that results from the carbon-carbon single bond free rotation by 0-360° are called conformations or conformational isomers or rotational isomers and this phenomenon is called conformational isomerism.

CONFORMATIONAL ISOMERISM

Newmann projection : Here two carbon atoms forming the σ bond are represented one by circle and other by centre of the circle. Circle represents rear side C and its centre represents front side carbon. The C–H bonds of front carbon are depicted from the centre of the circle while C–H bond of the back carbon are drawn from the circumference of the circle.



- ***Conformations of butane :*** $\overset{4}{CH_3} - \overset{3}{CH_2} - \overset{2}{CH_2} - \overset{1}{CH_3}$



- The order of stability of conformations of n-butane.
  Anti staggered > Gauche > Partially eclipsed > Fully eclipsed.
- Relative stability of various conformation of cyclohexane is
  Chair > twist boat > boat > half chair

REACTION MECHANISM

Electrophiles are electron deficient species.

eg. $H^{\oplus}$, $R^{\oplus}$, $NO_2^{\oplus}$, $X^{\oplus}$, PCl_3, PCl_5

($\overset{\oplus}{N}H_4$ and $H_3O^{\oplus}$ are not electrophile)

Nucleophiles are electron rich species.

e.g. $Cl^{\ominus}$, $\overset{\ominus}{C}H_3$, $\overset{\ominus}{O}H$, $RO^{\ominus}$, $\overset{\ominus}{C}N$, $\ddot{N}H_3$, $R\ddot{O}H$, $CH_2=CH_2$, $CH\equiv CH$

Relative electron withdrawing order (–I order)

$-\overset{\oplus}{N}F_3 > -\overset{\oplus}{N}R_3 > -\overset{\oplus}{N}H_3 > -NO_2 > -CN > -COOH > -X > -OR > -OH > -C\equiv CH > -NH_2 > -C_6H_5 > -CH=CH_2$

Relative electron releasing order (+I order)

$-\overset{\ominus}{N}H > -O^{\ominus} > -COO^{\ominus} > 3^{\circ}$ alkyl $> 2^{\circ}$ alkyl $> 1^{\circ}$ alkyl $> -CH_3$

RELATIVE STABILITY ORDER

(A) Stability of carbocation


$> (Ph)_3\overset{\oplus}{C} > (Ph)_2\overset{\oplus}{C}H > Ph-\overset{\oplus}{C}H_2 > CH_2=CH-\overset{\oplus}{C}H_2 >$

$(CH_3)_3\overset{\oplus}{C} > (CH_3)_2\overset{\oplus}{C}H > CH_3\overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_3 > CH_2=\overset{\oplus}{C}H > CH\equiv\overset{\oplus}{C}$

(B) Stability of free radical

$(Ph)_3\dot{C} > (Ph)_2\dot{C}H > Ph\dot{C}H_2 > CH_2=CH-\dot{C}H_2 >$

$(CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > CH_3\dot{C}H_2 > \dot{C}H_3$

(C) Stability of Carbanion

$(Ph)_3\overset{\ominus}{C} > (Ph)_2\overset{\ominus}{C}H > Ph-\overset{\ominus}{C}H_2 > CH_2=CH-\overset{\ominus}{C}H_2 >$

$\overset{\ominus}{C}H_3 > CH_3\overset{\ominus}{C}H_2 > (CH_3)_2\overset{\ominus}{C}H > (CH_3)_3\overset{\ominus}{C}$

BASIC STRENGTH $\propto K_b \propto \frac{1}{pK_b}$

- **Basic strength of amine :-**
  In aqueous medium
  $R \Rightarrow -CH_3$ $2^{\circ} > 1^{\circ} > 3^{\circ} > NH_3$
  $R \Rightarrow -CH_2CH_3$ $2^{\circ} > 3^{\circ} > 1^{\circ} > NH_3$
  In gaseous medium
  $R \Rightarrow -CH_3$ $3^{\circ} > 2^{\circ} > 1^{\circ} > NH_3$
  $R \Rightarrow -CH_2CH_3$ $3^{\circ} > 2^{\circ} > 1^{\circ} > NH_3$
- **Reactivity towards nucleophile (NAR)**
  (1) $HCHO > CH_3CHO > (CH_3)_2CO$
  (2) $CCl_3CHO > CHCl_2CHO > CH_2ClCHO$
- **Reactivity order towards acyl nucleophilic substitution reaction**
  Acid chloride > anhydride > ester > amide
- **Order of electronic effect**
  Mesomeric > Hyperconjugation > Inductive effect
- **Stability of alkene $\propto$ no. of α-hydrogen**

$R_2C=CR_2 > R_2C=CHR > R_2C=CH_2 > \underset{\text{trans form}}{RCH=CHR} > \underset{\text{cis form}}{RCH=CHR}$

$RCH=CH_2 > CH_2=CH_2$

- **Heat of hydrogenation** $\propto \frac{1}{\text{Stability of alkene}}$

ACIDIC STRENGTH $\propto$ Stability of conjugate base

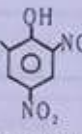
$\propto K_a \propto \frac{1}{pK_a}$

(i) $H_2O > CH\equiv CH > NH_3$

(ii) $CH\equiv CH > CH_2=CH_2 > CH_3-CH_3$

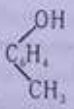
(iii) $R\text{-}SO_3H > R\text{-}COOH >$  $> R\text{-}OH$

(iv) $HCOOH > CH_3COOH > CH_3CH_2COOH$

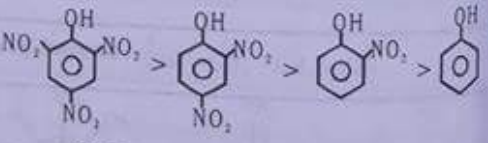
(v)  $> HCOOH > C_6H_5COOH > CH_3COOH$

(vi) $CCl_3COOH > CHCl_2COOH > CH_2ClCOOH$

(vii) $CH_3\text{-}\underset{F}{CH}\text{-}COOH > CH_3\text{-}\underset{F}{CH}\text{-}CH_2COOH > CH_2\text{-}\underset{F}{CH}CH_2COOH$

(viii)  Phenol > m > p > o

(ix)  p > o > m > Phenol

(x) 

(xi)  o > p > m > benzoic acid

(xii)  o > benzoic acid > m > p

(xiii)  o > m > benzoic acid > p

(xiv)  o > m > p > benzoic acid

PRACTICAL ORGANIC CHEMISTRY

PURIFICATION METHODS
DISTILLATION TECHNIQUES

Type :

(A) SIMPLE DISTILLATION

Conditions

(i) When liquid sample has non volatile impurities

(ii) When boiling point difference is 30 K or more.

Examples

(i) Mixture of chloroform (BP = 334K) and Aniline (BP = 457K)

(ii) Mixture of Ether (b.p. = 308K) & Toluene (b.p. = 384K)

(iii) Hexane (342K) and Toulene(384K)

(B) FRACTIONAL DISTILLATION

When b.p. difference is 10K

Examples

(i) Crude oil in petroleum industry

(ii) Acetone (329 K) and Methyl alcohol (338K)

(C) DISTILLATION UNDER REDUCED PRESSURE
(Vacuum distillation)

When liquid boils at higher temperature and it may decompose before b.p. is attained.

Example (i) Concentration of sugar juice
(ii) Recovery of glycerol from spent lye.
(iii) Glycerol

(D) STEAM DISTILLATION

When the substance is immiscible with water and steam volatile.

$$P = P_1 + P_2$$

Vapour pressure = Vapour pressure of Organic liquid + Vapour pressure of water

Example :

(i) Aniline is separated from water

(ii) Turpentine oil (iii) Nitro Benzene

(iv) Bromo Benzene (v) Naphthalene

(vi) o-Nitrophenol

LASSAIGNE'S METHOD
(detection of elements)

Element	Sodium extract	Confirmed test
Nitrogen	$Na + C + N \xrightarrow{\Delta} NaCN$	$(NaCN + FeSO_4 + NaOH)$ (boil and cool) $+ FeCl_3 + \text{conc. } HCl \rightarrow Fe_4[Fe(CN)_6]_3$ (Prussian blue colour)
Sulphur	$2Na + S \xrightarrow{\Delta} Na_2S$	(i) $Na_2S + Na_2[Fe(CN)_5NO]$ (sodium nitroprusside) $\rightarrow Na_4[Fe(CN)_5NOS]$ (a deep violet colour) (ii) $Na_2S + CH_3COOH + (CH_3COO)_2Pb \rightarrow$ (A black ppt. $PbS\downarrow$)
Halogen	$Na + X \xrightarrow{\Delta} NaX$	$NaX + HNO_3 + AgNO_3$ (i) White ppt. soluble in aq. NH_3 confirms Cl. (ii) Yellow ppt. partially soluble in aq. NH_3 confirms Br. (iii) Yellow ppt. insoluble in aq. NH_3 confirms I.
Nitrogen and sulphur together	$Na + C + N + S \xrightarrow{\Delta} NaCNS$ (Sodium thiocyanate (Blood red colour))	As in test for nitrogen; instead of green or blue colour, blood red colouration confirms presence of N and S both

QUANTITATIVE ANALYSIS OF ORGANIC COMPOUNDS

Estimation of carbon and hydrogen - Leebig's method

$$C_xH_y + O_2 \xrightarrow{\text{excess}} xCO_2 + y/2\,H_2O$$

$$\% \text{ of } C = \frac{12}{44} \times \frac{\text{wt. of } CO_2}{\text{wt. of org. compd}} \times 100$$

$$\% \text{ of } H = \frac{2}{18} \times \frac{\text{wt. of } H_2O}{\text{wt. of org compd}} \times 100$$

Note : This method is suitable for estimation if organic compound contains C and H only. In case if other elements e.g., N, S, halogens are also present the organic compound will also give their oxides which is being absorbed in KOH and will increase the percentage of carbon and therefore following modification should be made.

ESTIMATION OF NITROGEN

Duma's method :

The nitrogen containing organic compound yields nitrogen gas on heating it with copper (II) oxide in the presence of CO_2 gas. The mixture of gases is collected over potassium hydroxide solution in which CO_2 is absorbed and volume of nitrogen gas is determined.

$$\% \text{ of } N = \frac{28}{22400} \times \frac{\text{Vol. of } N_2 \text{ collected at N.T.P.}}{\text{Wt. of organic compound}} \times 100$$

Note : This method can be used to estimate nitrogen in all types of organic compounds

Kjeldahl's method :

In this method nitrogen containing compound is heated with conc. H_2SO_4 in presence of copper sulphate to convert nitrogen into ammonium sulphate which is decomposed with excess of alkali to liberate ammonia. The ammonia evolved is

$$\% \text{ of } N = \frac{1.4 \times \text{volume of acid (ml)} \times \text{normality of acid}}{\text{wt of organic compound}}$$

Note : This method is simpler and more convenient and is mainly used for finding out the percentage of nitrogen in food stuffs, soil, fertilizers and various agricultural products. This method cannot be used for compound having nitro groups, azo group (–N = N–) and nitrogen in the ring (pyridine, quinole etc.) Since nitrogen in these compounds is not quantitatively converted in to ammonium sulphate.

DISTINCTION BETWEEN PAIRS OF COMPOUNDS

UNSATURATION TEST

(a) Double/Triple bonded Compounds (C = C)/(C ≡ C) + Br_2 in CCl_4 (Brown colour) → Colourless compound

- $R-CH=CH-R + Br_2 \xrightarrow{CCl_4} R-\underset{Br}{\overset{Br}{CH}}-\underset{Br}{\overset{Br}{CH}}-R$
  (Alkene) (Brown) (Colourless)

- $R-C\equiv C-R + Br_2 \xrightarrow{CCl_4} R-\underset{Br}{\overset{Br}{C}}=\underset{Br}{\overset{Br}{C}}-R$
  (Alkyne) (Brown) (Colourless)

(b) Double/Triple bonded Compounds + Baeyer's reagent (Pink colour) ⟶ Brown precipitate

- $R-CH=CH-R + KMnO_4 \rightarrow R-\underset{OH}{\overset{OH}{CH}}-\underset{OH}{\overset{OH}{CH}}-R + MnO_2$
  (Alkene) (Cold, dilute) (Colourless) Brown ppt

- $R-C\equiv C-R' + KMnO_4 \rightarrow MnO_2 + RCOOH + R'COOH$
  (Hot, dilute) Brown ppt.

- $R-C\equiv C-H + KMnO_4 \rightarrow MnO_2 + RCOOH + CO_2 + H_2O$
  (Alkyne) (Hot, dilute) Brown ppt. (Colourless)

Baeyer's reagent is cold, dilute $KMnO_4$ solution having pink colour.

Note : The above test are not given by Benzene. Although it has unsaturation.

TEST FOR TERMINAL ALKYNE

Terminal alkyne

- Ammonical silver nitrate → White ppt.
- Ammonical cuprous chloride → Red ppt.

$NH_4NO_3 + H_2O + R-C\equiv C-Ag \xleftarrow{AgNO_3 + NH_4OH}$ White ppt.

$R-C\equiv CH$ Terminal alkyne

$NH_4Cl + H_2O + R-C\equiv C-Cu \xleftarrow{Cu_2Cl_2 + NH_4OH}$ Red ppt.

NATURE OF X-GROUP IN C–X BOND

$R-X$ + aqueous KOH ⟶ $R-OH + KX \xrightarrow[AgNO_3]{HNO_3}$ AgX Precipitate

If X is Cl, precipitate will be white and for Br yellow precipitate will be obtained.

DISTINCTION BETWEEN 1°, 2° AND 3° ALCOHOLS

- $R-\underset{R}{\overset{R}{\underset{|}{\overset{|}{C}}}}-OH \xrightarrow[\text{Room temperature}]{\text{Lucas reagent}} R-\underset{R}{\overset{R}{\underset{|}{\overset{|}{C}}}}-Cl$
  Tertiary alcohol — Cloudiness appears immediately

- $R-\underset{R}{\overset{R}{\underset{|}{\overset{|}{CH}}}}-OH \xrightarrow[\text{Room temperature}]{\text{Lucas reagent}} R-\underset{R}{\overset{R}{\underset{|}{\overset{|}{CH}}}}-Cl$
  Secondary alcohol — Cloudiness appears within five minutes

- $R-CH_2-OH \xrightarrow[\text{Heat}]{\text{Lucas reagent}} R-CH_2-Cl$
  Primary alcohol — Cloudiness appears after 30 minute

Lucas reagent is anhydrous $ZnCl_2$ + conc. HCl.

- $H_3C-\underset{OH}{\overset{OH}{CH}}-R$ type of alcohols give iodoform test.

- $H_3C-\underset{OH}{\overset{OH}{CH}}-R + I_2 \xrightarrow[\text{Iodoform test}]{NaOH} CHI_3 + RCOONa$
  Iodoform (Yellow ppt.)

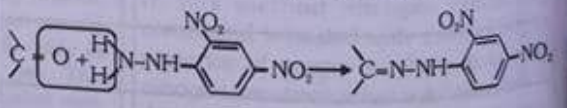
PHENOL

Phenol + ferric chloride ⟶ Violet colouration (neutral)

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

CARBONYL GROUP

- Carbonyl compound + 2, 4-Dinitrophenylhydrazine → Yellow/orange crystal (Brady's reagent)



- All aldehydes and only aliphatic methyl ketones + $NaHSO_3$ → White crystalline bisulphite.

$R-\underset{H}{\overset{R}{\underset{|}{\overset{|}{C}}}}=O + NaHSO_3 \rightarrow R-\underset{H}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-SO_3^-Na^+$
Aldehyde

$R-\underset{H_3C}{\overset{R}{\underset{|}{\overset{|}{C}}}}=O + NaHSO_3 \rightarrow R-\underset{CH_3}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-SO_3^-Na^+$
Methyl ketone

ALDEHYDE GROUP

Aldehyde + Tollen's reagent ⟶ Silver mirror

$RCHO + 3OH^- + 2[Ag(NH_3)_2]^+ \longrightarrow RCOO^- + 2H_2O + 4NH_3 + 2Ag\downarrow$ (silver mirror)

Aldehyde + Fehling's solution → Reddish brown precipitate

$RCHO + 2Cu^{2+} + 5OH^- \longrightarrow RCOO^- + 3H_2O + Cu_2O$ (Reddish brown ppt)

$H_3C-C(=O)-$ group also give iodoform test

$H_3C-C(=O)-R + I_2 + NaOH \xrightarrow{\text{Iodoform test}} CHI_3 + RCOONa$
Iodoform (Yellow ppt.)

AROMATIC ALDEHYDE GROUP

Aromatic aldehyde + Tollen's reagent → Silver mirror
Aromatic aldehyde + Fehling's solution → Negative test

Negative test ← (Fehling's solution) — C_6H_5CHO
$C_6H_5COO^-$ + Ag (Silver mirror) ← (Tollen's reagent)

CARBOXYLIC GROUP

Carboxylic acid + Sodium bicarbonate → effervescence
$RCOOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2\uparrow$

FORMIC ACID

$HCOOH$ (Formic acid)
- (Fehling's solution) → $H_2O + CO_3^{2-} + Cu_2O$ Red ppt.
- (Tollen's reagent) → $2Ag + CO_3^{2-} + H_2O$ Silver mirror

AMINES (1°)

Primary amine + KOH + $CHCl_3$ $\xrightarrow{\text{Carbylamine reaction}}$ Isonitrile (Offensive smell)

Amines (1°, 2° & 3°) (Hinsberg's test)

Primary amine + Benzenesulphonyl chloride → Precipitate $\xrightarrow{KOH}$ soluble

Secondary amine + Benzenesulphonyl chlorid → Precipitate $\xrightarrow{KOH}$ insoluble

Tertiary amine + Benzenesulphonyl chloride → No reaction

Note : Benzenesulphonyl chloride is called Hinsberg's reagent.

