Colourless – Sc^{3+}, Ti^{4+}, Zn^{2+} etc

Coloured – Fe^{3+} yellow , Fe^{2+} green, Cu^{2+} blue, Co^{3+} blue etc

Interstitial compounds : When less reactive nonmetals of small atomic size eg. H, B, N, C, Trapped in the interstitial space of transition metals, interstitial compounds are formed, like :-

TiC, Mn_4N, Fe_3H etc.

They are nonstoichiometric compounds.

They have high melting point than metals.

They are chemically inert.

Alloys :

Solid mixture of metals in a defenite ratio (15% differene in metallic radius)

They are hard and having high melting point.

eg. Brass (Cu + Zn)

Bronze (Cu + Sn) etc.

Hg when mix with other metals form semisolid amalgam except Fe,Co,Ni, Li.

Catalyst :

Transition metals & their compounds act as catalyst due to –

– Variable oxidation state

– Tendency to form complex

eg. V_2O_5 – Contact process

Fe – Haber process

Ni – Catalytic hydrogenation

Important reactions of d-block elements :

(a) $Cu^{2+} + 4I^- \longrightarrow Cu_2I_{2(s)} + I_2$

(b) $CuSO_4 + \underset{\text{Excess}}{KCN} \longrightarrow K_2SO_4 + \underset{\text{Unstable}}{Cu(CN)_2}$

$2Cu(CN)_2 \longrightarrow 2CuCN + \underset{\text{Cyanogen}}{(CN)_2}$

$CuCN + 3KCN \longrightarrow K_3[Cu(CN)_4]$

(c) $Cu \xrightarrow[\text{moist air}]{H_2O+CO_2} \underset{\text{green}}{CuCO_3.Cu(OH)_2}$

$Au \xrightarrow[(3HCl+HNO_3)]{\text{Aqua regia}} H[AuCl_4] + NOCl + H_2O$

(d) $AgNO_3 \xrightarrow{\text{Heating}} Ag + NO_2 + \frac{1}{2}O_2$

$AgCO_3 \xrightarrow{\text{Heating}} Ag + CO_2 + \frac{1}{2}O_2$

(e) $CuSO_4.5H_2O \xrightarrow{100°C} \underset{\text{light greenish blue}}{CuSO_4.H_2O} \xrightarrow{230°C} \underset{\text{Colourless}}{CuSO_4}$

$\xrightarrow{720°C} CuO + SO_2 + \frac{1}{2}O_2$

(f) $Hg_2Cl_2 + NH_4OH \longrightarrow \underset{\text{Black}}{Hg\begin{cases} NH_2 \\ Cl \end{cases}}$

(g) $NO_3^- / NO_2^- \xrightarrow{FeSO_4 + H_2SO_4} \left[Fe(H_2O)_5\,NO^+\right]SO_4$

Brown ring complex

(h) $AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$

Photographic
complex

METALLURGY

Branch of process to extract metal from their respective ore

Ore : Minerals from which metal can be extracted economically & easily.

Types of metallurgy

↓

- **Pyrometallurgy** → Temp. is involved → For heavy metals → eg. Fe, Zn, Cu, Hg, Sn, etc
- **Hydrometallurgy** → Solution is involved → According to E.C.S. → For metals placed below H → eg. Cu, Ag, Au
- **Electric metallurgy** → Electric involved → eg. IA, IIA, Al

Metallurgical process :

1. **Mining :** Ore obtain in big lumps (less reactive)

2. **Crushing/grinding/pulverization :** big lumps convert into powder (more reactive)

3. **Concentration :** To remove matrix/gangue (major impurities) from ore
To increase the concenration of ore particle in ore sample.

Concentration

(I) Physical process

- (a) Gravity separation /Hydrolic washing /Levigation
  ↓
  Based on diff. in sp. gravity
  ↓
  for oxides/ carbonates ore
- (b) Magnetic separation
  ↓
  Based on diff. in mag. properties
  ↓
  Used to separate s & p block compound from transitional elements compounds
- (c) Froath floatation
  ↓
  Based on diff. in wetting properties
  ↓
  Sulphide ores
  ↓
  Frother - pine oil
  Floating agent - sodium ethyl xanthate
  depressant - NaCN

(II) Chemical/leaching

↓

for $\boxed{Al}$ Ag, Au

$Al_2O_3 2H_2O$
- Red(Fe_2O_3)
  - Baeyer process (NaOH)
  - Hall process (Na_2CO_3)
- White(SiO_2)
  - Serpeck process (C & N)

Ag, Au, are concentrated by cyanide process.

(4) Calcination & Roasting

(I) Calcination

In absence of air

↓

for Carbonate /Hydroxide/Oxide ore

↓

CO_2 & H_2O are to be removed

↓

$MCO_3 \rightarrow MO + CO_2\uparrow$

↓

$M(OH)_2 \rightarrow MO + H_2O\uparrow$

(II) Roasting

In presence of air

↓

for Sulphide ore

↓

Impurity of S, P, As, SO_2 to be removed

↓

$MS + O_2 \rightarrow MO + SO_2\uparrow$

5. **Reduction :** To obtains metal (95 to 98%) from metal oxide.

(I) Chemical reduction

(a) by C (smelting)

↓

$MO + C + Flux \rightarrow M + CO_2\uparrow + Slag$

(b) by Al (Thermite process)

↓

$Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$

↓

$Mn_2O_3 + 2Al \rightarrow Al_2O_3 + 2Mn$

Flux - substance to convert non-fusible impurities to fusible one.

Flux

Acidic flux

↓

Removes basic impurities

↓

Non-metallic oxide (SiO_2)

Basic flux

↓

Removes acidic impurities

↓

Metallic oxide (CaO)

Imp. point – At high temp. C is reducing agent.
– At low temp. CO is reducing agent.

(II) Self reduction

↓

For Cu, Pb, Hg

↓

For sulphide ore only

(III) Metal displacement reduction

↓

Metal placed below H. in E.C.S.

↓

$\boxed{\text{Ag, Au,}}$ Cu

↓

(i) Cyano complex or Mac-Arther process

$$Ag_2S + NaCN \xrightarrow{O_2} Na_2[Ag(CN)_2] + Na_2SO_4$$

$$Au + 2KCN + H_2O \longrightarrow K[Ag(CN)_2]$$

(ii) Reduction to free metal

$$2Na[Ag(CN)_2]^{\bullet} + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag\downarrow$$

$$2K[Au(CN)_2] + Zn \longrightarrow K_2[Zn(CN)_4] + 2Au\downarrow$$

(IV) Electrolytic reduction

↓

For IA, IIA, Al

↓

Electolysis of molten sol.

↓

(i) Extraction of Al(Hall-Herault Process)

– Al can be extracted from Al_2O_3

– To decrease fusion temp. of Al_2O_3, $Na_3\,AlF_6$ & CaF_2 is to added

– $Na_3\,AlF_6$ & CaF_2 (Neutral flux) increase the conductivity & reduce the fusion temp.

(ii) Extraction of Na (Down cell process)

– Na can be extracted from NaCl

– Neutral flux ($CaCl_2$) to be added to decrease the fusion temp. of NaCl

– Neutral flux - substance used to increase the conductivity of NaCl

– decrease the fusion temp. of ionic compounds of (IA, IIA, Al) which is more than the melting point of metal.

Refining : To obtain metal (99.98%)

↓

(I) Physical Process

- (a) Liquation → Low M.P. metal Sn, Pb, As, Sb
- (b) Distillation → Low M.P. metal → Volatile metal (Zn, Cd, Hg)
- (c) Zone refining/ Fractional crystallization → Ultrapure metal → Volatile metal Ge, Ga, Si

(II) Chemical Process

- (a) Cupellation → For Ag having the imp. of Pb → Impure metal + O_2 →
  - pure metal + $O_2 \rightarrow \times$
  - imp. + $O_2 \rightarrow$ Volatile oxide
- (b) Polling → Cu, Pb having the imp. of their own oxide →

$$CuO + C \rightarrow Cu + CO\uparrow$$

$$CuO + H_2 \rightarrow Cu + H_2O\uparrow$$

- (c) Bessemerization → For Cu, Pb

(III) Thermal decomposition

(a) Van. arkel - Process

For Ti, Zr, Hf

↓

$$\underset{\text{Impure metal}}{Ti} + I_2 \rightarrow \underset{\text{Volatile}}{TiI_4} \rightarrow \underset{\text{Pure metal}}{Ti} + 2I$$

Impurity + $I_2 \rightarrow$ No reaction

Monds - Process

Ni, Pd

↓

$$\underset{\text{Impure metal}}{Ni + 4CO} \xrightarrow{\Delta} \underset{\text{Volatile carbonyl}}{Ni(CO)_4} \xrightarrow{\Delta} \underset{\text{Pure metal}}{Ni + 4CO}$$

Impurity + CO $\rightarrow$ No reaction

(IV) Electrolytic refining

↓

Anode – made up of impure metal
Cathode – made up of pure metal
(pure metal deposited)
Impurity deposited below anode as anode mud

Thermodynamics principle of metallurgy

- The graphical representationof Gibbs energy was first used by H.I.T. Ellingham. This provide a sound basis for considering te choice of reducing agent in the reduction of oxides. this is known as Ellingham diagram such diagram help us in predicting the feasibility of thermal reduction of an ore.
- The critesion of feasibility is that at a given temperatue, Gibbs energy of reaction must be negative.
- At high temperature 'C' is the best reducing agent.
- At low temperature 'CO' is the best redusing agent.
- In blast furnace reduction takes plae at low temperature i.e.

ORGANIC CHEMISTRY

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

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

Isomerism

Defination :

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

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

(A) **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} : $\boxed{CH_3 - CH_2 - CH_2 - CH_2 - CH_3}$

    n-pentane

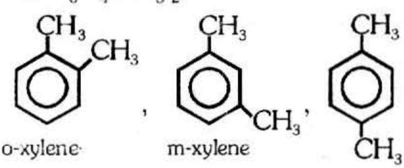
    $$\boxed{H_3C - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2 - CH_3}\ , \quad \boxed{H_3C - \overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}} - CH_3}$$

    iso-pentane neo-pentane

  - **Positional isomerism :** It occurs when functional groups or multiple bonds or substituents are in different position 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

  $CH_3-\underset{}{\overset{CH_3}{\overset{|}{N}}}-CH_3$, N, N-dimethylmethanamine

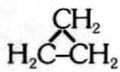
- **Metamerism :** This type of isomerism occurs when the isomers differ with respect to the nature of alkyl groups around the same polyvalent functional group.

  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

  
  cyclopropane

- **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 a $-\overset{O}{\overset{\|}{C}}-$ 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.

$$\underset{\text{keto form}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2COOC_2H_5} \rightleftharpoons \underset{\text{enol form}}{CH_3-\overset{OH}{\overset{|}{C}}=CHCOOC_2H_5}$$

Enol content $\propto$ Acidity of α-H of keto form

$\propto$ Intra molecular H-Bonding in enol form

$\propto$ Resonance in enol form

$\propto$ Aromatisation in enol form

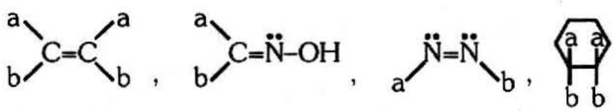
1. For chain, positional and metamerism, functional group must be same.

2. Metamerism may also show chain and position isomerism but priority is given to metamerism.

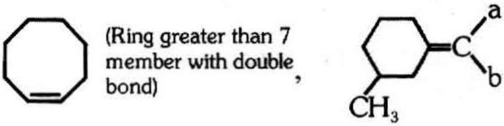
(B) Stereoisomerism : Compounds with the same molecular formula and structural formula but having difference in the spatial arrangement of atoms or groups are called stereoisomers and the phenomenon is called stereoisomerism.

❑ **Types of stereoisomerism**

● **Geometrical isomerism :** It is due to restricted rotation and is observed in following systems :-

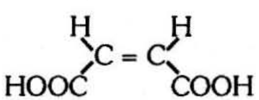


(Ring greater than 7 member with double bond),

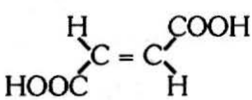


○ **Cis-trans isomerism :** The cis compound is the one with the same groups on the same side of the bond, and the trans has the same groups on the opposite sides. Both isomers have different physical and chemical properties.

e.g.



cis
maleic acid



trans
fumaric acid

○ 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 = no. 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.

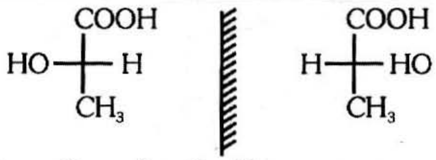
- The carbon atom linked to four different groups is called **chiral carbon.**

- **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)

  $\overset{3}{C}H_3 - \underset{\substack{|\\OH}}{\overset{2}{C}H} - \overset{1}{C}OOH$:



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 ①→②→③ Clockwise → R; Anti clockwise → S

Rule-3 If lowest priority ④ is bonded to horizontal line then moving ①→②→③ Clockwise → S; Anti clockwise → R

Determination of D/L system :

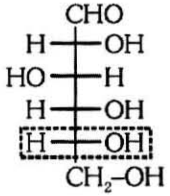
- Reference molecule glyceraldehyde
- It is used to assign configuration in carbohydrate, amino acid and similar compounds

Rule: Arrange parent carbon chain on the vertical line

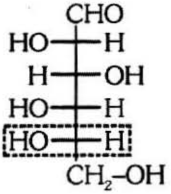
- Placed most oxidised carbon on the top or nearest to top.
- On highest IUPAC numbered chiral carbon

  If OH group on RHS $\longrightarrow$ D

  If OH group on LHS $\longrightarrow$ 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 2^{nd} 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 direcion.

- **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 necessory condition.

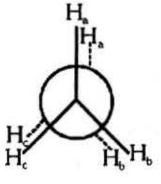
Calculation of number of optical isomers

The compound if contains	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	$2^{(n-1)} - 2^{(n-1)/2}$	$2^{(n-1)/2}$

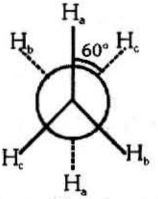
* Where n = no. of chiral carbon

- **Conformational isomerism :** 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.

- **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.



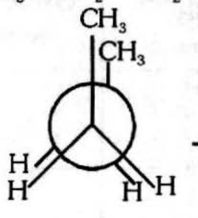
Eclipsed form (least stable)



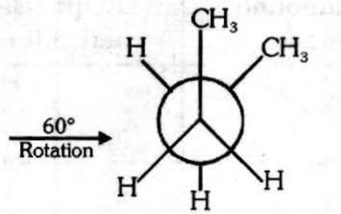
Staggered form (most stable)

- **Conformations of butane :**

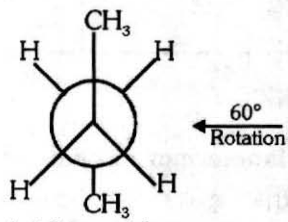
$\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{C}H_3$



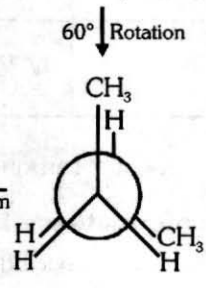
Fully eclipsed (less stable)



Gauche (more stable)



Anti Staggered-form (most stable)



Partially Eclipsed form

- 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.