Chloroethane and chlorobenzene

- $C_2H_5-Cl + aq.\ KOH \xrightarrow{Boil} C_2H_5-OH + KCl \xrightarrow[AgNO_3]{HNO_3} AgCl$ White ppt.
- $C_6H_5-Cl + aq.\ KOH \xrightarrow[AgNO_3,\ HNO_3]{Boil}$ No reaction

Chlorocyclohexane and chlorobenzene

- $C_6H_{11}-Cl + aq.\ KOH \xrightarrow{Boil} C_6H_{11}-OH + KCl \xrightarrow[AgNO_3]{HNO_3} AgCl$ White ppt.
- $C_6H_5-Cl + aq.\ KOH \xrightarrow[AgNO_3,\ HNO_3]{Boil}$ No reaction

Chloroethane and bromoethane

- $C_2H_5-Cl + aq.\ KOH \xrightarrow{Boil} C_2H_5-OH + KCl \xrightarrow[AgNO_3]{HNO_3} AgCl$ White ppt.
  (Chloroethane)
- $C_2H_5-Br + aq.\ KOH \xrightarrow{Boil} C_2H_5-OH + KBr \xrightarrow[AgNO_3]{HNO_3} AgBr$ Yellow ppt.
  (Bromoethane)

Benzyl chloride and chlorobenzene

- $C_6H_5CH_2Cl + aq.\ KOH \xrightarrow{Boil} C_6H_5CH_2OH + KCl$
  (Benzyl chloride)
  $AgCl \xleftarrow[AgNO_3]{HNO_3}$ White ppt.
- $C_6H_5-Cl + aq.\ KOH \xrightarrow[HNO_3,\ AgNO_3]{Boil}$ No reaction
  Chlorobenzene

Ethyl chloride and vinyl chloride

- $C_2H_5-Cl + aq.KOH \xrightarrow{Boil} C_2H_5-OH + KCl$
  (Ethyl chloride)
  $AgCl \xleftarrow[AgNO_3]{HNO_3}$ (White ppt.)
- $H_2C=CH-Cl + aq.KOH \xrightarrow[HNO_3,\ AgNO_3]{Boil}$ No reaction
  Vinyl chloride

n-Propyl alcohol and iso-propyl alcohol

- $CH_3CH_2CH_2OH + HCl \xrightarrow{ZnCl_2} CH_3CH_2CH_2Cl$
  No cloudiness at room temp.
- $H_3C-\underset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow[HCl]{ZnCl_2} H_3C-\underset{Cl}{\underset{|}{CH}}-CH_3$
  Cloudiness within 5 minutes

Ethyl alcohol and methyl alcohol (Iodoform test)

- $CH_3CH_2OH + 4I_2 + 6NaOH \longrightarrow \underset{\text{Yellow ppt.}}{CHI_3} + HCOONa$
- $CH_3OH + 4I_2 + 6NaOH \longrightarrow$ No yellow ppt.

Ethyl alcohol and acetone (2, 4 – DNP)

- 

- $C_2H_5OH \xrightarrow{2,4\text{-DNP}}$ No reaction

Phenol and ethyl alcohol (Neutral $FeCl_3$)

- Phenol + Neutral ferric chloride $\longrightarrow$ Violet colouration

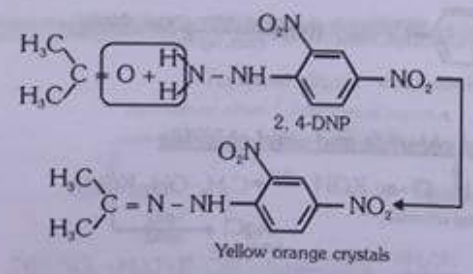
$$6\,C_6H_5OH + FeCl_3 \longrightarrow \underset{\text{Violet colouration}}{3H^+ + [Fe(OC_6H_5)_6]^{3-}} + 3HCl$$

- CH_3CH_2OH + Neutral ferric chloride $\longrightarrow$ No violet colouration

Benzoic acid and phenol ($NaHCO_3$)

- Benzoic acid + Sodium bicarbonate $\longrightarrow$ effervescence
  $C_6H_5COOH + NaHCO_3 \rightarrow C_6H_5COONa + CO_2\uparrow + H_2O$
- Phenol + Sodium bicarbonate $\rightarrow$ No effervescence
  (Phenol is less acidic than benzoic acid)

Propanone and propanol (2, 4 - DNP)

- 

- Propanol + 2,4-Dinitrophenylhydrazine $\longrightarrow$ No crystals

Ethanal and propanal (Iodoform test)

- $H_3C-\overset{O}{\overset{\|}{C}}-H + I_2 + NaOH \xrightarrow{\text{Iodoform test}} \underset{\text{Iodoform (Yellow ppt.)}}{CHI_3} + HCOONa$
  (Ethanal)
- $H_3C-CH_2-\overset{O}{\overset{\|}{C}}-H + I_2 + NaOH \xrightarrow{\text{Iodoform test}}$ No yellow ppt.
  (Propanal)

Propanal and propanone (Tollen's and Fehling reagent)

- Propanal + Tollen's reagent $\longrightarrow$ Silver mirror

$$H_3C-CH_2-\overset{O}{\overset{\|}{C}}H + 3OH^- + 2[Ag(NH_3)_2]^+ \longrightarrow CH_3CH_2COO^- + 2H_2O + 4NH_3 + 2Ag\downarrow$$
(Silver mirror)

- Propanal + Fehling's solution $\rightarrow$ Reddish brown precipitate

$$H_3C-CH_2-\overset{O}{\overset{\|}{C}}H + 2Cu^{2+} + 5OH^- \longrightarrow CH_3CH_2COO^- + 3H_2O + Cu_2O$$
(Reddish brown ppt.)

- Propanone
  - Fehling's solution $\rightarrow$ Negative test
  - Tollen's reagent $\rightarrow$ Negative test

Pentan-2-one and pentan-3-one (Iodoform test)

- $H_3C-CH_2-CH_2-\underset{\text{(Pentan-2-one)}}{\overset{O}{\overset{\|}{C}}}-CH_3 + I_2 + NaOH \xrightarrow{\text{Iodoform test}} \underset{\text{Iodoform (Yellow ppt.)}}{CHI_3} + CH_3CH_2CH_2COONa$
- $H_3C-CH_2-\underset{\text{Pentan-3-one}}{\overset{O}{\overset{\|}{C}}}-CH_2-CH_3 + I_2 + NaOH \xrightarrow{\text{Iodoform test}}$ No yellow ppt.

Propanal and benzaldehyde (Fehling solution)

- Propanal + Fehling's solution $\rightarrow$ Reddish brown precipitate

$$H_3C-CH_2-\underset{\text{Fehling's solution}}{\overset{O}{\overset{\|}{C}}}-H + 2Cu^{2+} + 5OH^- \longrightarrow CH_3CH_2COO^- + 3H_2O + Cu_2O$$

- Benzaldehyde + Fehling's solution $\rightarrow$ No precipitate

$$C_6H_5CHO + 2Cu^{2+} + 5OH^- \longrightarrow \text{No reaction}$$

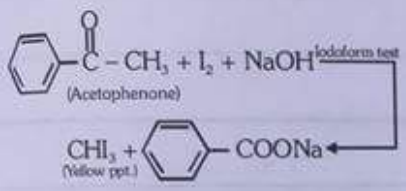
Methanoic acid and ethanoic acid (Tollen's & Fehling solution)

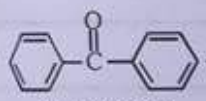
- $HCOOH$ (Methanoic acid)
  - Fehling's solution $\rightarrow H_2O + CO_3^{2-} + Cu_2O$
  - Tollen's reagent $\rightarrow 2Ag\downarrow + CO_3^{2-} + H_2O$
- Ethanoic acid
  - Fehling's solution $\rightarrow$ No brown ppt.
  - Tollen's reagent $\rightarrow$ No silver mirror

Ethanal and methanal (Iodoform test)

- $CH_3CHO + I_2 + NaOH \xrightarrow{\text{Iodoform test}} CHI_3 + HCOONa$
  Ethanal — Iodoform (Yellow ppt.)
- $HCHO + I_2 + NaOH \xrightarrow{\text{Iodoform test}}$ No yellow ppt.
  Methanal

Acetophenone and benzophenone (Iodoform test)

- 

- 

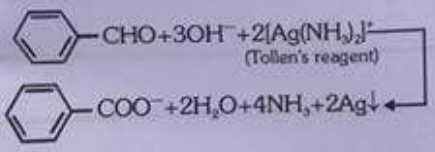
  No ppt.

Benzoic acid and ethylbenzoate

- $C_6H_5COOH + NaHCO_3 \rightarrow C_6H_5COONa + CO_2\uparrow + H_2O$
  effervescence
- Ethyl benzoate + Sodium bicarbonate → No effervescence

Benzaldehyde and acetophenone (Tollen's test)

- Benzaldehyde + Tollen's reagent → Silver mirror

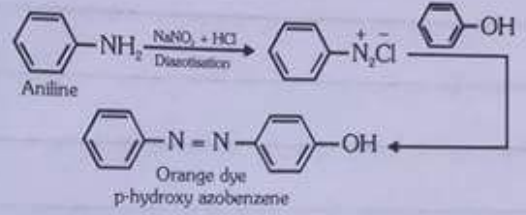


- Acetophenone + Tollen's reagent ⟶ No silver mirror

Methyl amine and dimethyl amine (Isocyanide test)

- $CH_3NH_2 + CHCl_3 + 3KOH \xrightarrow{\text{(alc.)}} CH_3NC + 3KCl + 3H_2O$
  Methyl amine — Methyl isocyanide (Offensive smell)
- $H_3C-\underset{\displaystyle CH_3}{\underset{|}{N}}H + CHCl_3 + 3KOH\ \text{(alc.)} \longrightarrow$ No offensive smell
  Di-methyl amine

Aniline and ethyl amine (Diazotisation)

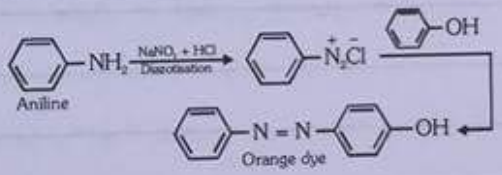
- 

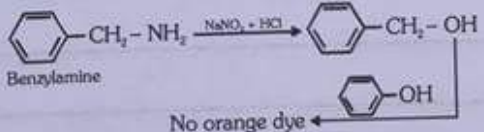
- $CH_3CH_2NH_2 \xrightarrow{NaNO_2 + HCl} CH_3CH_2OH$ (OH) ⟶ No Orange dye
  Ethyl amine

Aniline and N-methylaniline (Isocyanide test)

- $NH_2 + CHCl_3 + 3KOH \xrightarrow{\text{(alc.)}} NC + 3KCl + 3H_2O$
  Aniline — Phenyl isocyanide (Offensive smell)
- $NH - CH_3 + CHCl_3 + 3KOH \xrightarrow{\text{(alc.)}}$ No offensive smell
  N-Methylaniline

Aniline and Benzylamine (Diazotisation + phenol)

- 

- 

Glucose and fructose

- Glucose + Br_2 + H_2O ⟶ Gluconic acid + 2HBr
  (Brown colour) — (Colourless)
- Fructose + Br_2 + H_2O ⟶ Brown colour
  (Brown colour) — (no change in colour)

Glucose and sucrose

- Glucose + Tollen's reagent ⟶ Silver mirror
- Sucrose + Tollen's reagent ⟶ No silver mirror

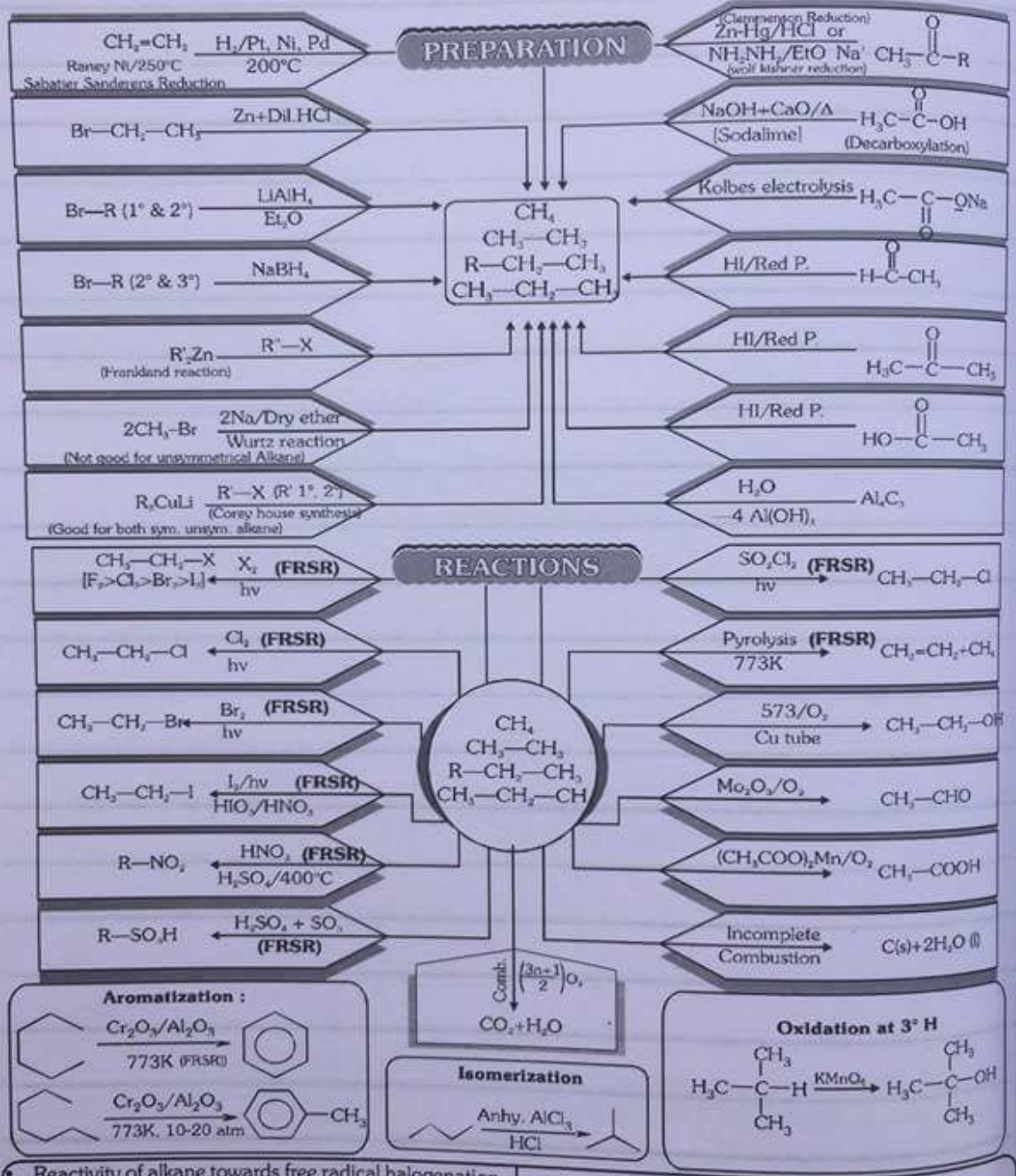
Glucose and starch

- Glucose + Fehling's solution ⟶ Red ppt.
- Starch + Fehling's solution ⟶ No red ppt.

OR

- Glucose + I_2 solution ⟶ No blue colour
- Starch + I_2 solution ⟶ Blue colour

HYDROCARBON - ALKANE



- Reactivity of alkane towards free radical halogenation is ∝ stability of free radical
  $C_6H_5-CH_3>CH_2=CH-CH_3>(CH_3)_3CH$
  $>CH_3-CH_2-CH_3>CH_3-CH_3>CH_4$
- Reactivity of halogen towards free radical substitution
  $F_2>Cl_2>Br_2>I_2$
- Knocking tendency of petroleum as fuel decrease with increase in side chain. Straight chain > Branched chain

Knocking tendency is in the order
Olefin > cycloalkane > aromatic

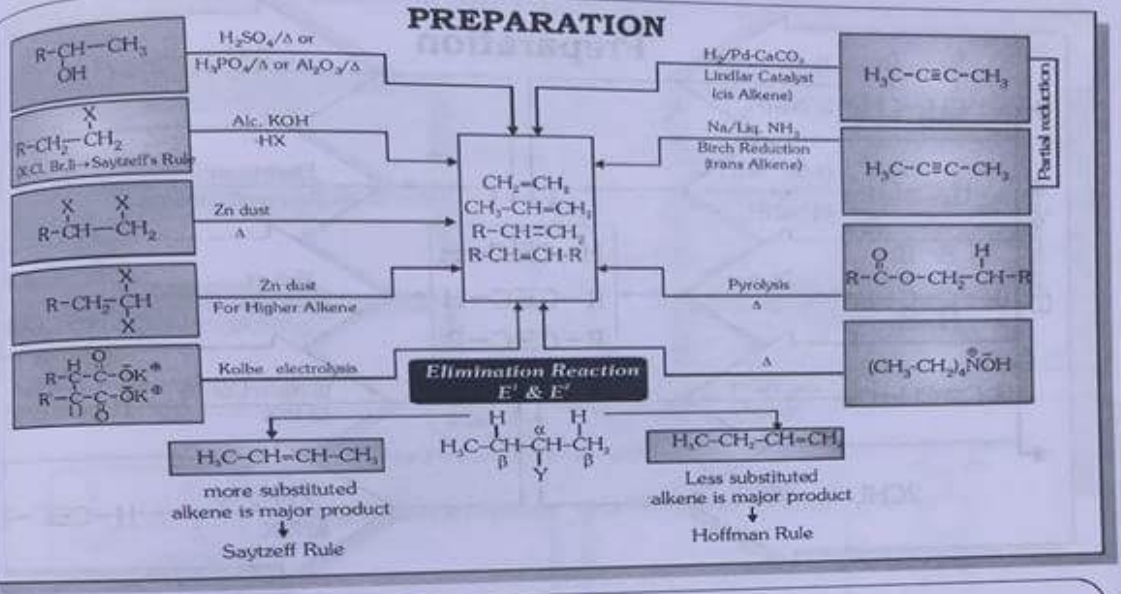
- Boiling point decrease with increase in number of side chain.

$CH_3-CH_2-CH_2-CH_2-CH_3>CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_3>CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3$

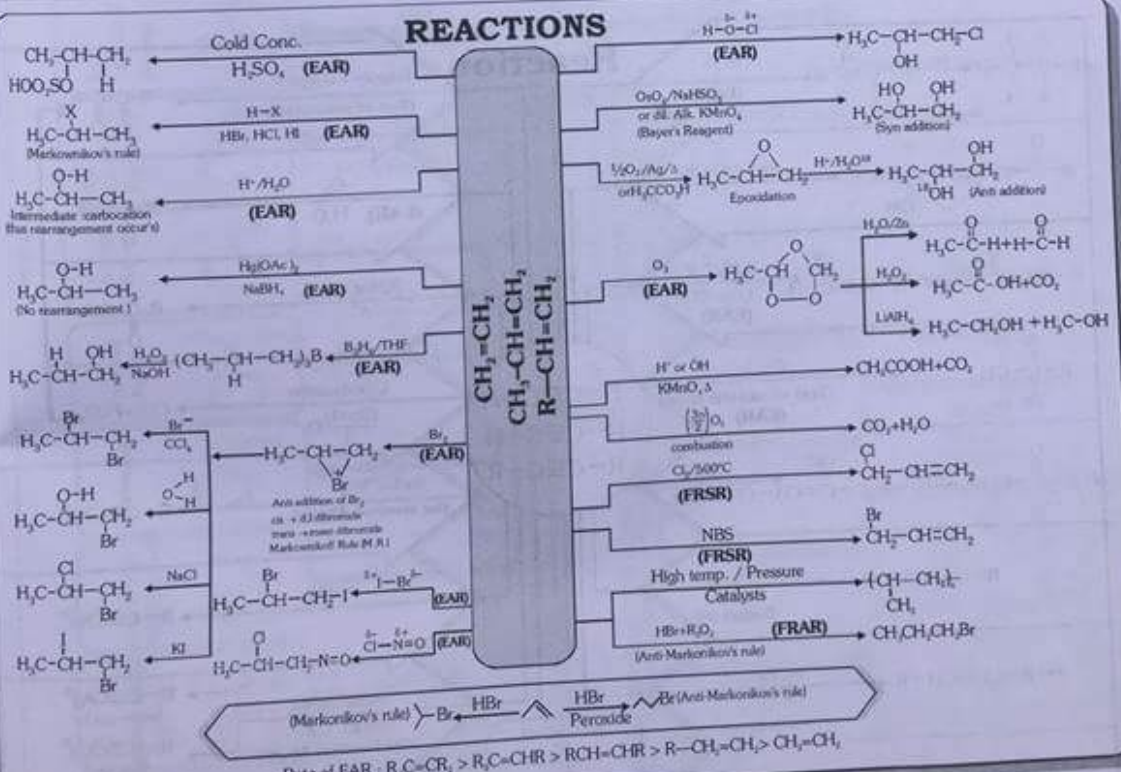
normal iso neo

HYDROCARBON - ALKENE

PREPARATION



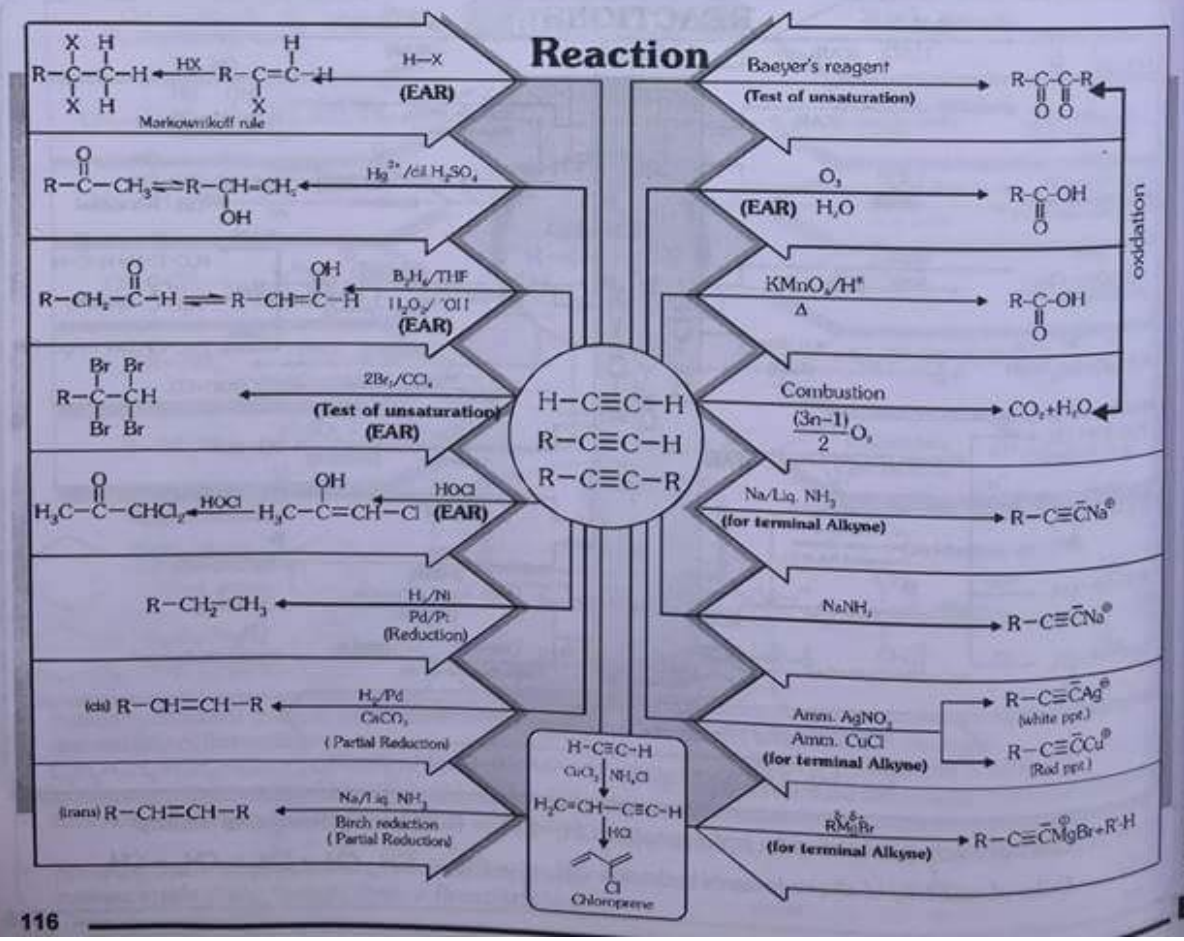
REACTIONS



- Order of reactivity of olefins for hydrogenation $CH_2=CH_2 > R\text{-}CH=CH_2$ (Reverse of stability)
- Order of reactivity of alkene towards hydration $CH_3\text{-}\underset{CH_3}{\overset{CH_3}{C}}=CH_2 > CH_3\text{-}CH=CH_2 > CH_2=CH_2$

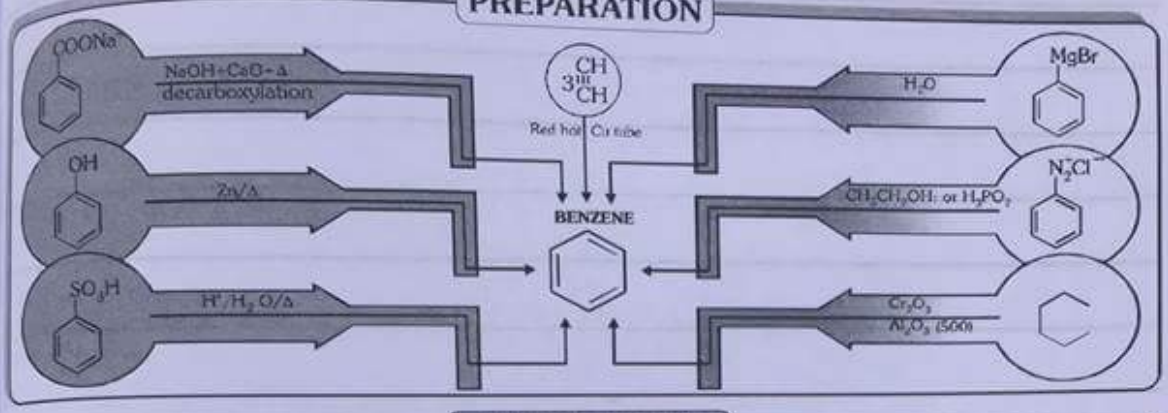
CHAPTER 6

HYDROCARBON - ALKYNE



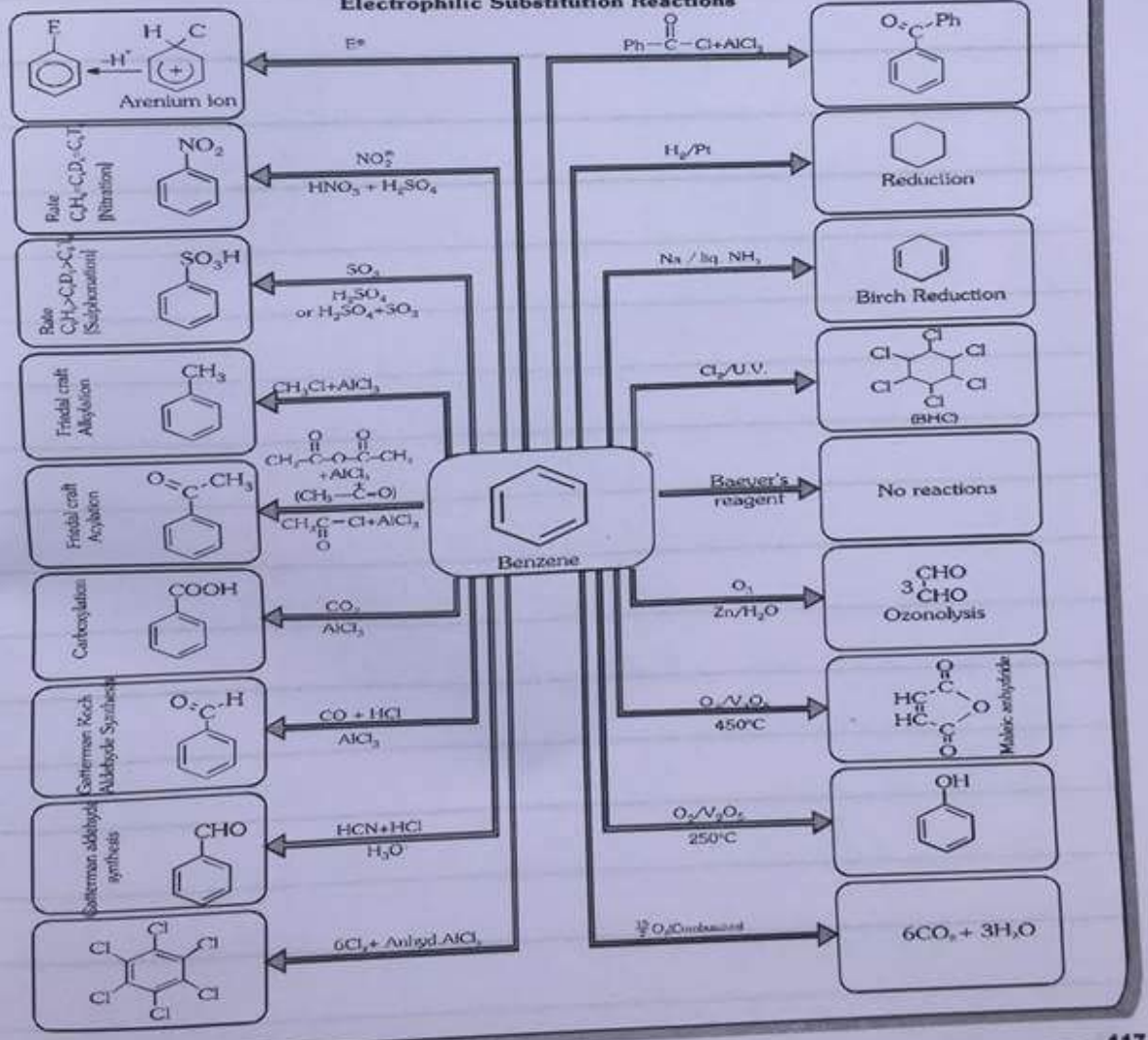
HYDROCARBON - BENZENE

PREPARATION

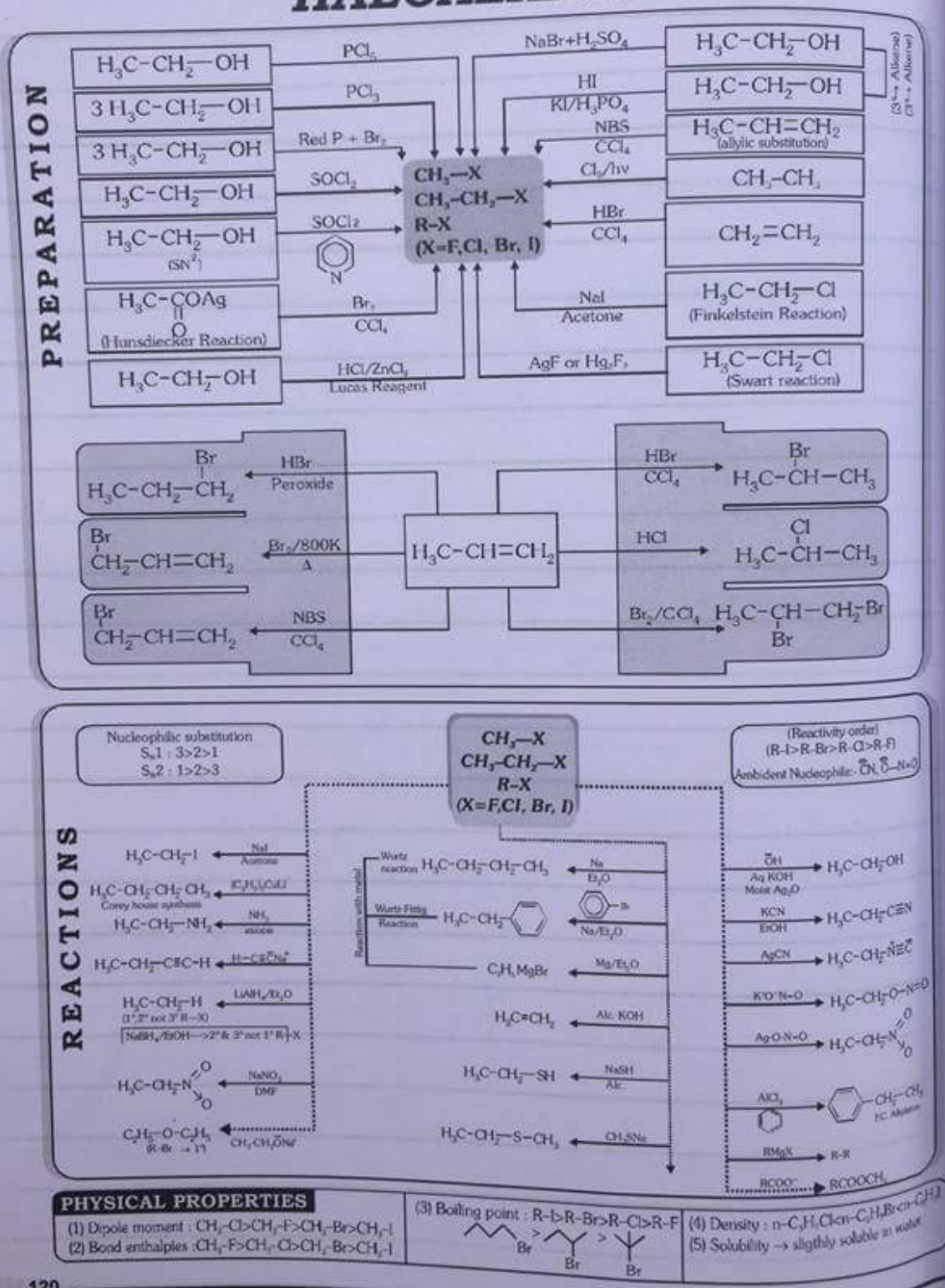


REACTIONS

Electrophilic Substitution Reactions



HALOALKANE



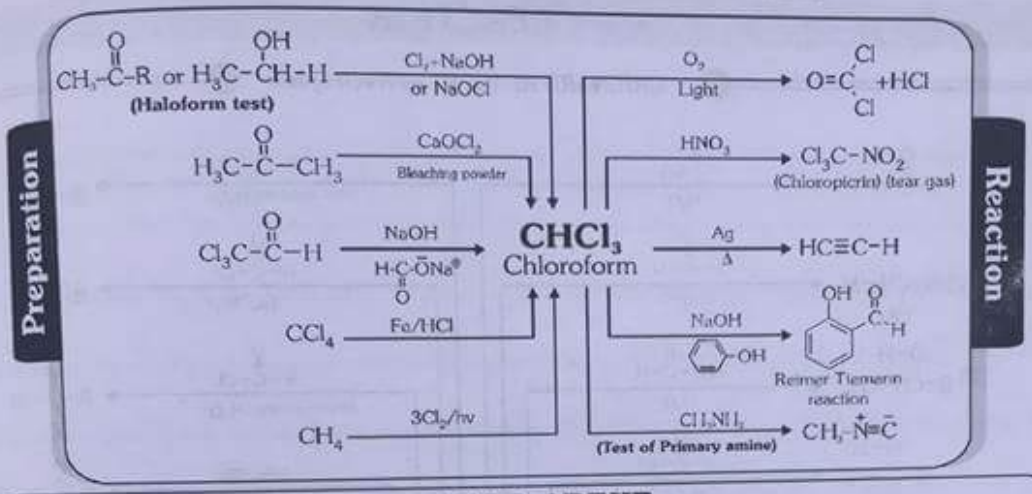
PHYSICAL PROPERTIES

(1) Dipole moment : $CH_3-Cl>CH_3-F>CH_3-Br>CH_3-I$
(2) Bond enthalpies : $CH_3-F>CH_3-Cl>CH_3-Br>CH_3-I$

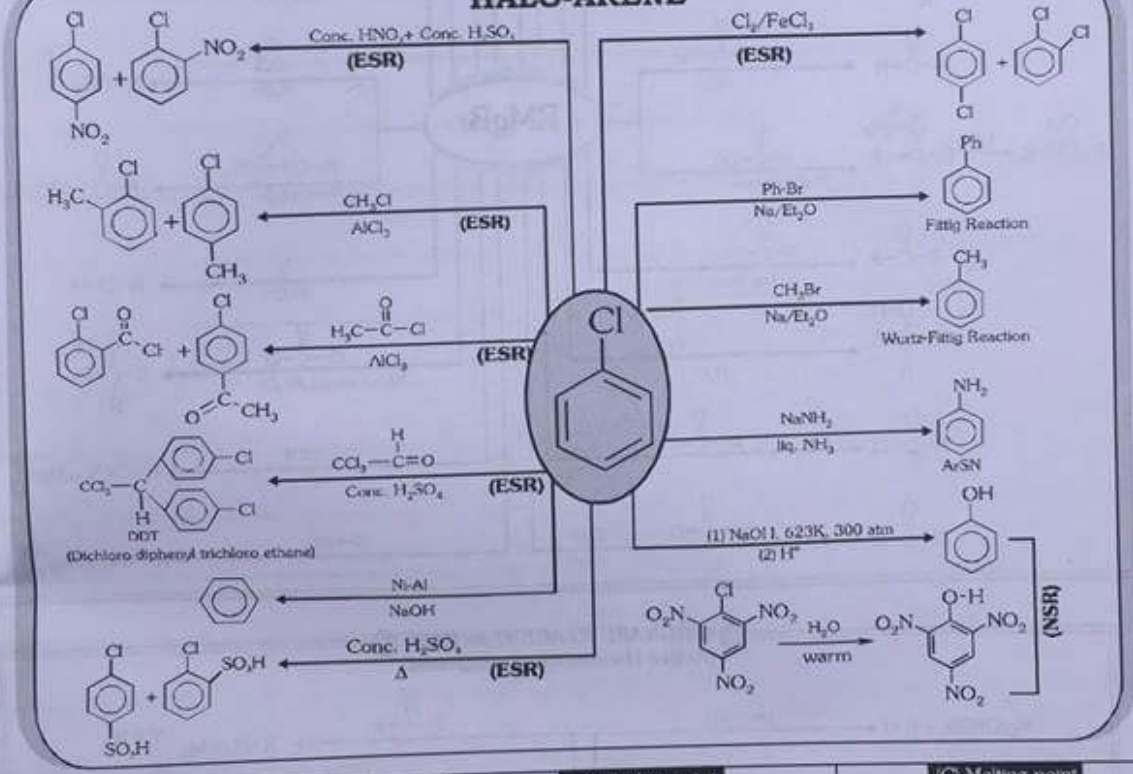
(3) Boiling point : R-I>R-Br>R-Cl>R-F

(4) Density : $n-C_3H_7Cl<n-C_3H_7Br<n-C_3H_7I$
(5) Solubility → slightly soluble in water