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

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)

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

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

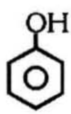
$$(Ph)_3\overset{\ominus}{C} > (Ph)_2\overset{\ominus}{C}H > Ph-\overset{\ominus}{C}H_2 > CH_2=CH-\overset{\ominus}{C}H_2 > \overset{\ominus}{C}H_3 >$$

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

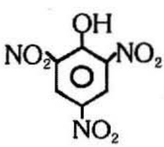
Acidic strength $\propto$ Stability of conjugate base $\propto K_a \propto \dfrac{1}{pK_a}$

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

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

(iii) $R-SO_3H > R-COOH >$  $> R-OH$

(iv) $HCOOH > CH_3COOH > CH_3CH_2COOH$

(v)  $> HCOOH > C_6H_5COOH > CH_3COOH$

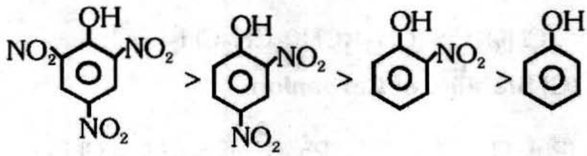
(vi) $CCl_3COOH > CHCl_2COOH > CH_2ClCOOH$

(vii) $CH_3-CH_2-\underset{F}{\underset{|}{C}H}-COOH > CH_3-\underset{F}{\underset{|}{C}H}-CH_2COOH >$

$\underset{F}{\underset{|}{C}H_2}-CH_2CH_2COOH$

(viii) $C_6H_4(OH)(CH_3)$ Phenol > m > p > o

(ix) $C_6H_4(OH)(NO_2)$ p > o > m > Phenol

(x) 

(xi) $C_6H_4(COOH)(NO_2)$ o > p > m > benzoic acid

(xii) $C_6H_4(COOH)(CH_3)$ o > benzoic acid > m > p

(xiii) $C_6H_4(COOH)(OCH_3)$ o > m > benzoic acid > p

(xiv) $C_6H_4(COOH)(Cl)$ o > m > p > benzoic acid

Basic strength $\propto K_b \propto \dfrac{1}{pK_b}$

Basic strength of amine :-

In aqueous medium

$R \Rightarrow -CH_3$ $2° > 1° > 3° > NH_3$

$R \Rightarrow -CH_2CH_3$ $2° > 3° > 1° > NH_3$

In gaseous medium

$R \Rightarrow -CH_3$ $\quad 3° > 2° > 1° > NH_3$

$R \Rightarrow -CH_2CH_3$ $\quad 3° > 2° > 1° > NH_3$

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 ∝ 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 $\propto \dfrac{1}{\text{Stability of alkene}}$

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.

$$\underset{\text{normal}}{CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_3} > \underset{\text{iso}}{CH_3{-}\underset{\substack{|\\ CH_3}}{CH}{-}CH_2{-}CH_3} > \underset{\text{neo}}{CH_3{-}\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}{-}CH_3}$$

Alkene

- Order of reactivity of olefins for hydrogenation

  $CH_2=CH_2 > R-CH=CH_2$ (Reverse of stability)

- Order of reactivity of alkene towards hydration

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

Alkyl halide

- Order of reactivity of alkyl halide towards

  $S_{N^1} \propto$ Benzylic > Allylic > 3° > 2° > 1°

  $S_{N^1} \propto$ Stability of carbocation

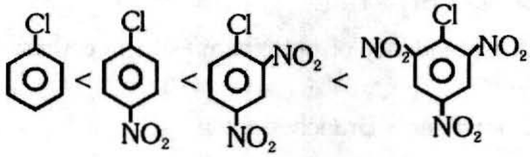
  $S_{N^2} \propto$ 1° > 2° > 3°

  $$S_{N^2} \propto \frac{1}{\text{Steric hindrance}}$$

- Reactivity order towards S_{N^1} or S_{N^2} 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.



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)

PURIFICATION METHODS

Distillation Techniques :

Type	Conditions	Examples
(A) Simple distillation	(i) When liquid sample has non volatile impurities (ii) When boiling point difference is 30 K or more.	(i) Mixture of chloroform (BP = 334K) and Aniline (BP = 457K) (ii) Mixture of Ether (BP = 308K) & Toluene (BP = 384K) (iii) Hexane (342K) and Toulene(384K)
(B) Fractional distillation	When BP difference is 10K	(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 BP is attained.	(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. $\underset{\text{Vapour pressure}}{P} = \underset{\text{Vapour pressure of Organic liquid}}{P_1} + \underset{\text{Vapour pressure of water}}{P_2}$	(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 $+ FeCl_3 +$ conc. HCl $\longrightarrow Fe_4[Fe(CN)_6]_3$ Prussian blue colour
Sulphur	$2Na + S \xrightarrow{\Delta} Na_2S$	(i) $Na_2S + \underset{\text{sodium nitrosopruside}}{Na_2[Fe(CN)_5NO]} \longrightarrow \underset{\text{a deep violet colour}}{Na_4[Fe(CN)_5NOS]}$ (ii) $Na_2S + CH_3COOH + (CH_3COO)_2Pb \longrightarrow$ 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	$Na+C+N+S \xrightarrow{\Delta} \underset{\text{Sodium thiocyanate (Blood red colour)}}{NaCNS}$	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

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

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

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

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 :** In this method a nitrogen containing compound is strongly heated with CuO in the atmosphere of CO_2 to get free nitrogen along with CO_2 and water.

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

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

$$\% \text{ of } N = \frac{1.4 \times \text{vol. of acid used in ml} \times \text{normality of acid}}{\text{wt. of organic compound}}$$

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 $(C=C)/(C\equiv C)$ + Br_2 in CCl_4 (Brown colour) ⟶ Colourless compound

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

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

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

- $\underset{\text{(Alkene)}}{R-CH=CH-R} + \text{(Cold, dilute) } KMnO_4 \longrightarrow$

$$\underset{\text{(Colourless)}}{R-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-R} + \underset{\text{Brown ppt}}{MnO_2}$$

- $R-C\equiv C-R' + \text{(Hot, dilute) } KMnO_4 \longrightarrow$

$$\underset{\text{Brown ppt.}}{MnO_2} + RCOOH + R'COOH$$

- $\underset{\text{(Alkyne)}}{R-C\equiv C-H} + \text{(Hot, dilute) } KMnO_4 \longrightarrow$

$$\underset{\text{Brown ppt.}}{MnO_2} + RCOOH + \underset{\text{(Colourless)}}{CO_2 + H_2O}$$

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	Ammonical cuprous chloride
↓	↓
White ppt.	Red ppt.

- $$\underset{\text{White ppt.}}{NH_4NO_3 + H_2O + R-C\equiv C-Ag} \xleftarrow{AgNO_3 + NH_4OH} \underset{\text{Terminal alkyne}}{R-C\equiv CH} \xrightarrow{Cu_2Cl_2 + NH_4OH} \underset{\text{Red ppt.}}{NH_4Cl + H_2O + R-C\equiv C-Cu}$$

Nature of X-group in C – X bond

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

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

Distinction between 1°, 2° and 3° alcohols

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

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

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

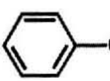
Lucas reagent is anhydrous $ZnCl_2$ + conc. HCl.

$H_3C-\overset{\displaystyle OH}{\overset{|}{C}H}-R$ type of alcohols give iodo form test.

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

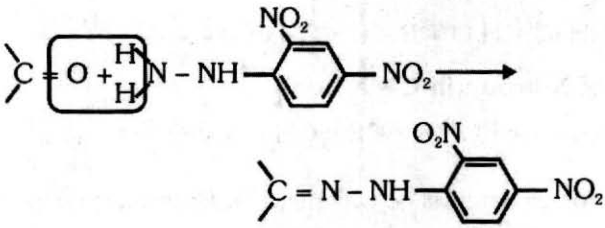
Phenol

$$\text{Phenol} + \underset{\text{(neutral)}}{\text{ferric chloride}} \longrightarrow \text{Violet colouration}$$

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

Carbonyl group

- Carbonyl compound + 2, 4-Dinitrophenylhydrazine (Bredy's reagent) $\longrightarrow$ Yellow/orange crystal



- $\left(\begin{array}{l}\text{All aldehydes and only}\\ \text{aliphatic methyl ketones}\end{array}\right)$ + $NaHSO_3$ $\rightarrow$ White crystalline bisulphite.