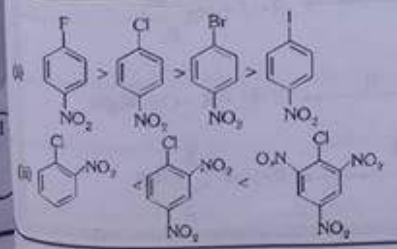
TRI-HALO ALKANE



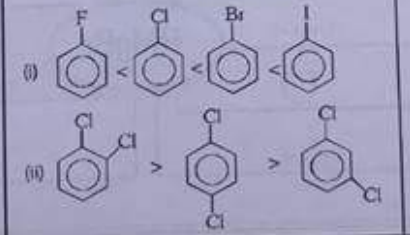
HALO-ARENE



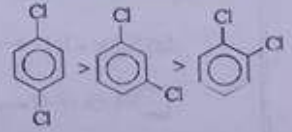
(A) [Reactivity toward Nucleophile]



(B) Boiling point



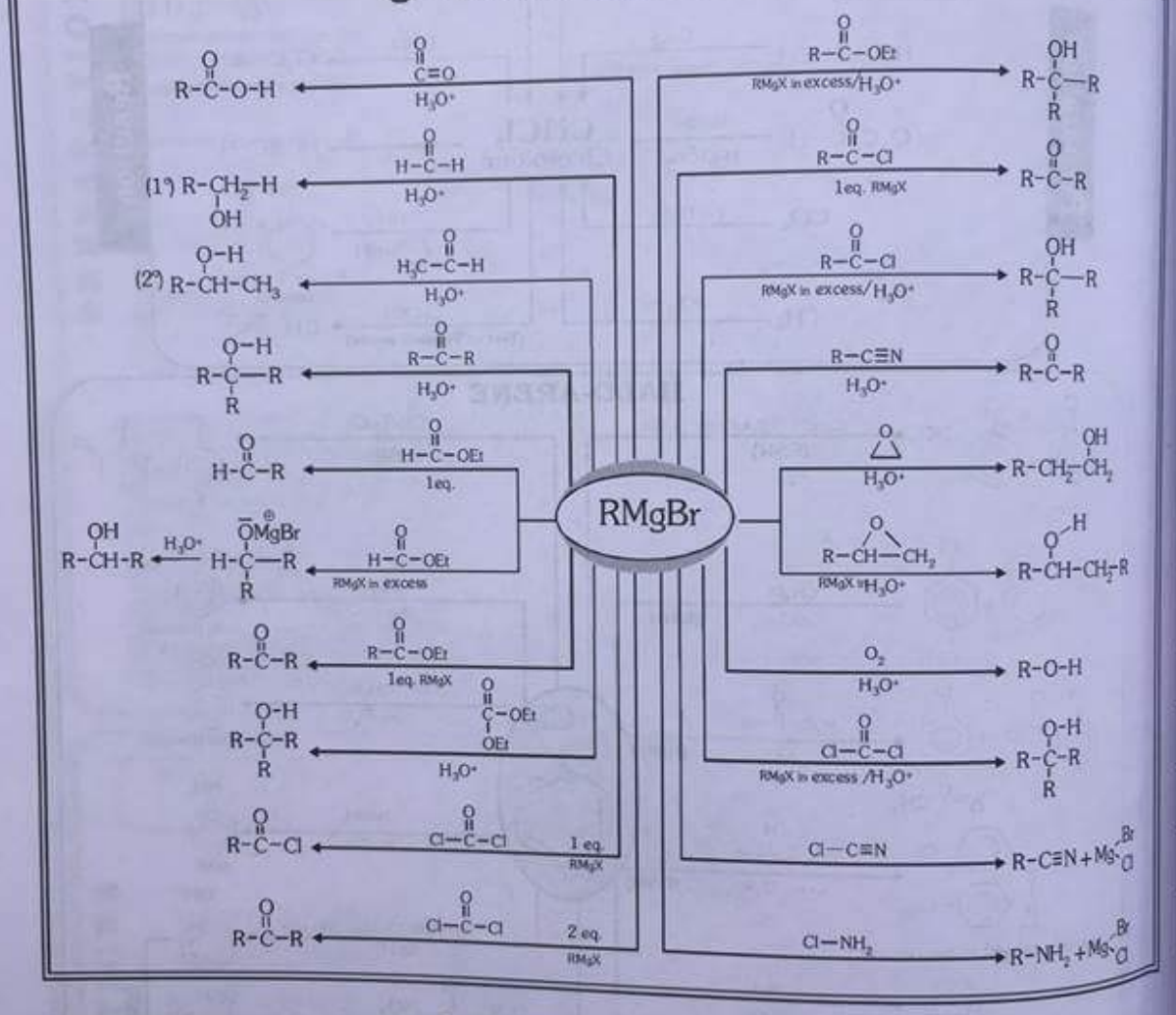
(C) Melting point



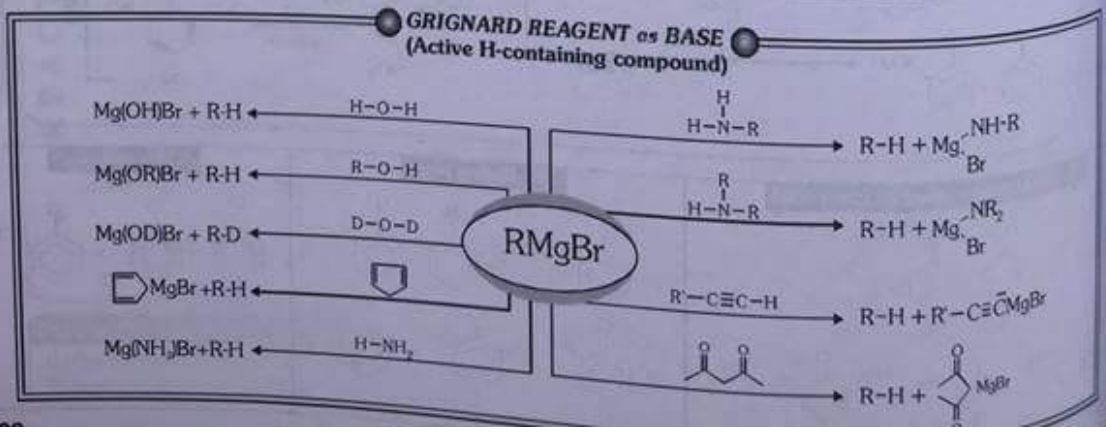
GRIGNARD REAGENT

REACTION

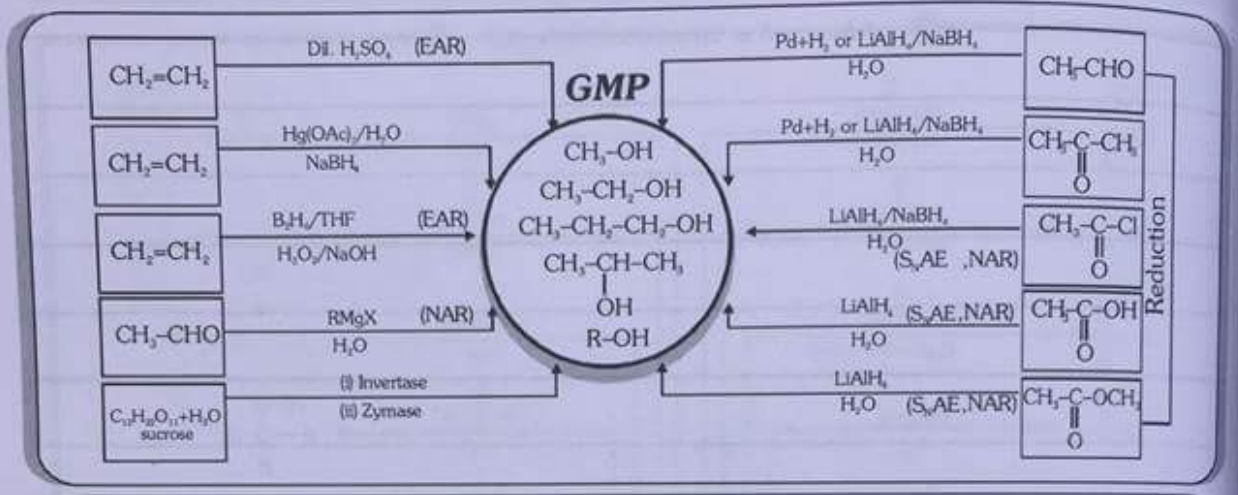
GRIGNARD REAGENT as Nucleophile

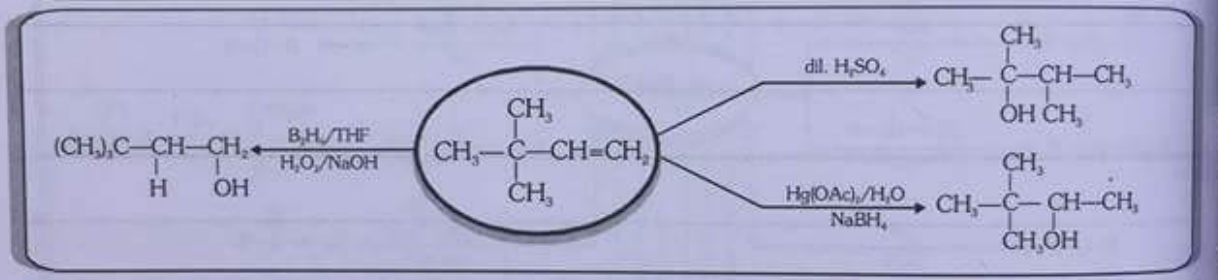


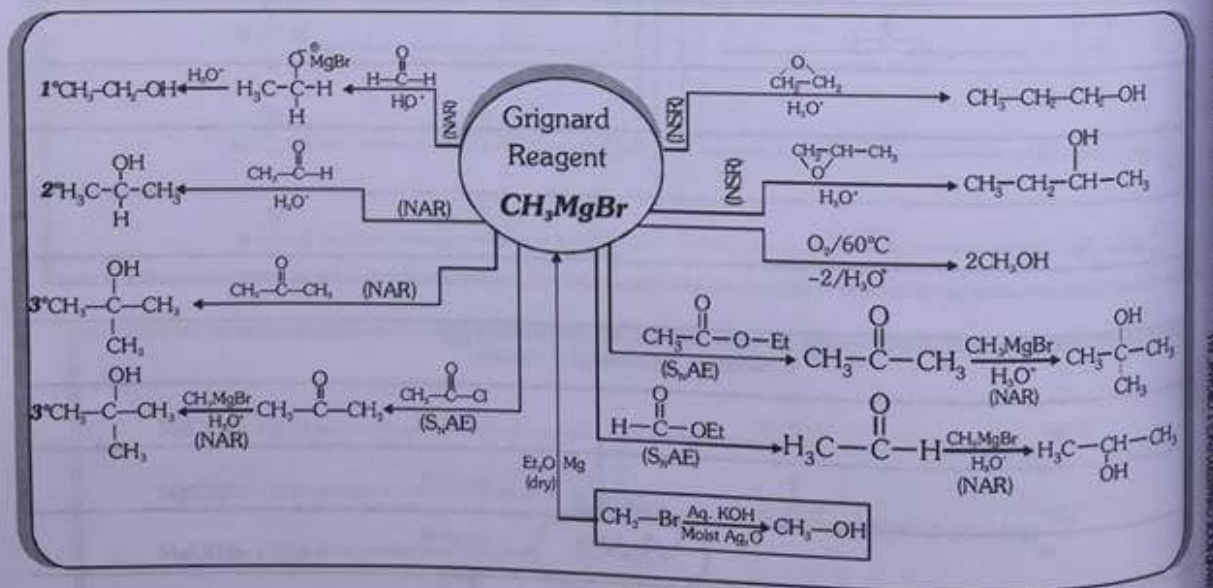
GRIGNARD REAGENT as BASE
(Active H-containing compound)



ALCOHOL



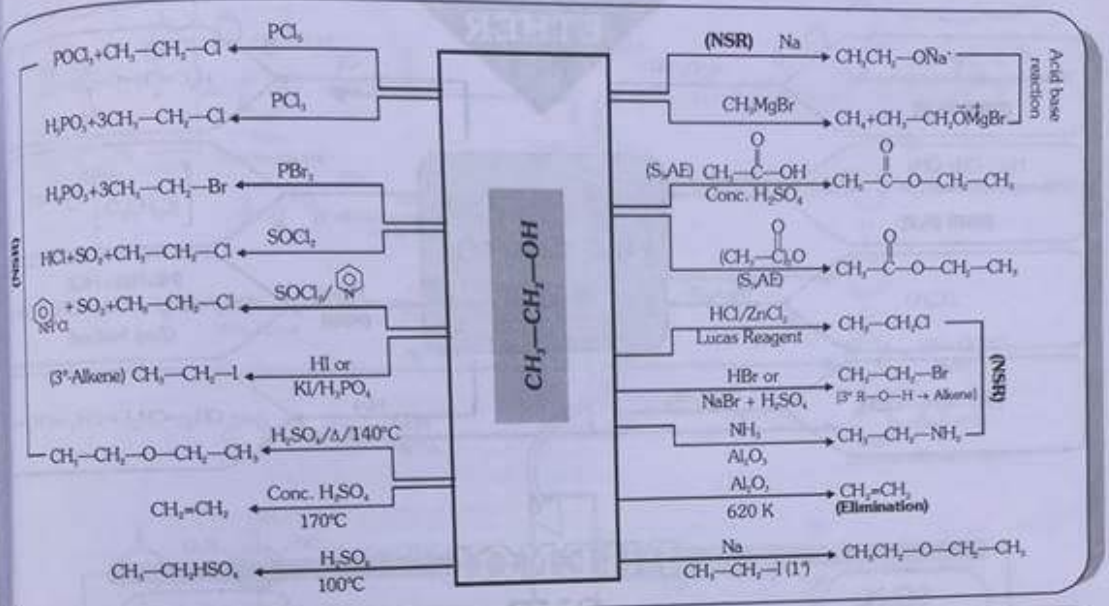




- Solubility of alcohol increase with increase in branching n < iso < neo (isomeric)
- Relative order of reactivity

(i) 1° > 2° > 3° (O–H bond fission) (ii) 3° > 2° > 1° (C–O bond fission) (iii) 3° > 2° > 1° (Dehydration)

ALCOHOL

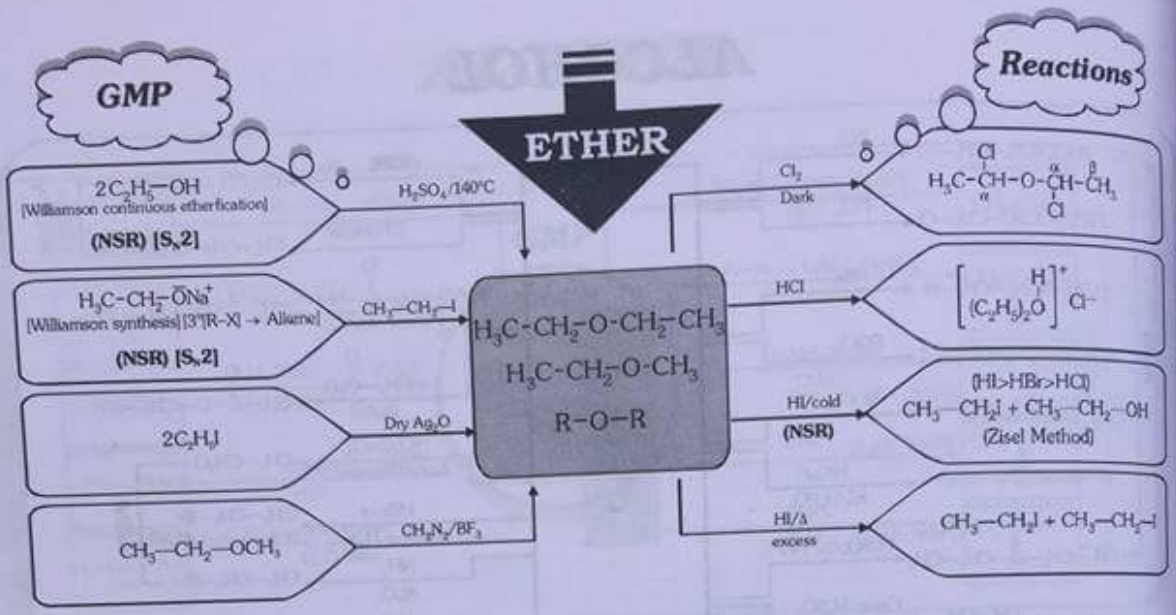


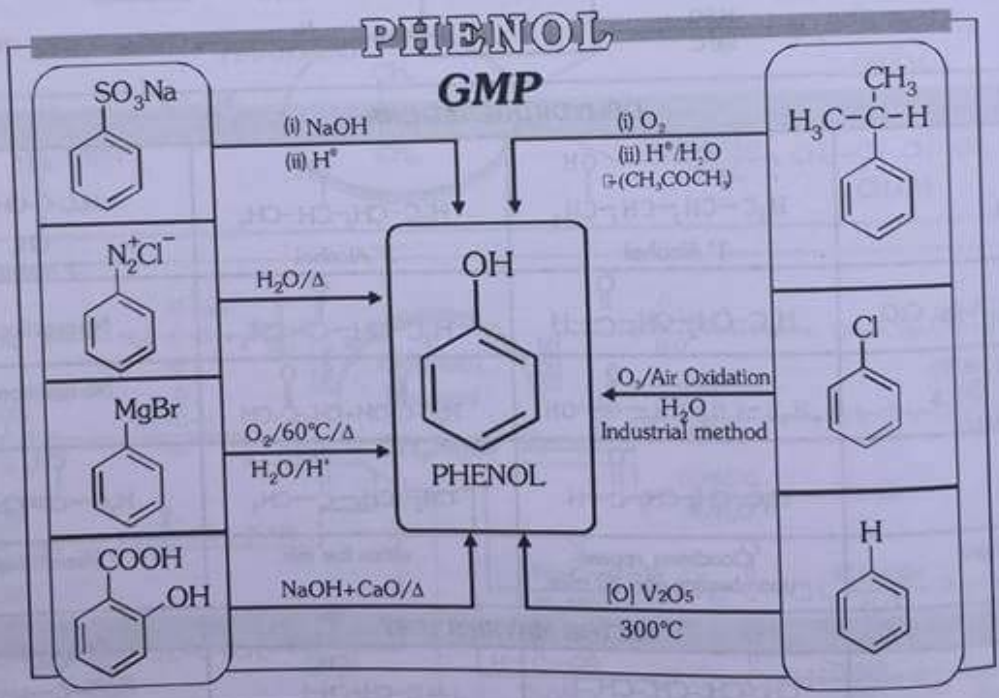
DEHYDROGENATIONS

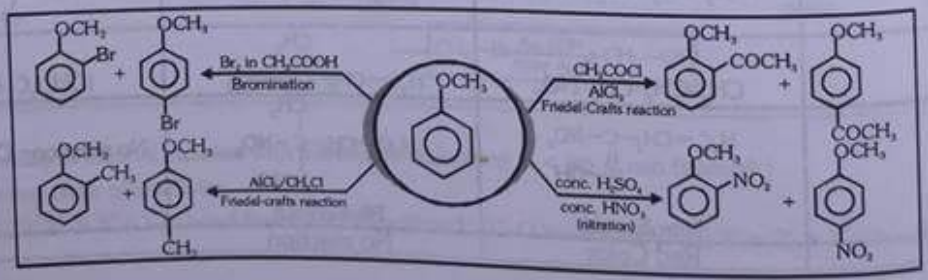
eagent	$H_3C-CH_2-CH_2-CH_2-OH$ 1° Alcohol	$H_3C-CH_2-CH(OH)-CH_3$ 2° Alcohol	$H_3C-C(CH_3)_2-OH$ 3° Alcohol
CC/PDC Anhy. CrO_3	$H_3C-CH_2-CH_2-CHO$	$H_3C-CH_2-CO-CH_3$	No reaction
$K_2Cr_2O_7/H^\oplus$ $MnO_4/H^+/\bar{O}H/\Delta$ ones Reagent	$H_3C-CH_2-CH_2-COOH$	$H_3C-COOH+CH_3-COOH$	No reaction
u/500°C	$H_3C-CH_2-CH_2-CHO$	$CH_3-CH_2-CO-CH_3$	$H_3C-C(CH_3)=CH_2$
Lucas Reagent $HCl/ZnCl_2$	Cloudiness appear upon heating after 30 mins.	within five min.	Immediately

VICTOR MAYER'S TEST

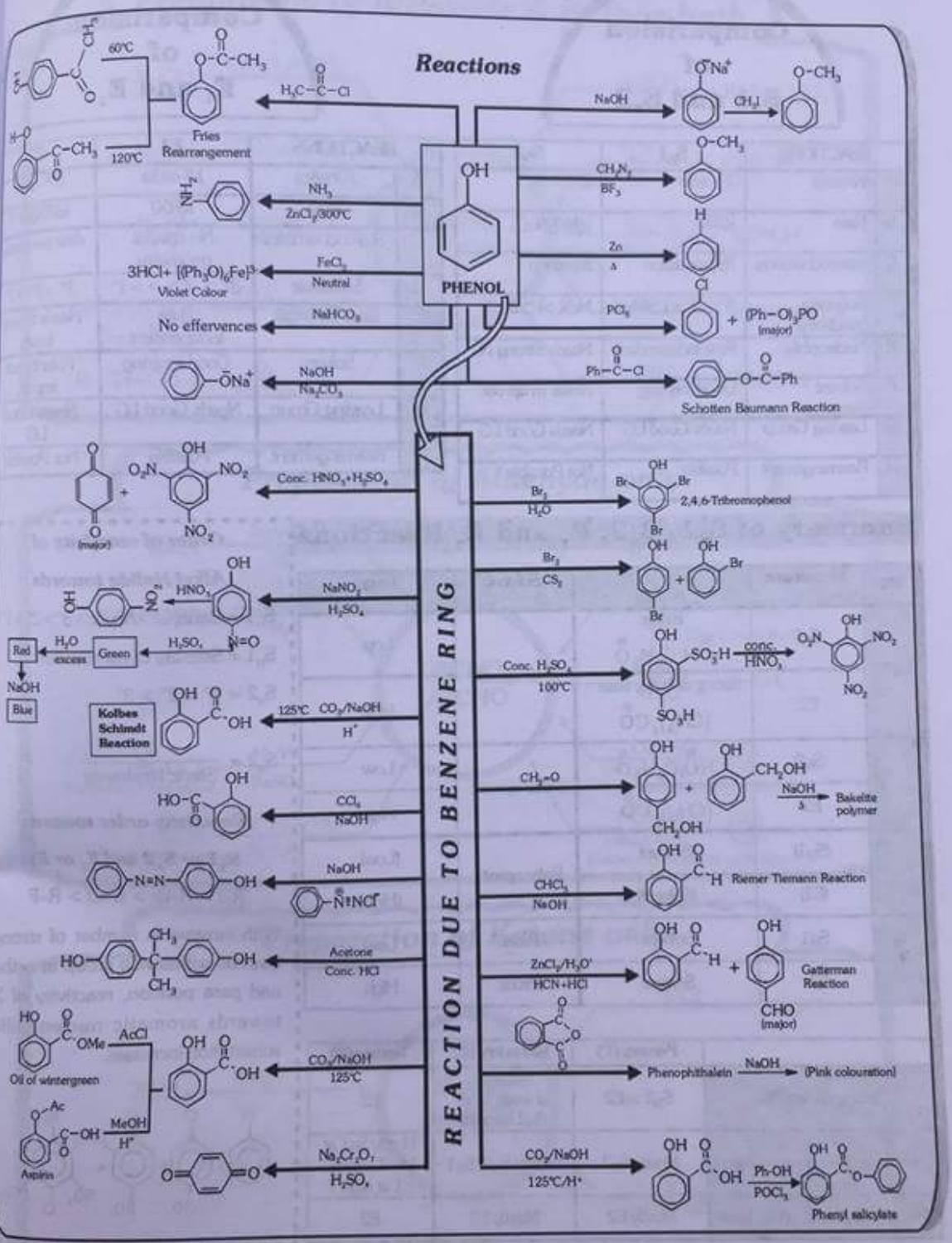
PI_2	$CH_3-CH_2-CH_2-CH_2-I$	$H_3C-CH_2-CH(CH_3)-I$	$H_3C-C(CH_3)_2-I$
$AgNO_2$	$CH_3-CH_2-CH_2-NO_2$	$H_3C-CH_2-CH(CH_3)-NO_2$	$(CH_3)_3C-NO_2$
HNO_2	$H_3C-CH_2-C(=N-OH)-NO_2$ Nitrolic acid	$H_3C-CH_2-C(CH_3)(N=O)-NO_2$ Blue colour	No reaction : Colourless
NaOH	Red Color	No reaction	


GMP
ETHER
Reactions
2C2H5–OH
[Williamson continuous etherfication]
(NSR) [Sn2]
H2SO4/140°C
H3C-CH2-ONa+
[Williamson synthesis] [3°R-X → Alkene]
(NSR) [Sn2]
CH3–CH2–I
2C2H5I
Dry Ag2O
CH3–CH2–OCH3
CH2N2/BF3
H3C-CH2-O-CH2-CH3
H3C-CH2-O-CH3
R–O–R
Cl2
Dark
HCl
HI/cold
(NSR)
HI/Δ
excess
(HI>HBr>HCl)
CH3–CH2I + CH3–CH2–OH
(Zisel Method)
CH3–CH2I + CH3–CH2–I


PHENOL
GMP
SO3Na
(i) NaOH
(ii) H+
(i) O2
(ii) H+/H2O
(CH3COCH3)
N2+Cl−
H2O/Δ
OH
PHENOL
MgBr
O2/60°C/Δ
H2O/H+
O2/Air Oxidation
H2O
Industrial method
COOH
OH
NaOH+CaO/Δ
[O] V2O5
300°C
Cl
H


Br2 in CH3COOH
Bromination
CH3COCl
AlCl3
Friedel-Crafts reaction
AlCl3/CH3Cl
Friedel-crafts reaction
conc. H2SO4
conc. HNO3
(nitration)

PHENOL


Reactions
PHENOL
REACTION DUE TO BENZENE RING
Fries Rearrangement
60°C
120°C
NaOH
CH3I
NH3
ZnCl2/300°C
CH2N2
BF3
Zn
Δ
FeCl3
Neutral
3HCl+ [(Ph3O)6Fe]3
Violet Colour
NaHCO3
No effervences
PCl5
(Ph–O)3PO
(major)
NaOH
Na2CO3
Ph–C(=O)–Cl
Schotten Baumann Reaction
Conc. HNO3+H2SO4
(major)
Br2
H2O
2,4,6-Tribromophenol
Br2
CS2
NaNO2
H2SO4
HNO2
H2O
excess
Red
Green
H2SO4
NaOH
Blue
Conc. H2SO4
100°C
conc. HNO3
Kolbes Schmidt Reaction
125°C CO2/NaOH
H+
CCl4
NaOH
CH2=O
NaOH
Δ
Bakelite polymer
NaOH
Riemer Tiemann Reaction
CHCl3
NaOH
Acetone
Conc. HCl
ZnCl2/H2O
HCN+HCl
Gattermann Reaction
(major)
Oil of wintergreen
AcCl
MeOH
H+
Aspirin
CO2/NaOH
125°C
Phenophthalein
NaOH
(Pink colouration)
Na2Cr2O7
H2SO4
CO2/NaOH
125°C/H+
Ph-OH
POCl3
Phenyl salicylate

Comparision of S_N1 and S_N2

	REACTIONS	S_N1	S_N2
A	Kinetics	1st order	2nd order
B	Rate	k[RX]	k[RX][Nu:$^{\ominus}$]
C	Stereochemistry	Racemisation	Inversion
D	Substrate (reactivity)	3°> 2°>1°>MeX	MeX >1°>2°>3°
E	Nucleophile	Rate Independent	Needs Strong Nu
F	Solvent	Good ionizing	Faster in aprotic
G	Leaving Group	Needs Good LG	Needs Good LG
H	Rearrangement	Possible	Not Possible

Comparision of E_1 and E_2

	REACTIONS	E1	E2
A	Kinetics	1st order	2nd order
B	Rate	k[RX]	k[RX][B:$^{-}$]
C	Stereochemistry	No special geometry	Anti-periplanar
D	Substrate	3° > 2°>>>1°	3° >2° >1°
E	Base Strength	Rate Independent	Needs Strong bases
F	Solvent	Good ionizing	Polarity not import
G	Leaving Group	Needs Good LG	Needs Good LG
H	Rearrangement	Possible	Not Possible

Summary of S_N1, S_N2, E_1 and E_2 Reactions

RX	Mechanism	$\overset{\ominus}{Nu}/\overset{\ominus}{B}$	Solvent	Temp.
1°	S_N2	Better $\overset{\ominus}{O}H, C_2H_5\overset{\ominus}{O}$	Polar aprotic	Low
	E2	Strong & bulky base $(CH_3)_3C\overset{\ominus}{O}$		High
2°	S_N2	$\overset{\ominus}{H}O, C_2H_5\overset{\ominus}{O}$	Polar aprotic	Low
	E2	$(CH_3)_3C\overset{\ominus}{O}$		High
	(S_N1)	(Solvent	Polar aprotic	(Low)
	(E1)	(Solvent)		(High)
3°	S_N1	Solvent	Protic	Low
	E1	Solvent	Protic	High

	Primary (1°)	Secondary (2°)	Tertiary (3°)
Strong nucleophile	S_N2 >>E2	$S_N2 + E_2$ (If weak base, S_N2 favored)	E2
Weak nucleophile weak base	Mostly S_N2	Mostly S_N2/S_N1	Mostly S_N1 at low T mostly E1 at high T
Weak nucleophile strong base	Mostly E2	Mostly E2	E2

Order of reactivity of Alkyl Halide towards

$S_N1 \propto$ Benzylic>Allylic>3°>2°>1°

$S_N1 \propto$ Stability of carbocation

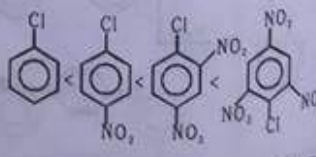
$S_N2 \propto 1° > 2° > 3°$

$$S_N2 \propto \frac{1}{\text{Steric hindrance}}$$

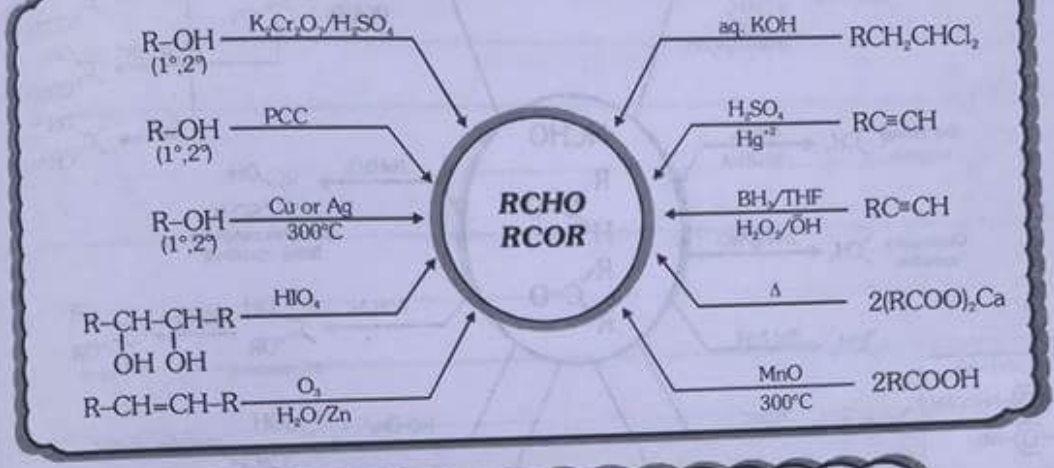
Reactivity order towards S_N1 or S_N2 and E_1 or E_2

R–I > R–Br > R–Cl > R–F

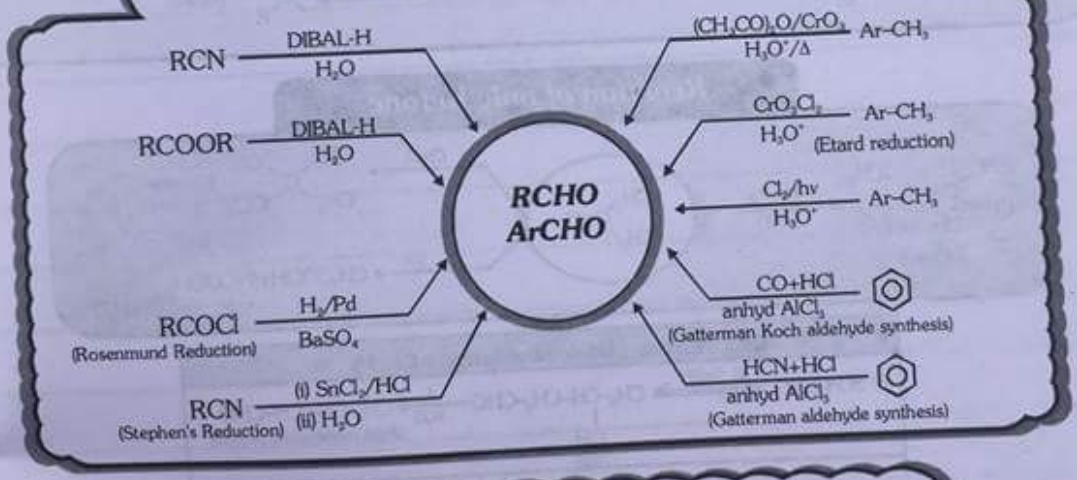
With increase in number of strong electron withrawing group at ortho and para position, reactivity of X towards aromatic nucleophilic substitution increases.