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

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

Aldehyde group

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

$$R-\overset{O}{\overset{\|}{C}}-H + 3OH^{\ominus} + 2[Ag(NH_3)_2]^+ \longrightarrow$$

$$RCOO^{\ominus} + 2H_2O + 4NH_3 + \underset{\text{(silver mirror)}}{2Ag\downarrow}$$

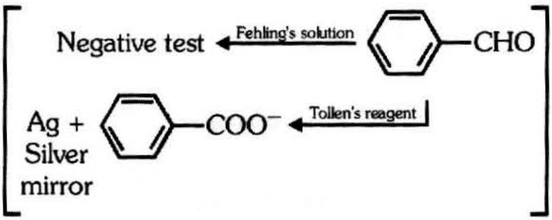
- Aldehyde + Fehling's solution $\longrightarrow$ Reddish brown precipitate

$$R-\overset{O}{\overset{\|}{C}}-H + 2Cu^{2+} + 5OH^- \longrightarrow RCOO^{\ominus} + 3H_2O + \underset{\text{(Reddish brown ppt)}}{Cu_2O}$$

- $H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-$ group also give iodoform test

$$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-R + I_2 + NaOH \xrightarrow{\text{Iodoform test}} \underset{\substack{\text{Iodoform} \\ \text{(Yellow ppt.)}}}{CHI_3} + RCOONa$$

- **Aromatic aldehyde group**
  - Aromatic aldehyde + Tollen's reagent $\longrightarrow$ Silver mirror
  - Aromatic aldehyde + Fehling's solution $\longrightarrow$ Negative test



- **Carboxylic group**

Carboxylic acid + Sodium bicarbonate $\longrightarrow$ effervescence

$$RCOOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2\uparrow$$

- **Formic acid**

$$\underset{\text{Formic acid}}{HCOOH} \xrightarrow{\text{Fehling's solution}} H_2O + CO_3^{2-} + \underset{\text{Red ppt.}}{Cu_2O}$$

$$\underset{\text{Formic acid}}{HCOOH} \xrightarrow{\text{Tollen's reagent}} \underset{\text{Silver mirror}}{2Ag} + CO_3^{2-} + H_2O$$

- **Amines (1°)**

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

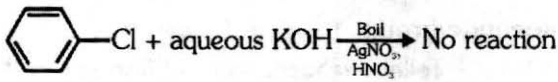
- **Amines (1°, 2° & 3°) (Hinsberg's test)**
  - Primary amine + Benzenesulphonyl chloride $\longrightarrow$ Precipitate $\xrightarrow{KOH}$ soluble
  - Secondary amine + Benzenesulphonyl chloride $\longrightarrow$ Precipitate $\xrightarrow{KOH}$ insoluble

- Tertiary amine + Benzenesulphonyl chloride $\longrightarrow$ No reaction

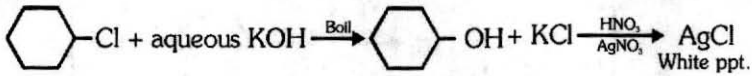
Note : Benzenesulphonyl chloride is called Hinsberg's reagent.

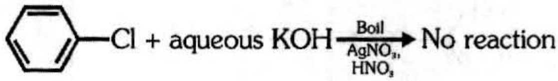
1. Chloroethane and chlorobenzene

- $C_2H_5{-}Cl$ + aqueous KOH $\xrightarrow{\text{Boil}}$ C_2H_5-OH + KCl $\xrightarrow[AgNO_3]{HNO_3}$ AgCl (White ppt.)

- 

2. Chorocyclohexane and chlorobenzene

- 

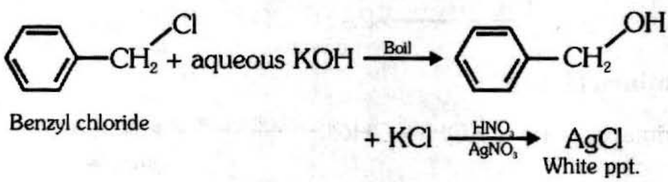
- 

3. Chloroethane and bromoethane

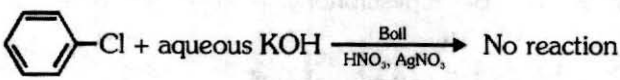
- $C_2H_5{-}Cl$+aqueous KOH $\xrightarrow{\text{Boil}}$ $C_2H_5{-}OH$+KCl $\xrightarrow[AgNO_3]{HNO_3}$ AgCl (White ppt.)
  Chloroethane

- $C_2H_5{-}Br$+aqueous KOH $\xrightarrow{\text{Boil}}$ $C_2H_5{-}OH$+KBr $\xrightarrow[AgNO_3]{HNO_3}$ AgBr (Yellow ppt.)
  Bromoethane

4. Benzyl chloride and chlorobenzene

- 

Benzyl chloride

- 

Chlorobenzene

5. Ethyl chloride and vinyl chloride

- $\underset{\text{Ethyl chloride}}{C_2H_5-Cl} + \text{aqueous KOH} \xrightarrow{\text{Boil}} C_2H_5-OH + KCl$

  $\xrightarrow[AgNO_3]{HNO_3} \underset{\text{White ppt.}}{AgCl}$

- $\underset{\text{Vinyl chloride}}{H_2C=CH-Cl} + \text{aq.KOH} \xrightarrow[HNO_3,\ AgNO_3]{\text{Boil}} \text{No reaction}$

6. n-Propyl alcohol and iso-propyl alcohol

- $CH_3CH_2CH_2OH + HCl \xrightarrow{ZnCl_2} CH_3CH_2CH_2Cl$

  No cloudiness at room temp.

- $H_3C-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_3 \xrightarrow[HCl]{ZnCl_2} H_3C-\overset{\overset{\displaystyle Cl}{|}}{C}H-CH_3$

  Cloudiness within 5 minutes

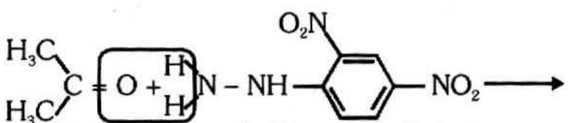
7. Ethyl alcohol and methyl alcohol (Iodoform test)

- $CH_3CH_2OH + 4I_2 + 6NaOH \longrightarrow CHI_3 + HCOONa$

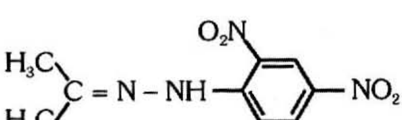
  Yellow ppt.

- $CH_3OH + 4I_2 + 6NaOH \longrightarrow \text{No yellow ppt.}$

8. Ethyl alcohol and acetone (2, 4 – DNP)

- 

  Acetone 2, 4-Dinitrophenylhydrazine

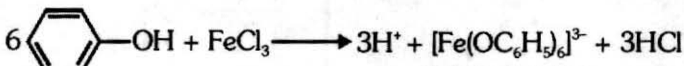


(yellow orange crystals)

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

9. Phenol and ethyl alcohol (Neutral $FeCl_3$)

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



Violet colouration

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

10. Benzoic acid and phenol ($NaHCO_3$)

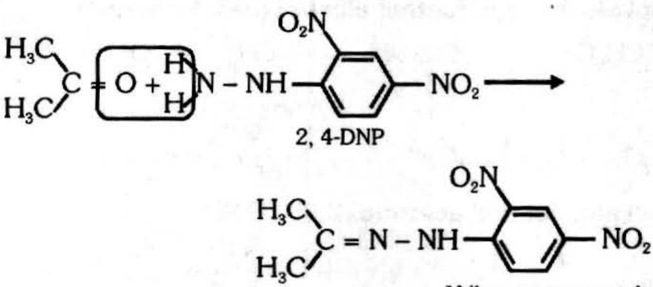
- Benzoic acid + Sodium bicarbonate $\longrightarrow$ effervescence

$$C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + CO_2\uparrow + H_2O$$

- Phenol + Sodium bicarbonate $\longrightarrow$ No effervescence

(Phenol is less acidic than benzoic acid)

11. Propanone and propanol (2, 4 - DNP)

- 

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

12. Propanal and propanone (Tollen's and Fehling reagent)

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

$$H_3C - CH_2 - \overset{\overset{\displaystyle O}{\|}}{C}H + 3OH^- + 2[Ag(NH_3)_2]^+ \longrightarrow$$

$$CH_3CH_2COO^- + 2H_2O + 4NH_3 + 2Ag\downarrow$$

(Silver mirror)