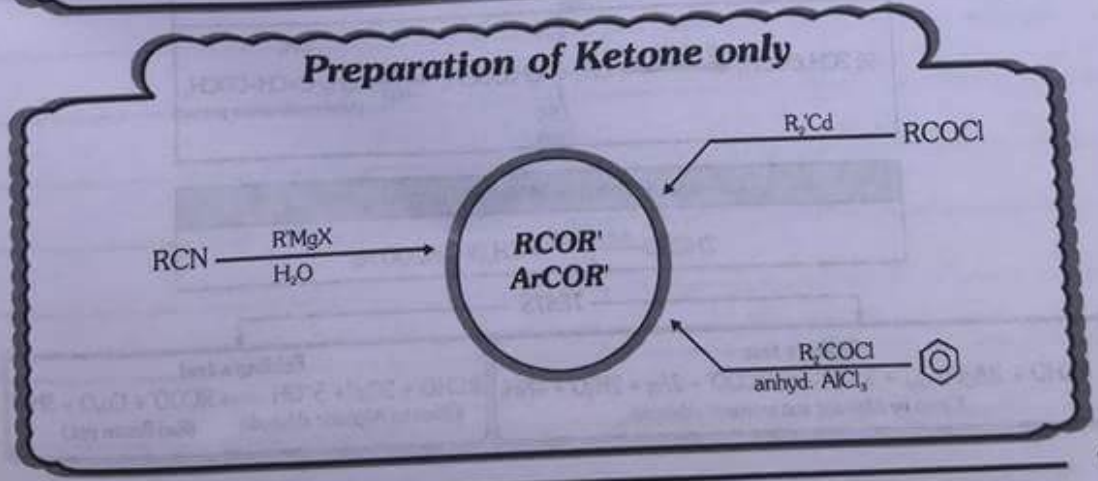
Preparation of Aldehyde & Ketone both



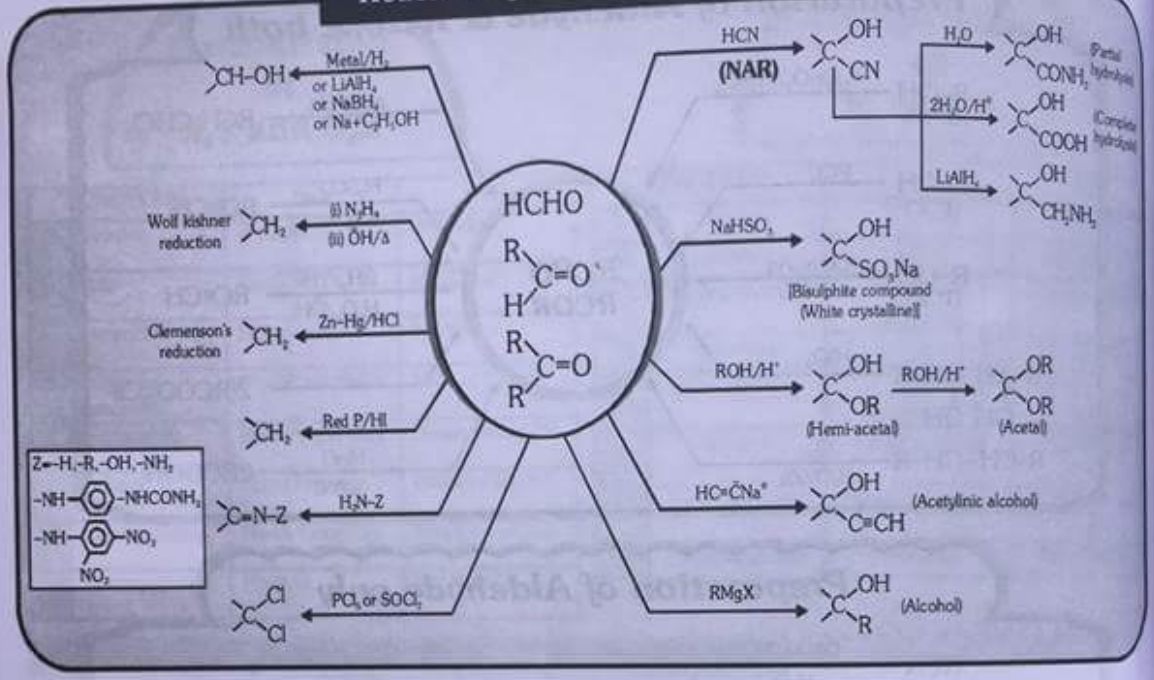
Preparation of Aldehyde only



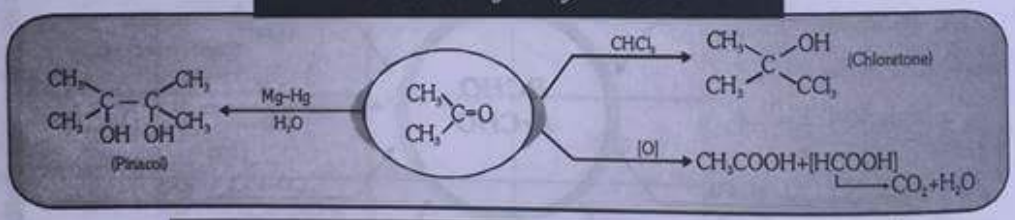
Preparation of Ketone only



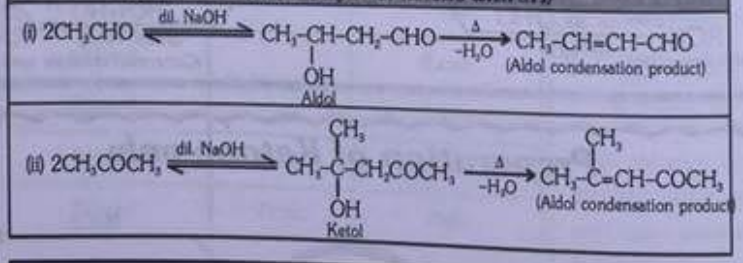
Reaction of Aldehyde & Ketone



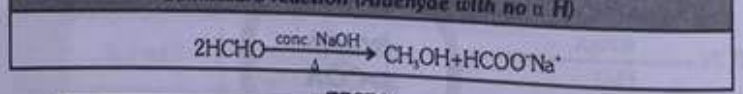
Reaction of only Ketone



Aldol Reaction (Aldehyde or ketone with α H)



Cannizzaro reaction (Aldehyde with no α H)



TESTS

Tollen's test :-

$RCHO + 2[Ag(NH_3)_2]^+ + 3\ ^-OH \longrightarrow RCOO^- + 2Ag + 2H_2O + 4NH_3$

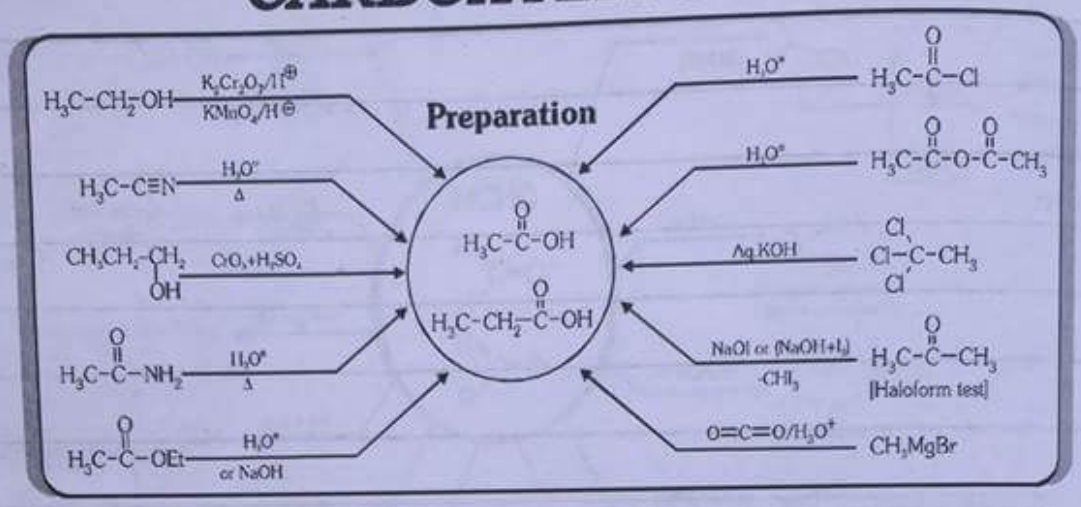
(Given by Aliphatic and aromatic aldehyde)

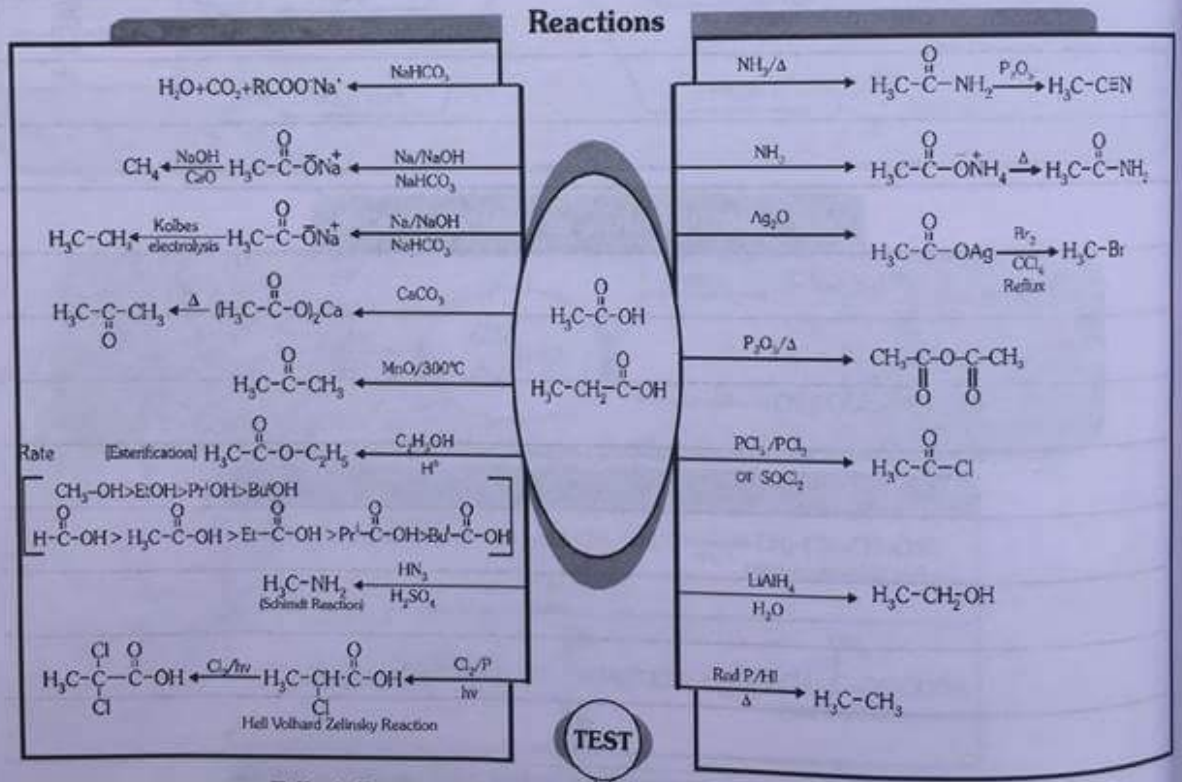
Fehling's test

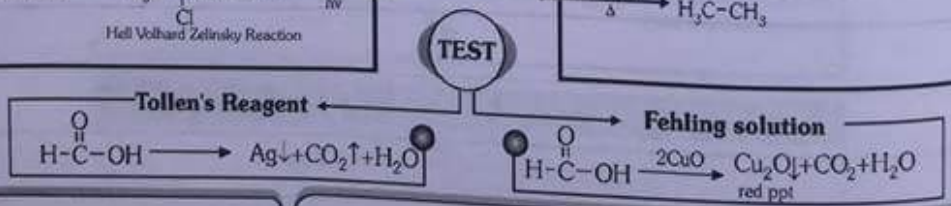
$RCHO + 2Cu^{+2} + 5\ ^-OH \longrightarrow RCOO^- + Cu_2O + 3H_2O$

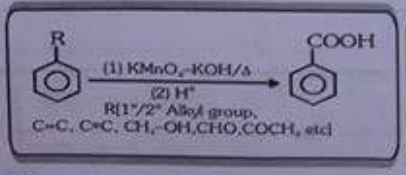
(Given by Aliphatic aldehyde) (Red-Brown ppt.)

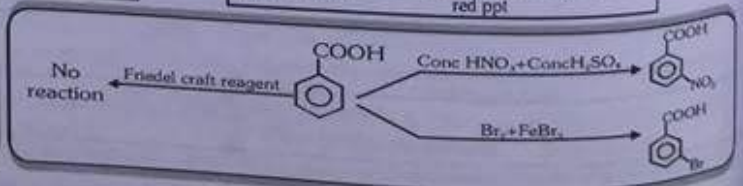
CARBOXYLIC ACID





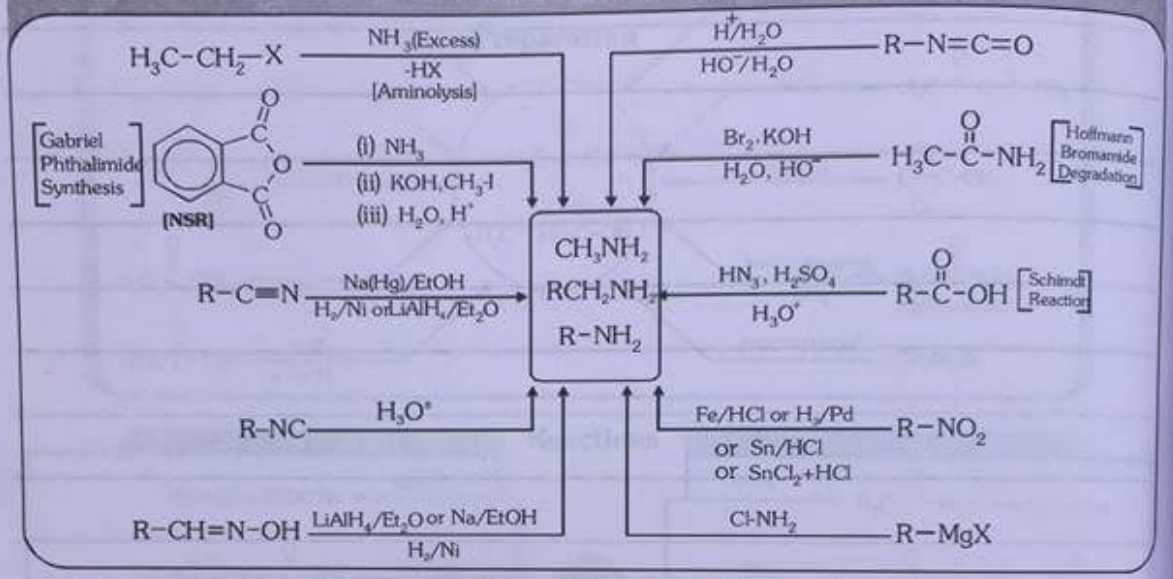




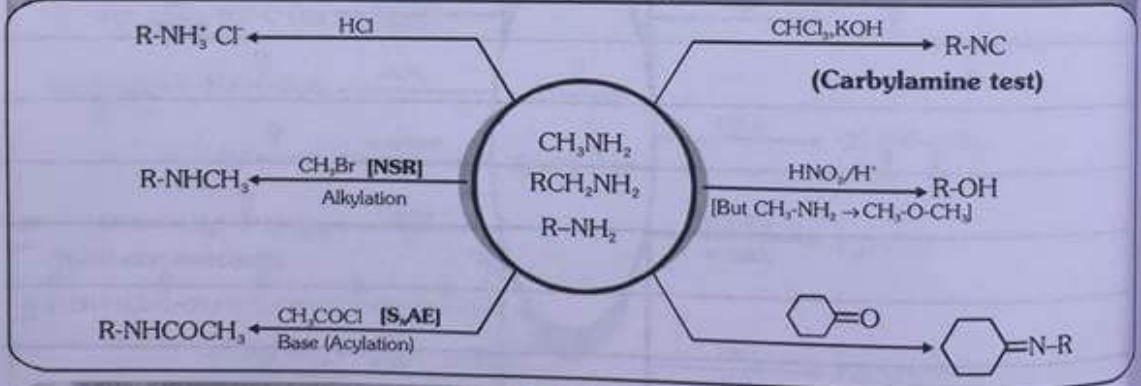


AMINES

PREPARATION



REACTION

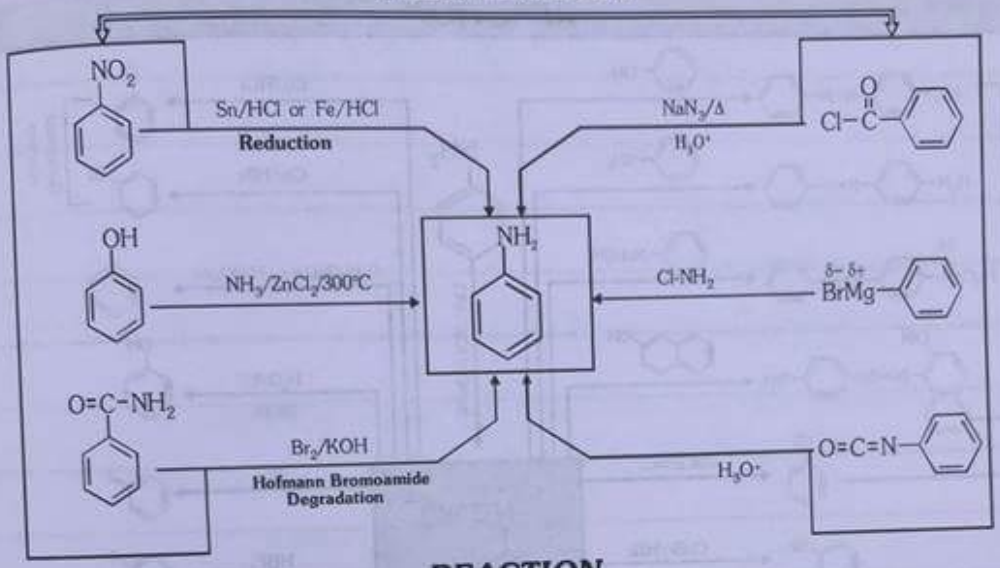


TEST

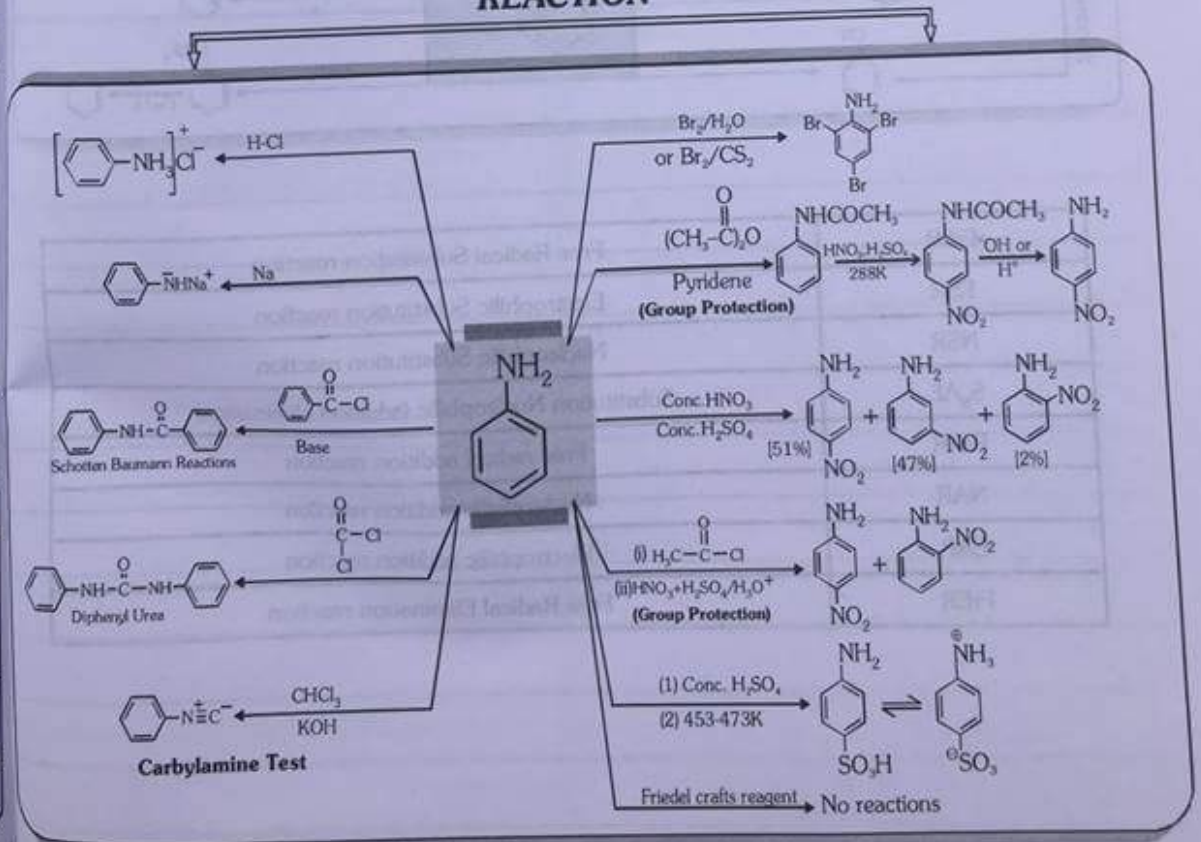
Reagent	$R-\ddot{N}H_2$(1°)	$R_2\ddot{N}H$(2°)	$R_3\ddot{N}$(3°)	$\ddot{N}H_2$
$Ph-SO_2Cl$ (Hinsberg reagent)	$R-\underset{H}{\overset{}{N}}-SO_2-Ph$ soluble $\xrightarrow{NaOH}$ $[R-\overset{\ominus}{N}-SO_2-Ph]Na^+$	$R_2N-\overset{O}{\overset{\|}{S}}-Ph$ $\xrightarrow[O]{NaOH}$ Insoluble	No reaction	$NH-SO_2-Ph$
$C=S$ $\Delta/HgCl_2$ Mustard oil test	$R-NH-\overset{S}{\overset{\|}{C}}-SH$ $\xrightarrow[\Delta]{HgCl_2}$ $R-N=C=S+HgS$	$R_2N-\overset{S}{\overset{\|}{C}}-SH$ $\xrightarrow[\Delta]{HgCl_2}$ No reaction	No reaction	$\xrightarrow{KOH}$ $Ph-N=C=S+HgS$