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

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

- Propanone $\xrightarrow{\text{Fehling's solution}}$ Negative test

  Propanone $\xrightarrow{\text{Tollen's reagent}}$ Negative test

13. Ethanal and propanal (Iodoform test)

- $$\underset{\text{Ethanal}}{H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-H} + I_2 + NaOH \xrightarrow{\text{Iodoform test}} \underset{\substack{\text{Iodoform}\\ \text{(Yellow ppt.)}}}{CHI_3} + HCOONa$$

- $$\underset{\text{Propanal}}{H_3C-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H} + I_2 + NaOH \xrightarrow{\text{Iodoform test}} \text{No yellow ppt.}$$

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

- $$\underset{\text{Pentan-2-one}}{H_3C-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + I_2 + NaOH$$

$$\xrightarrow{\text{Iodoform test}} \underset{\substack{\text{Iodoform}\\ \text{(Yellow ppt.)}}}{CHI_3} + CH_3CH_2CH_2COONa$$

- $$\underset{\text{Pentan-3-one}}{H_3C-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_3} + I_2 + NaOH$$

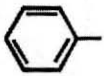
$$\xrightarrow{\text{Iodoform test}} \text{No yellow ppt.}$$

15. Propanal and benzaldehyde (Fehling solution)

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

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

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


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

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

- $\underset{\text{Methanoic acid}}{HCOOH}$ $\xrightarrow{\text{Fehling's solution}} H_2O + CO_3^{2-} + Cu_2O$
  $\xrightarrow{\text{Tollen's reagent}} 2Ag\downarrow + CO_3^{2-} + H_2O$

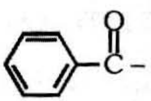
- Ethanoic acid $\xrightarrow{\text{Fehling's solution}}$ No brown ppt.
  $\xrightarrow{\text{Tollen's reagent}}$ No silver mirror

17. Ethanal and methanal (Iodoform test)

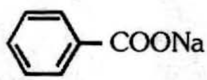
- $\underset{\text{Ethanal}}{CH_3CHO} + I_2 + NaOH \xrightarrow{\text{Iodoform test}} \underset{\substack{\text{Iodoform}\\ \text{(Yellow ppt.)}}}{CHI_3} + HCOONa$

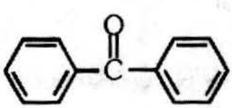
- $\underset{\text{Methanal}}{HCHO} + I_2 + NaOH \xrightarrow{\text{Iodoform test}}$ No yellow ppt.

18. Acetophenone and benzophenone (Iodoform test)

- 
$+ I_2 + NaOH \xrightarrow{\text{Iodoform test}}$

Acetophenone

$\underset{\text{(Yellow ppt.)}}{CHI_3}$ +


- 
$+ I_2 + NaOH \xrightarrow{\text{Iodoform test}}$ No ppt.

Benzophenone

19. Benzoic acid and ethylbenzoate ($NaHCO_3$)

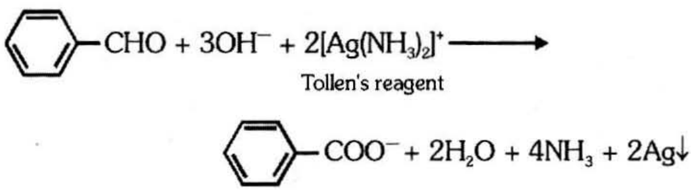
- Benzoic acid + Sodium bicarbonate $\longrightarrow$ effervescence

  $C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + CO_2 + H_2O$

- Ethyl benzoate + Sodium bicarbonate $\longrightarrow$ No effervescence

20. Benzaldehyde and acetophenone (Tollen's test)

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



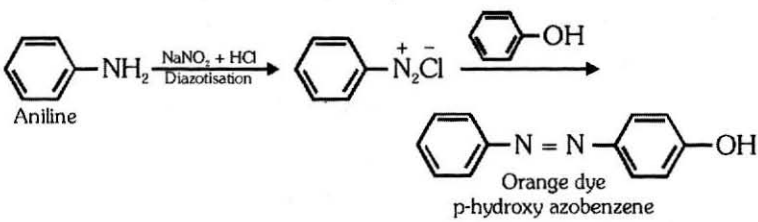
- Acetophenone + Tollen's reagent $\longrightarrow$ No silver mirror

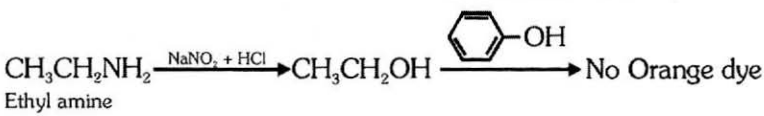
21. Methyl amine and dimethyl amine (Isocyanide test)

- $\underset{\text{Methyl amine}}{CH_3NH_2} + CHCl_3 + \underset{\text{(alc.)}}{3KOH} \longrightarrow \underset{\substack{\text{Methyl isocyanide}\\\text{(Offensive smell)}}}{CH_3NC} + 3KCl + 3H_2O$

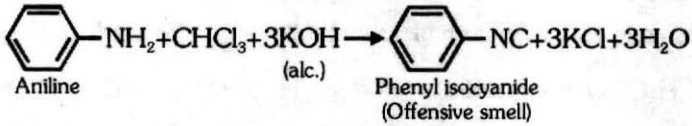
- $\underset{\text{Di-methyl amine}}{H_3C-\overset{\overset{\displaystyle CH_3}{|}}{N}H} + CHCl_3 + 3KOH\text{ (alc.)} \longrightarrow$ No offensive smell

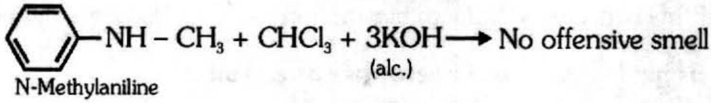
22. Aniline and ethyl amine (Diazotisation)



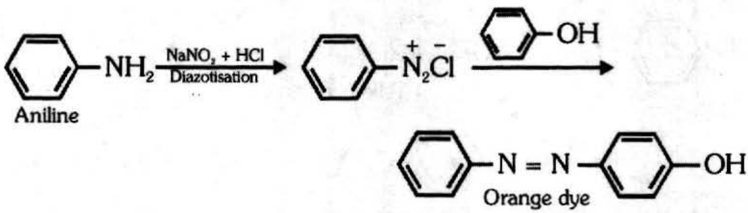


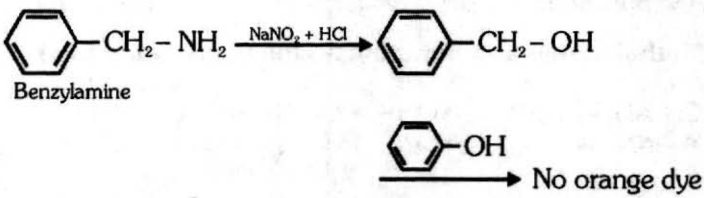
23. Aniline and N-methylaniline (Isocyanide test)

- 

- 

24. Aniline and Benzylamine (Diazotisation + phenol)

- 

- 

25. Glucose and fructose

- Glucose + Br_2 + H_2O $\longrightarrow$ Gluconic acid + 2HBr
  (Brown colour) (Colourless)
- Fructose + Br_2 + H_2O $\longrightarrow$ Brown colour (no change in colour)
  (Brown colour)

26. Glucose and sucrose

- Glucose + Tollen's reagent $\longrightarrow$ Silver mirror
- Sucrose + Tollen's reagent $\longrightarrow$ No silver mirror

27. Glucose and starch

- Glucose + Fehling's solution $\longrightarrow$ Red ppt.
- Starch + Fehling's solution $\longrightarrow$ No red ppt.

OR

- Glucose + I_2 solution $\longrightarrow$ No blue colour
- Starch + I_2 solution $\longrightarrow$ Blue colour

ALKANES

Methods of preparation

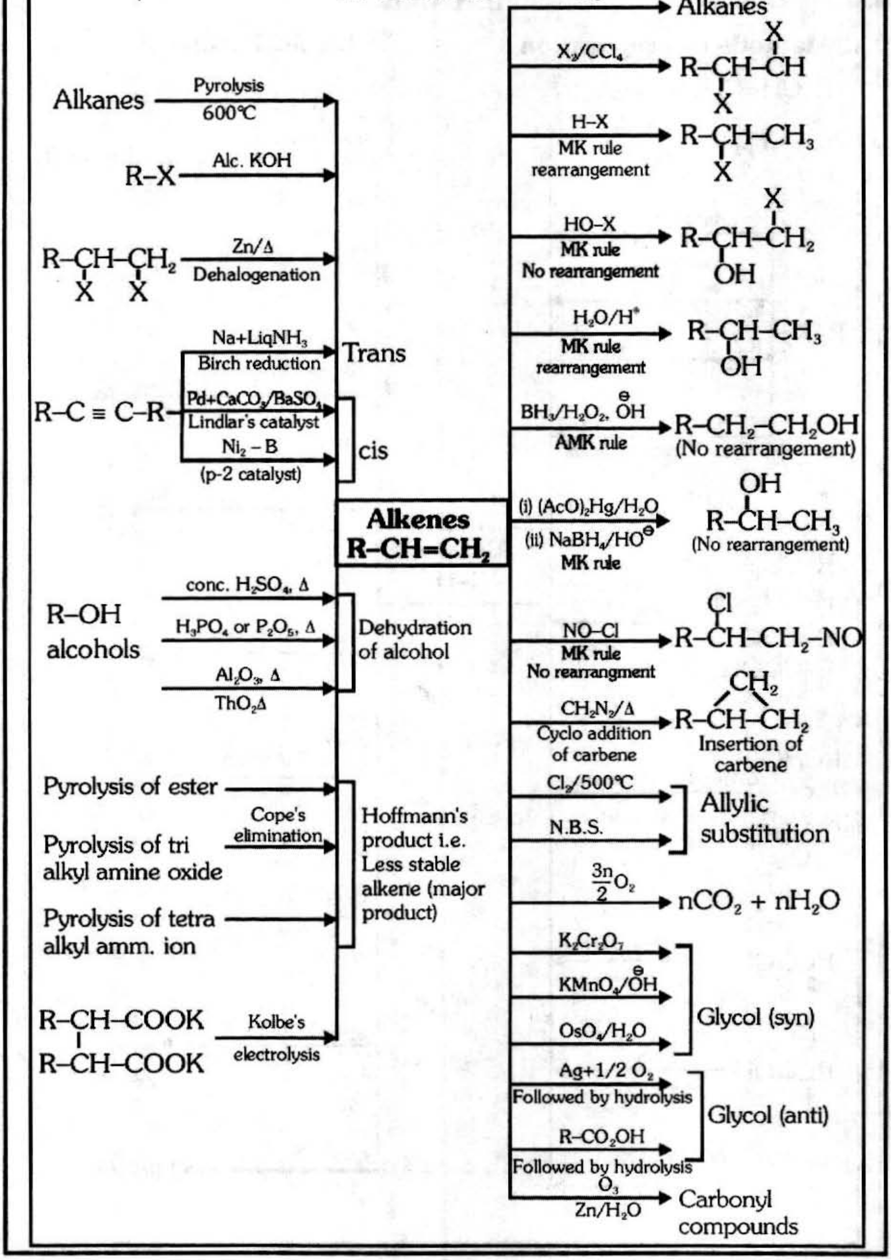
- $R-CH=CH_2$ / $R-C\equiv C-H$ $\xrightarrow[Pt]{H_2}$ Alkanes
- $R-X$:
  - $\xrightarrow{\text{Reducing agent}}$ Alkanes
  - $\xrightarrow{\text{Na-dry ether, wurtz reaction}}$ Alkanes
  - $\xrightarrow{\text{Zn, R'-X/ } R_2Zn\text{-Frankland reagent}}$ Alkanes
  - $\xrightarrow[R_2CuLi\text{-Gillmann's reagent}]{\text{Li.CuI, R'-X/Corey house}}$ Alkanes
- $R-CH_2-I$, $R-CH_2-OH$, $R-CHO$, $R-COOH$ $\xrightarrow{\text{Red P + HI}}$ Alkanes
- $RCHO$ or $R-\underset{\underset{O}{\parallel}}{C}-R$ $\xrightarrow[\text{NH}_2\text{-NH}_2/\overset{\ominus}{O}H \text{ Wolf Kishner}]{\text{Zn+Hg/HCl-Clemmensen}}$ Alkanes
- $RCOOH \xrightarrow[\text{Sodalime}/\Delta \text{ (Decarboxylation)}]{NaOH + CaO}$ Alkanes
- $RCOOH \xrightarrow[\text{electrolysis}]{\text{Kolbe's}}$ Alkanes
- $R-MgX \xrightarrow[\text{(Active-H)}]{H-Z}$ Alkanes

Alkanes R-H

Chemical properties

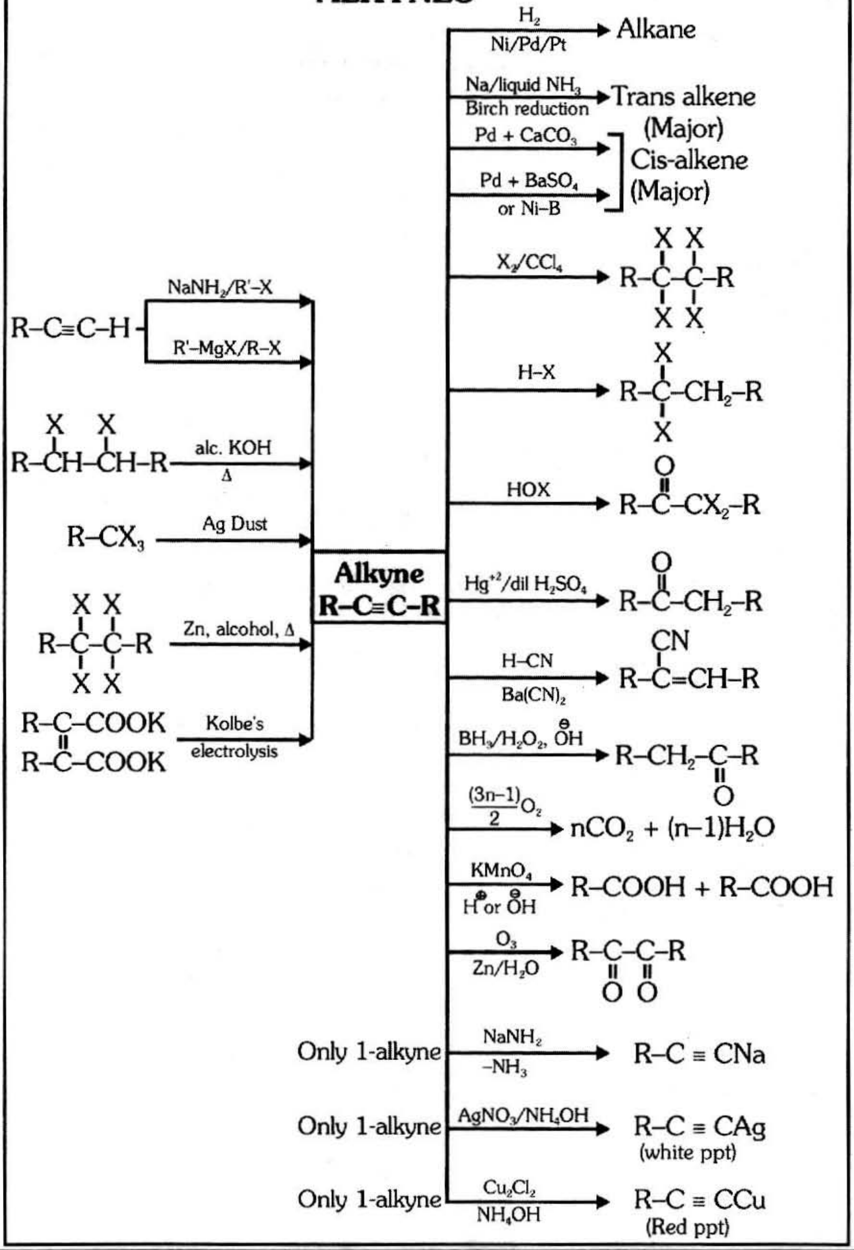
- $\xrightarrow[\text{Complete oxidation}]{\frac{(3n+1)}{2}O_2}$ $nCO_2 + (n+1)H_2O$
- $\xrightarrow[KMnO_4]{\text{Catalytic oxidation}}$ R_3C-OH
- $\xrightarrow{X_2/h\nu\ (F_2 > Cl_2 > Br_2 > I_2)}$ $R-X$
- $\xrightarrow[450°C]{HNO_3 \text{ (vapours)}}$ $R-NO_2$
- $\xrightarrow{\text{conc. } H_2SO_4 + SO_3}$ $R-SO_3H$
- $\xrightarrow[\text{isomerisation}]{AlCl_3/HCl,\ \Delta}$ Isomeric alkanes
- $\xrightarrow[\text{aromatization}]{Cr_2O_3 + Al_2O_3,\ 600°C}$ Aromatic hydrocarbon
- $\xrightarrow{\text{Pyrolysis}}$ Alkenes + alkanes
- $\xrightarrow[\text{insertion of carbene}]{CH_2N_2/\Delta}$ Higher alkanes