ANILINE

PREPARATION

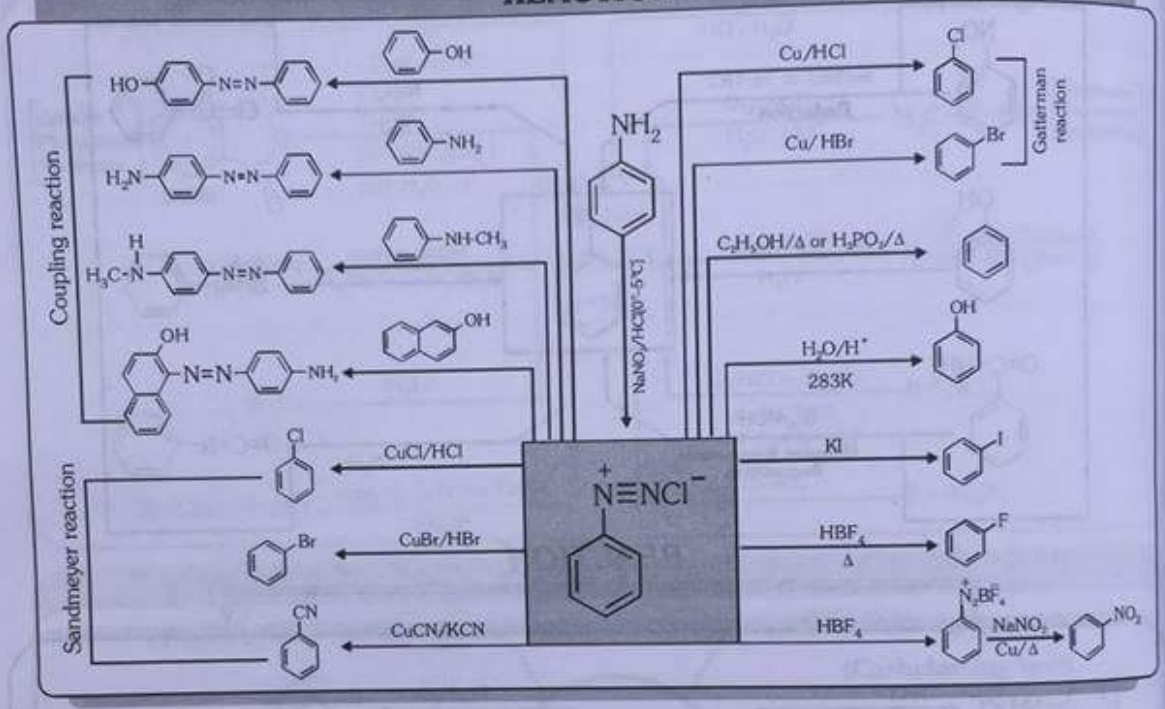


REACTION



BENZENE DIAZONIUM CHLORIDE

REACTION



FrSR	Free Radical Substitution reaction
ESR	Electrophilic Substitution reaction
NSR	Nucleophilic Substitution reaction
S_NAE	Substitution Nucleophilic (addition elimination)
FrAR	Free radical addition reaction
NAR	Nucleophilic addition reaction
EAR	Electrophilic addition reaction
FrER	Free Radical Elimination reaction

CHAPTER 13

Nutshell review & preview of ORGANIC REAGENTS

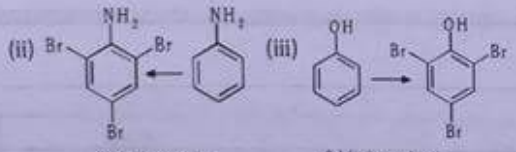
1. Alcoholic KOH
R—X → Alkene ; Elimination

2. Aluminium Ethoxide
$RCH{=}O \longrightarrow R{-}\underset{\underset{O}{\|}}{C}{-}O{-}CH_2R$ (Tischenko Reaction)
(Aldehyde) (Ester)

3. Aqueous KOH/NaOH
R—X → ROH
Nucleophilic substitution reaction also used for Cannizzaro reaction with aldehyde.

4. Baeyer's Reagent (Alkaline cold dilute $KMnO_4$)
$RCH{=}CHR' \longrightarrow RCH(OH){-}CHR'(OH)$ (Syn)
alkene ⟶ 1, 2 diol
(used to detect unsaturation)

5. Bromine water
(i) used to detect unsaturation;

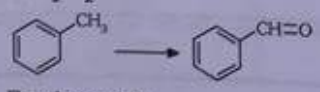


2,4,6-tribromoaniline 2,4,6-tribromophenol

6. Benedict's solution
Used to detect aldehyde group RCHO → RCO_2^-
[ketone gives -ve test]

7. Cu_2Cl_2 + NH_4OH
Used to Detect Terminal Alkyne
Red Precipitate observed

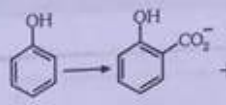
8. CrO_2Cl_2



Etard reaction

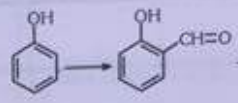
9. CrO_3
(i) $RCH_2OH \rightarrow RCHO$,
(ii) $R_2CHOH \rightarrow R_2C{=}O$
(iii) R_3COH → no reaction

10. CCl_4 + OH^- (Reimer Tiemann)



+ p-Product

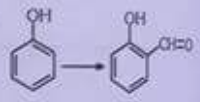
11. CO + HCl + $AlCl_3$



+ p-Product

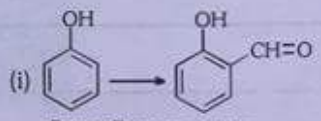
Gatterman koch reaction

12. HCN + HCl + $AlCl_3$



Gatterman Aldehyde Synthesis

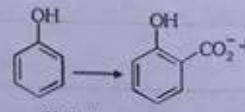
13. $CHCl_3$ + KOH



Reimer Tiemann reaction

(ii) $RNH_2 \rightarrow RNC$ ***(Carbyl amine reaction)***
(used to detect 1° Amine) (Isocyanide test)

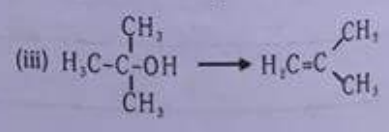
14. CO_2 + OH^- *(high temp. + Pressure)*



+ p-Product

Kolbe's reaction

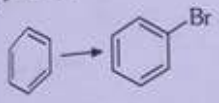
15. Cu/Δ
(i) $RCH_2OH \rightarrow RCHO$,
(ii) $R_2CHOH \rightarrow R_2C{=}O$



16. 2,4 – D.N.P.
used to detect carbonyl group (orange ppt observed)

17. DMSO
Polar aprotic solvent: favour S_N2 mechanism

18. $Fe + Br_2/FeBr_3$



19. Fehling solution

used to identify – CH=O group.
PhCHO gives –ve test
Observation: red ppt of Cu_2O formed

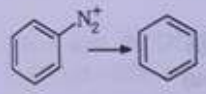
20. Grignard Reagent

Follows (i) Acid base reaction (ii) NAR (iii) NSR

21. $H_2(Pd/CaCO_3)$ Quinoline (Lindlar catalyst)

$R-C\equiv C-R \rightarrow R-CH=CH-R$ (cis)

22. H_3PO_2



23. $HN_3 + H_2SO_4$

$$R-\underset{\underset{O}{\|}}{C}-OH \longrightarrow RNH_2$$

(Schmidt Reaction)

24. H_3PO_4/Δ

$H_3PO_4 \Rightarrow$ Same as H_2SO_4/Δ

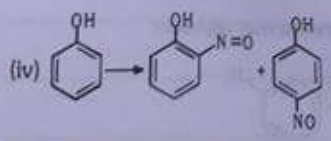
25. H_2SO_4/Δ

$$R\underset{\underset{OH}{|}}{C}H-CH_3 \longrightarrow RCH=CH_2$$

Saytzeff product; C^+ mechanism;
Rearranged alkene can be formed

26. HNO_2 ($NaNO_2 + HCl$)

(i) $RNH_2 \rightarrow R-OH$;
(ii) $PhNH_2 \rightarrow PhN_2^+$ (0 – 5°C)
(iii) $PhNH_2 \rightarrow PhOH$ (high temperature)

(iv) 

27. HIO_4 (Periodic acid)

$$RCH(OH)-CH(OH)-R' \longrightarrow RCH=O + R'CH=O$$

Oxidative cleavage of diol

28. $H_2(Ni)$ can reduce

(i) $R-\underset{\underset{O}{\|}}{C}-R \longrightarrow R_2CHOH$

(ii) $R-\underset{\underset{O}{\|}}{C}-H \longrightarrow RCH_2OH$

(iii) $RCN \rightarrow RCH_2NH_2$; $-C\equiv C- \rightarrow -CH_2-CH_2-$,
$-HC=CH- \rightarrow -CH_2-CH_2-$

29. $H_2(Pd/BaSO_4)$
Quinoline

$$R-\underset{\underset{O}{\|}}{C}-Cl \longrightarrow RCH=O$$

(Rosenmund reduction)

30. Jones Reagent (CrO_3 + dil. H_2SO_4 + acetone)

(i) $RCH_2OH \rightarrow RCH=O$; (ii) $R_2CHOH \rightarrow R_2C=O$

31. $KHSO_4$ Dehydrating Reagent

$$CH_2(OH)-CH(OH)-CH_2-OH \longrightarrow CH_2=CH-CH=O$$

32. $K_2Cr_2O_7/H^+$

(i) $RCH_2OH \rightarrow RCO_2H$; (ii) $R_2CHOH \rightarrow R_2C=O$

33. MnO_2

(i) $CH_3-CH=CH-CH_2-OH \rightarrow CH_3-CH=CH-CH=O$
(ii) $PhCH_2OH \rightarrow PhCH=O$
To oxidise allylic / benzylic hydroxyl group into corresponding carbonyl.

34. $NaHCO_3$

$$RCO_2H \xrightarrow{NaH\overset{14}{C}O_3} RCO_2^-Na^+ + \overset{14}{C}O_2\uparrow$$

35. $NaHSO_3$

$$R-\underset{\underset{O}{\|}}{C}-R \rightarrow RC(OH)(SO_3Na^+)$$

[White crystals, soluble in water used to separate carbonyl from noncarbonyl compound]

36. NaOH(aq)

(i) $R-X \rightarrow R-OH$

(ii) $$R-\underset{\underset{O}{\|}}{C}-OR' \xrightarrow[H_2O]{NaOH} R-\underset{\underset{O}{\|}}{C}-O^- + R'OH$$

Basic hydrolysis of ester

(iii) $HCHO \xrightarrow{OH^-} HCO_2^- + CH_3OH$ (cannizaro)

(iv) $H_3C-CH=O \xrightarrow[\Delta]{OH^-} H_3C-CH=CH-CH=O$
(Aldol condensation)

37. Ninhydrin
Detection of amino acid
Observation : Purple coloured ion

38. NaOR
Strong base :

(i) $RCH(X)-CH_2-R \longrightarrow RCH=CH-R$
(Saytzeff Product : E_2 elimination)

(ii) $H_3C-\underset{\underset{O}{\|}}{C}-OEt \longrightarrow H_3C-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-OEt$
(claisen condensation) (β keto ester)

39. NaOH + X_2 or NaOX

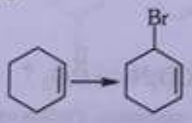
(i) $R\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[-CHI_3]{} RCO_2^-$ (Haloform reaction)

(ii) $R-\underset{\underset{O}{\|}}{C}-NH_2 \longrightarrow RNH_2$ (Hoffman Degradation)

40. NaOH + CaO
$RCO_2H \rightarrow RH$

41. MnO / 300°C
used for $-CO_2$ & $-H_2O$ in carboxylic acid.

42. NBS

(i)  ; (ii) $PhCH_3 \rightarrow PhCH_2-Br$

43. $NaNO_2$ + HCl
$RNH_2 \rightarrow R-OH$

44. $NaNH_2$ in paraffin
Non-terminal Alkyne → Terminal Alkyne
(2-Butyne → 1-butyne)

45. Na/EtOH
Reduce all except c/c double & triple bond

46. Zn(Hg) + HCl [Clemmensen's reduction]

$R-\underset{\underset{O}{\|}}{C}-R \longrightarrow R-CH_2-R$

47. NH_2 -NH_2/OH^- [Wolf Kishner reduction]
$R-CO-R \rightarrow R-CH_2-R$

48. Na in Liq. NH_3 [Birch reduction]

$R-C\equiv CR \longrightarrow \underset{H}{\overset{R}{}}C=C\underset{R}{\overset{H}{}}$
(trans alkene)

49. OsO_4 + H_2O

$RCH=CHR \longrightarrow RCH(OH)-CH(OH)-R$
(syn addition)

50. O_3 : $R-CH=CH-R \xrightarrow[H_2O\,/\,Zn]{O_3} R-CHO + R-CHO$
(Ozonolysis process)

51. Oxirane followed by H^+
$RMgX \rightarrow RCH_2-CH_2-OH$

52. PCC
(i) $RCH_2OH \rightarrow RCHO$,
(ii) $R_2CHOH \rightarrow R_2C=O$
(iii) $R_3COH \rightarrow$ no reaction
(Mild oxidizing reagent)

53. P(red) + Br_2
(i) $CH_3CO_2H \rightarrow H_2C(Br)-CO_2H$ (HVZ reaction)
(ii) $ROH \rightarrow R-Br$

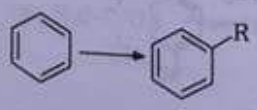
54. P (red) + HI
$CH_3CO_2H \rightarrow CH_3-CH_3$
$CH_3CH=O \rightarrow CH_3-CH_3$
$CH_3CH_2OH \rightarrow CH_3-CH_3$
(strong reducing agent can reduce any oxygen or halogen containing compound to alkane)

55. Perbenzoic acid [Baeyer Villiger Oxidation]

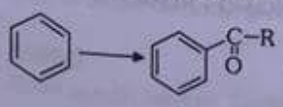
$R-\underset{\underset{O}{\|}}{C}-R' \longrightarrow R-\underset{\underset{O}{\|}}{C}-OR'$

R' having more migrating tendency than R

56. RCl+$AlCl_3$ [Friedel craft alkylation]



57. RCOCl + $AlCl_3$ [Friedel craft acylation]

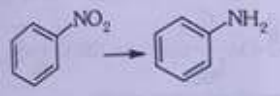


58. $ROH + R-\underset{\underset{O}{\|}}{C}-OH \xrightarrow[H_2SO_4]{conc.} R-\underset{\underset{O}{\|}}{C}-OR$

Ester formed (Esterification reaction)

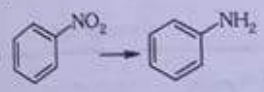
59. **$SnCl_2$ + HCl**

(i) $R-N=N-R' \rightarrow RNH_2 + R'NH_2$

(ii) 

(iii) $RCN \rightarrow RCH=O$ [Stephen reduction]

60. **Sn + HCl**

(i) 

(ii) $RCN \rightarrow R\text{-}CH_2NH_2$

61. **Silver salt RCOOAg** (Hunsdiecker reaction)

$Br_2/CCl_4/\Delta \rightarrow RBr + CO_2 + AgBr$

62. **AgOH/moist Ag_2O**; $R_4\overset{+}{N}\overset{-}{X} \rightarrow R_4\overset{+}{N}\overset{-}{O}H$

63. **$SOCl_2$**

$R-\underset{\underset{O}{\|}}{C}-OH/R-OH \longrightarrow R-\underset{\underset{O}{\|}}{C}-Cl/R-Cl$

64. ***Tollens Reagent Test***

(i) Terminal alkyne gives
(ii) Aldehyde Group gives
(iii) Ketone gives –ve test
(iv) α-hydroxy ketone gives
(v) HCOOH gives
(vi) Hemi acetal gives
(vii) PhNH-OH gives

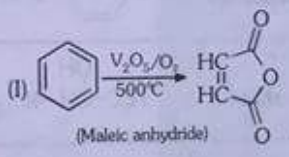
65. ***Benzene sulphonyl chloride***

It is used to distinguish and separate (Hinsberg reagent) 1°, 2° and 3° amines.