ALKENES

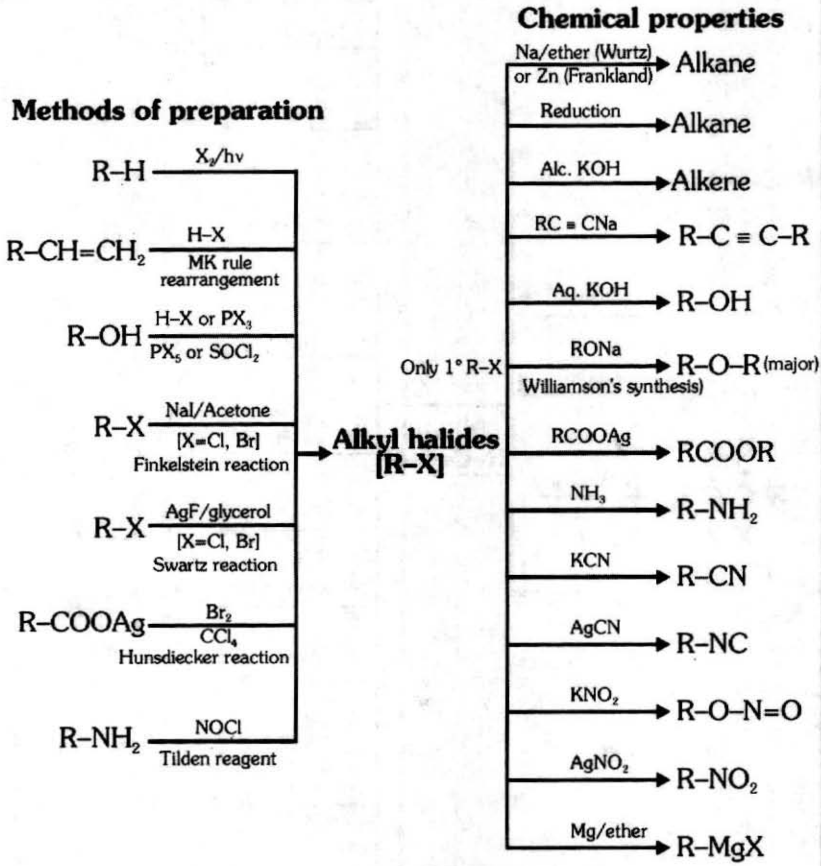


Alkanes
Pyrolysis
600°C
R–X
Alc. KOH
R–CH–CH2 X X
Zn/Δ
Dehalogenation
Na+LiqNH3
Birch reduction
Trans
R–C ≡ C–R
Pd+CaCO3/BaSO4
Lindlar's catalyst
Ni2 – B
(p-2 catalyst)
cis
Alkenes
R–CH=CH2
R–OH
alcohols
conc. H2SO4, Δ
H3PO4 or P2O5, Δ
Al2O3, Δ
ThO2Δ
Dehydration of alcohol
Pyrolysis of ester
Cope's elimination
Pyrolysis of tri alkyl amine oxide
Pyrolysis of tetra alkyl amm. ion
Hoffmann's product i.e. Less stable alkene (major product)
R–CH–COOK
R–CH–COOK
Kolbe's electrolysis
H2
Alkanes
X2/CCl4
H–X
MK rule
rearrangement
HO–X
MK rule
No rearrangement
H2O/H+
MK rule
rearrangement
BH3/H2O2, OH⊖
AMK rule
R–CH2–CH2OH
(No rearrangement)
(i) (AcO)2Hg/H2O
(ii) NaBH4/HO⊖
MK rule
(No rearrangement)
NO–Cl
MK rule
No rearrangment
CH2N2/Δ
Cyclo addition of carbene
Insertion of carbene
Cl2/500°C
N.B.S.
Allylic substitution
3n/2 O2
nCO2 + nH2O
K2Cr2O7
KMnO4/OH⊖
OsO4/H2O
Glycol (syn)
Ag+1/2 O2
Followed by hydrolysis
R–CO2OH
Followed by hydrolysis
Glycol (anti)
O3
Zn/H2O
Carbonyl compounds