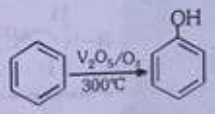
66. ***Tetra ethyl lead (TEL)***

Used as antiknock compound

67. **V_2O_5**

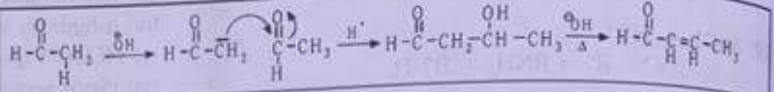
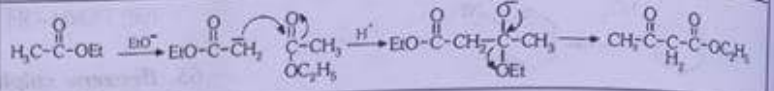
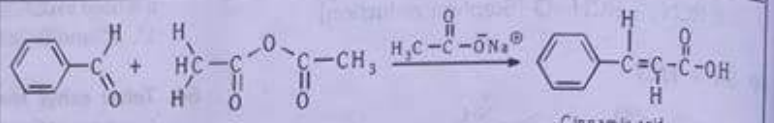
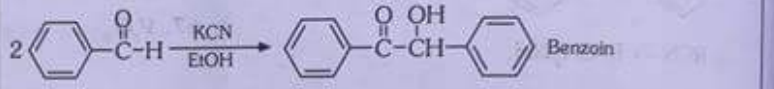
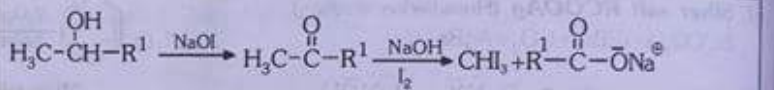
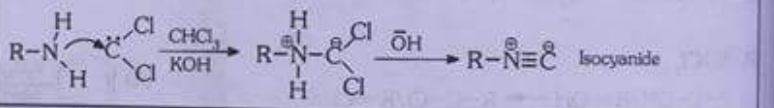
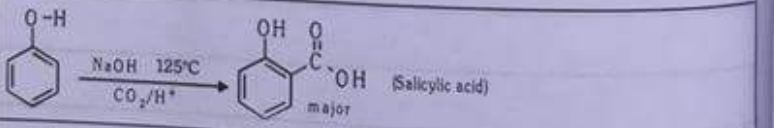
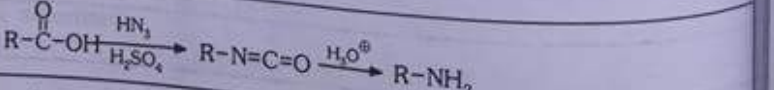
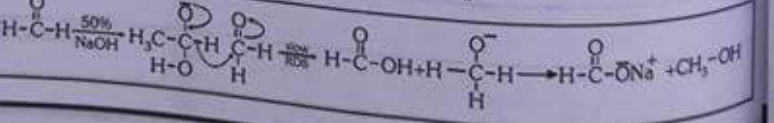
(I) 

(Maleic anhydride)

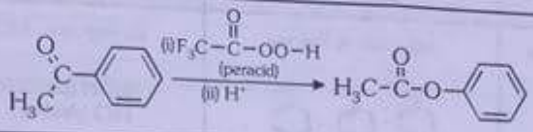
(II) 

IMPORTANT NOTES

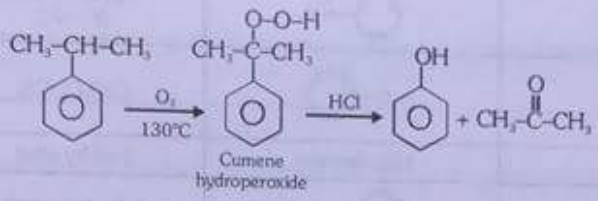
Nutshell review & preview of
ORGANIC NAME REACTIONS

• **Aldol Condensation**	
• **Claisen Condensation**	
• **Perkin Condensation**	
• **Benzoin Condensation**	
• **Haloform Reaction**	
• **Carbylamine Test**	
• **Reimer Tiemman Reaction**	
• **Kolbe's Schimdt Reaction**	
• **Hoffmann Bromamide Degradation**	
• **Curtius Reaction**	
• **Schimdt Reaction**	
• **Cannizzaro reaction**	

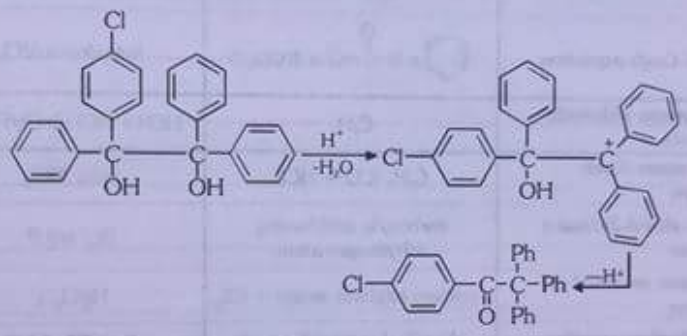
- **Bayer villiger oxidation**



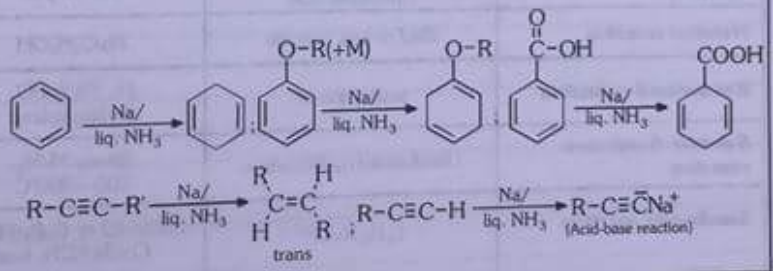
- **Cumene**



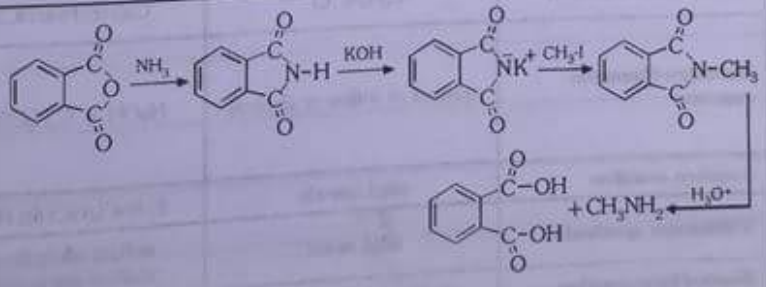
- **Pinacol-Pincolone rearrangement**



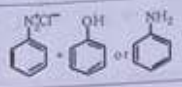
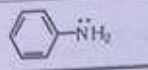
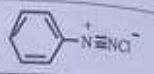
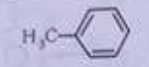
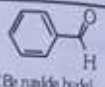
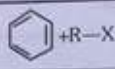
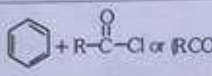
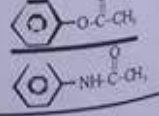
- **Birch Reduction**



- **Gabriel Synthesis**



NAME REACTIONS

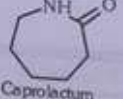
Name	Reactant	Reagent	Product
Clemmensen Reduction	Aldehyde & Ketone	Zn-Hg/conc. HCl	Alkane
Coupling Reaction		NaOH (phenol) HCl (Aniline)	Azo Dye (Detection of OH or NH_2 gr)
Diazotization		$NaNO_2$ + HCl $0° - 5°C$	
Etard reaction		CrO_2Cl_2/CS_2	 (Benzaldehyde)
Fittig Reaction	Halo benzene	Na/Dry ether	Diphenyl
Friedel Craft alkylation		Anhydrous $AlCl_3$	Alkyl Benzene
Friedel Craft acylation		Anhydrous $AlCl_3$	Acyl Benzene
Gattermann aldehyde synthesis	C_6H_6	$HCN + HCl / ZnCl_2/H_3O^+$	Benzaldehyde
Gattermann-Koch reaction	C_6H_6 (CO + HCl)	anhy $AlCl_3$	Benzaldehyde
Hell-Volhard-Zelinsky reaction	carboxylic acid having α-hydrogen atom	Br_2/ red P	α– halogenated carboxylic acid
Hoffmann mustard oil reaction	primary aliphatic amine + CS_2	$HgCl_2/\Delta$	CH_3CH_2—N=C=S + HgS (black)
Hunsdiecker reaction	Ag salt of carboxylic acid	Br_2/CCl_4, 80°C	alkyl or aryl bromide
Kolbe electrolytic reaction	alkali metal salt of carboxylic acid	electrolysis	alkane, alkene and alkyne
Mendius reaction	alkyl or aryl cyanide	Na/C_2H_5OH	primary amine
Rosenmund reduction	acid chloride	H_2, Pd/$BaSO_4$ boiling xylene	aldehyde
Sabatier-Senderens reaction	Unsaturated hydrocarbon	Raney Ni/H_2, 200—300°C	Alkane
Sandmeyer reaction	$C_6H_5\overset{+}{N}_2Cl^-$	CuCl/HCl or CuBr/HBr or CuCN/KCN, heat	Halo or cyanobenzene
Gattermann Reaction	$C_6H_5N_2^+Cl^-$	Cu/HX(HBr/HCl)	Halobenzene
Schotten-Baumann reaction	(phenol or aniline or alcohol)	NaOH + C_6H_5COCl	benzoylated product 
Stephen reaction	alkyl cyanide	(i) $SnCl_2$/HCl (ii) H_2O	Aldehyde
Williamson synthesis	alkyl halide	sodium alkoxide or sodium phenoxide	Ether
Wurtz-Fittig reaction	alkyl halide + aryl halide	Na/dry ether	alkyl benzene

POLYMERS

ADDITION POLYMERS

S.No	Name of Polymer	Starting Materials	Nature of Polymer
	I. Polyolefins		
1.	Polyethylene or Polyethene	$CH_2=CH_2$	Low density homopolymer (branched chain growth
2.	Polypropylene or Polypropene	$CH_3CH=CH_2$	Homopolymer, linear, chain growth
3.	Polystyrene	$C_6H_5CH=CH_2$	Homopolymer, linear, chain growth
	II. Polydiences		
1.	Neoprene	$CH_2=CH-\underset{Cl}{C}=CH_2$ Chloroprene or 2-Chloro-1,3-butadiene	Homopolymer, chain growth
2	Buna S (Styrene-Butadiene, Rubber) SBR or GRS	$CH_2=CH-CH=CH_2$ (1,3-butadiene) and $C_6H_5CH=CH_2$ (Styrene)	Copolymer, chain growth
	III. Polyacrylates		
1.	Polymethylmethacrylate (Flexiglass Lucite, Acrylite or Perspex PMMA	$H_2C=\underset{CH_3}{C}-COOCH_3$	Homopolymer
2.	Polyethylacrylate	$H_2C=CH-COOC_2H_5$	Homopolymer
3.	Polyacrylonitrile or Orlon PAN	$CH_2=CH-CN$	Homopolymer
	IV. Polyhalofins		
1.	Polyvinyl chloride PVC	$CH_2=CH-Cl$	Homopolymer, chain growth
2.	Polytetrafluoroethylene or Teflon PTFE	$F_2C=CF_2$	Homopolymer
3.	Polymonochlorotrifluoro-ethylene PCTFE	$ClFC=CF_2$	Homopolymer

CONDENSATION POLYMERS

S.No	Name of Polymer	Starting Materials	Nature of Polymer
	I. Polyesters		
1.	Terylene or Dacron	$HO-CH_2-CH_2-OH$ (Ethylene glycol or Ethane-1,2-diol) And Terephthalic acid or Benzene-1,4-dicarboxylic acid	Copolymer, step growth, linear
2.	Glyptal or Alkyl resin	$HO-CH_2-CH_2-OH$ (Ethylene glycol) and Phthalic acid or Benzene-1,2-dicarboxylic acid	Copolymer, linear step growth
	II. Polyamides		
1.	Nylon-6,6	$HO-\overset{O}{\overset{\|}{C}}(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH$ (Adipic acid) and $H_2N-(CH_2)_6-NH_2$ (Hexamethylenediamine)	Copolymer, linear, step growth
2	Nylon-6,10	$H_2N(CH_2)_6NH_2$ (Hexamethylene diamine) and $HOOC(CH_2)_8COOH$ (Sebacic acid)	Copolymer, linear, step growth
3.	Nylon-6	 Caprolactum	Homopolymer, linear
	Formaldehyde resins		
1.	Phenolformaldehye resin or Bakelite	Phenol and formaldehyde	Copolymer, step growth
2.	Melamine formaldehyde resin	Melamine and formaldehyde	Copolymer, step growth

CHAPTER 16

CARBOHYDRATES

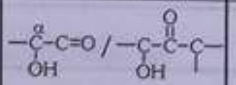
- Carbodydrates are defined as optically active polyhydroxy aldehydes or ketones or the compound which produce such units on hydrolysis.
- ***Monosaccharide*** ($C_nH_{2n}O_n$) : single unit, can't be hydrolysed : Glucose and fructose.
- ***Oligosaccharides*** gives two to ten monosaccharides on hydrolysis.
- ***Disaccharides*** (by glycosydic linkage)

  Sucrose $\xrightarrow{H_3O^+}$ α–D. Glucose + β–D. Fructose;

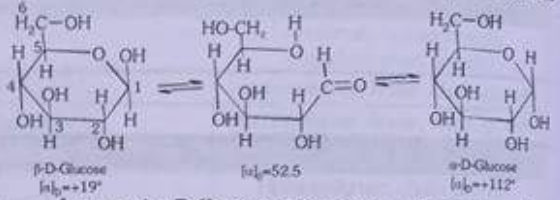
  Maltose $\xrightarrow{H_3O^+}$ 2 α–D. Glucose unit

  Lactose $\xrightarrow{H_3O^+}$ β–D. Glucose + β–D. Galactose
- ***Polysaccharide*** : Contain more than ten monosaccharide units

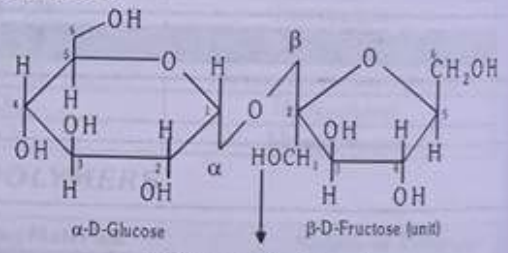
  $(C_6H_{10}O_5)_n$: Starch & cellulose.

TYPE OF SUGAR		
Give Test	**Reducing**	**Non Reducing**
Tollen's Reagent	+ve test	–ve test
Fehling Reagent	+ve test	–ve test
Benedict Test	+ve test	–ve test
Mutarotation	Yes	No
Functional Unit	  Hemiacetal  Hemiketal	 Acetal  Ketal
Example	All monosaccharides Glucose Fructose Mannose Galactose Disaccharide Maltose lactose	Disaccharide Sucrose Polysaccharide Starch cellulose

- ***Mutarotation:*** When either form of D-glucose is placed in aq. solution it slowly form the other via open chain aldehyde and gradual change in specific rotation until specific rotation (± 52.5°) is reached.

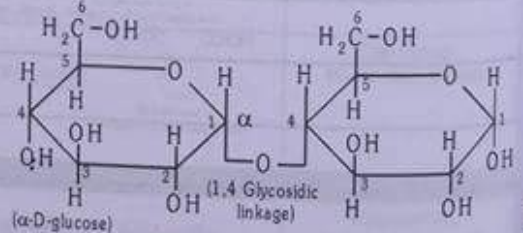


- ***Anomer's*** : Differ in configuration at 1st carbon due to hemi (acetal or ketal) ring formation. The new asymmetric carbon is referred to as Anomeric carbon.
- ***Epimer's*** : Diastereomer's which differ in conformation at any one chiral carbon
  eg. D-Glucose & D-mannose
  D-Glucose & D-Galactose
- ***Sucrose :***



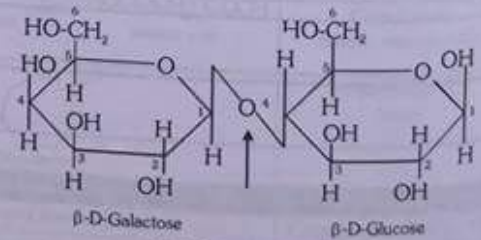
(1,2 Glycosidic linkage)

- ***Maltose***



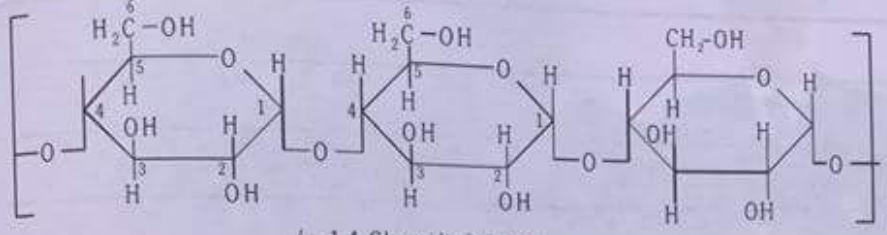
Two α-D-Glucose unit

- ***Lactose :***



(1,4 Glycosidic linkage)

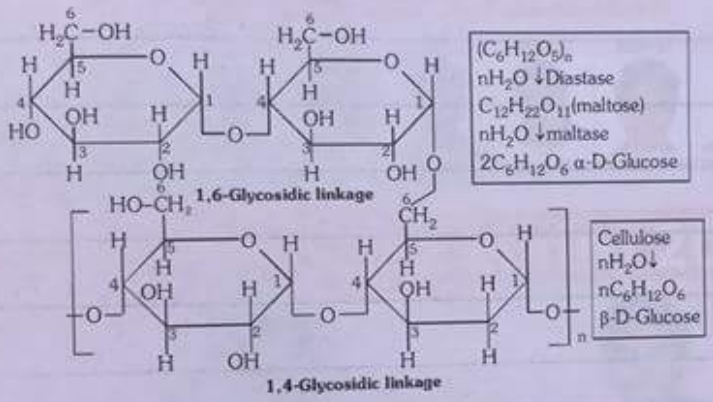
- **Starch** : (Amylose & Amylopectin)
- **Amylose : (Straight Chain) :**



(α-1,4 Glycosidic linkage)

(i) Soluble in H_2O & gives blue colour with I_2

- **Amylopectin (Branch chain) : $(C_6H_{12}O_5)_n$**



$(C_6H_{12}O_5)_n$
nH_2O ↓Diastase
$C_{12}H_{22}O_{11}$(maltose)
nH_2O ↓maltase
$2C_6H_{12}O_6$ α-D-Glucose

Cellulose
nH_2O↓
$nC_6H_{12}O_6$
β-D-Glucose

REACTION OF GLUCOSE (OPEN CHAIN STRUCTURE)

* Fructose doesn't react with Br_2/H_2O