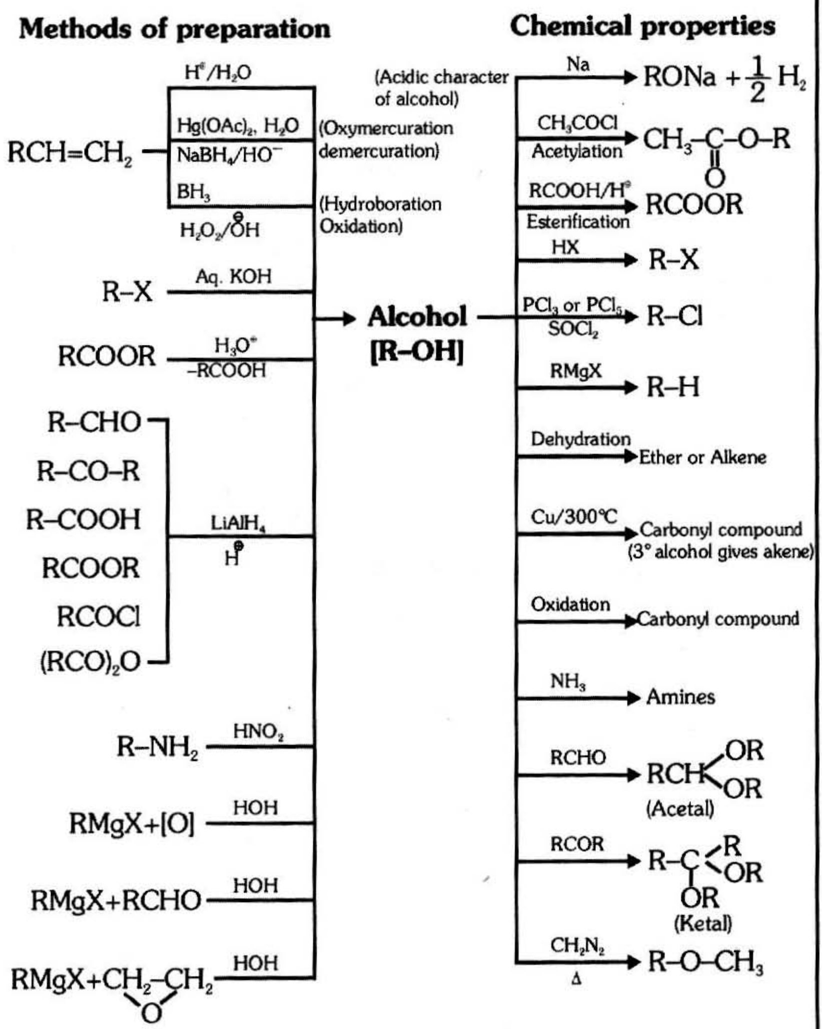
ALKYNES


NaNH2/R'–X
R–C≡C–H
R'–MgX/R–X
R–CH–CH–R
alc. KOH
Δ
R–CX3
Ag Dust
Zn, alcohol, Δ
R–C–COOK
R–C–COOK
Kolbe's
electrolysis
Alkyne
R–C≡C–R
H2
Ni/Pd/Pt
Alkane
Na/liquid NH3
Birch reduction
Trans alkene
(Major)
Pd + CaCO3
Pd + BaSO4
or Ni–B
Cis-alkene
(Major)
X2/CCl4
H–X
R–C–CH2–R
HOX
R–C–CX2–R
Hg+2/dil H2SO4
R–C–CH2–R
H–CN
Ba(CN)2
R–C=CH–R
BH3/H2O2, OH
R–CH2–C–R
(3n–1)/2 O2
nCO2 + (n–1)H2O
KMnO4
H or OH
R–COOH + R–COOH
O3
Zn/H2O
R–C–C–R
Only 1-alkyne
NaNH2
–NH3
R–C ≡ CNa
Only 1-alkyne
AgNO3/NH4OH
R–C ≡ CAg
(white ppt)
Only 1-alkyne
Cu2Cl2
NH4OH
R–C ≡ CCu
(Red ppt)

ALKYL HALIDES



ALCOHOL



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ETHER

Methods of preparation

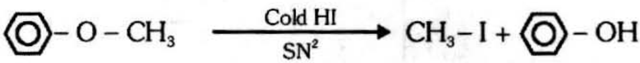
- $R-X + RONa \xrightarrow{\text{(Williamson's synthesis)}}$ Ether (R–O–R)
- $R-OH \xrightarrow[140^\circ]{\text{Conc. } H_2SO_4}$ Ether (R–O–R) (Williamson's continuous synthesis)
- $R-X \xrightarrow{\text{Dry } Ag_2O}$ Ether (R–O–R)
- $R-OH \xrightarrow[\Delta]{CH_2N_2}$ Ether (R–O–R)

Chemical properties

- Ether (R–O–R) $\xrightarrow{HCl}$ $[R-\overset{\oplus}{\underset{H}{O}}-R]\overset{\ominus}{Cl}$
- Ether (R–O–R) $\xrightarrow[\Delta]{\text{dil. } H_2SO_4}$ R–OH
- Ether (R–O–R) $\xrightarrow[\Delta]{PCl_5}$ RCl
- Ether (R–O–R) $\xrightarrow[\text{Cold}]{HI}$ R–OH+R–I
- Ether (R–O–R) $\xrightarrow[\text{[long contact]}]{O_2}$ Hydro Peroxide
- Ether (R–O–R) $\xrightarrow[\text{Hot}]{HI}$ $2R-I + H_2O$

Reaction with cold HI (Zeisel's method)

$$CH_3-O-CH_2-CH_3 \xrightarrow[SN^2]{\text{Cold HI}} CH_3-I + CH_3CH_2OH$$



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_3 \xrightarrow[SN^1]{\text{Cold HI}} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-I + CH_3-OH$$

$$CH_3-\overset{CH_3}{CH}-O-CH_3 \xrightarrow[SN^2]{\text{Cold HI}} CH_3-I + (CH_3)_2CH-OH$$

$$CH_2=CH-CH_2-O-CH_3 \xrightarrow[SN^1]{\text{Cold HI}} CH_2=CH-CH_2-I+CH_3-OH$$

PHENOL

Methods of preparation

- $C_6H_5Cl \xrightarrow[\text{(II) } H^+]{\text{(I) NaOH/High T \& P}}$ [Phenol] C_6H_5OH
- $C_6H_5MgBr \xrightarrow[H^{\oplus}/H_2O]{[O]}$ [Phenol] C_6H_5OH
- $C_6H_5\overset{\oplus}{N}_2\overset{\ominus}{Cl} \xrightarrow[\Delta]{H_2O}$ [Phenol] C_6H_5OH
- $C_6H_5CH(CH_3)_2 \xrightarrow[\text{(ii) } H_2O/H^{\oplus}]{\text{(i) } O_2}$ [Phenol] C_6H_5OH
- $C_6H_4(OH)(COOH) \xrightarrow[\Delta]{\text{Soda lime}}$ [Phenol] C_6H_5OH
- $C_6H_5SO_3H \xrightarrow[H_3O^{\oplus}]{\text{NaOH [Fusion]}}$ [Phenol] C_6H_5OH

Chemical properties

[Phenol] C_6H_5OH

- $\xrightarrow{Na} C_6H_5ONa$
- $\xrightarrow{Zn} C_6H_6 + ZnO$
- $\xrightarrow{PCl_5} (C_6H_5)_3PO_4$
- $\xrightarrow[ZnCl_2]{NH_3} C_6H_5NH_2$
- $\xrightarrow{FeCl_3}$ Violet colour
- $\xrightarrow{Br_2/CCl_4}$ o- and p-Bromophenol
- $\xrightarrow{Br_2/H_2O}$ 2,4,6-Tribromophenol (White ppt.)
- $\xrightarrow{\text{dil. } HNO_3}$ o and p-nitrophenol
- $\xrightarrow{\text{Conc. } HNO_3}$ 2,4,6-Trinitrophenol (Picric acid)
- $\xrightarrow{CH_3Cl/AlCl_3}$ o and p-Cresol
- $\xrightarrow[ZnCl_2]{CH_3COCl/AlCl_3}$ o and p-hydroxy acetophenone
- $\xrightarrow[\text{(Reimer tiemann)}]{CHCl_3/NaOH}$ Salicylaldehyde
- $\xrightarrow[\text{(Reimer tiemann)}]{CCl_4/NaOH}$ Salicylic acid
- $\xrightarrow[\Delta]{CO_2/NaOH}$ Salicylic acid (Kolbe's reaction)

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CARBONYL COMPOUNDS

Methods of preparation

- Alkenes $\xrightarrow{\text{Ozonolysis}}$
- Alkynes $\xrightarrow[\text{HgSO}_4]{\text{dil. } H_2SO_4}$
- Gemdihalides $\xrightarrow{\text{Hydrolysis}}$
- Alcohols $\xrightarrow[300°C]{\text{Cu}}$
- $R-CH_2-OH \xrightarrow{\text{PCC}}$
- $R-\underset{\displaystyle OH}{\underset{|}{CH}}-R \xrightarrow{H^{\oplus}/K_2Cr_2O_7}$
- $R-COOH \xrightarrow[300°C]{\text{MnO}}$
- $(RCOO)_2Ca \xrightarrow{\text{Dry distillation}}$
- Esters $\xrightarrow{\text{Grignard reagent}}$
- Alkyl cyanide $\xrightarrow[\text{(ii) } H_3O^+]{\text{(i) Grignard reagent}}$
- $RCOCl \xrightarrow[\text{(Rosenmund's reduction)}]{H_2/Pd/BaSO_4}$
- $R-C\equiv N \xrightarrow[\text{(ii) Hydrolysis}]{\text{(i) } SnCl_2/HCl}$ (Stephen's reaction)

$\longrightarrow$ **Carbonyl Compounds [Aldehydes, Ketones]**

Chemical properties

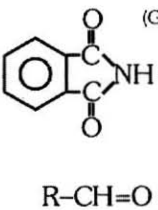
- $\xrightarrow{HCN}$ $R_2C(OH)CN$ (Cyanohydrin)
- $\xrightarrow{NaHSO_3}$ $R_2C(OH)SO_3Na$
- $\xrightleftharpoons{H^{\oplus}/H_2O}$ $R_2C(OH)OH$ (Unstable)
- $\xrightarrow{H^{\oplus}/ROH}$ $R_2C(OR)OR$
- $\xrightarrow[\text{(Ammonia derivatives)}]{H_2N-Z}$ $R_2C=N-Z$
- $\xrightarrow[\text{Tischenko reaction}]{Al(OEt)_3}$ Ester (Given by all aldehydes)
- $\xrightarrow{\overset{\ominus}{O}H}$ α–H containing carbonyl compounds give Aldol reaction
- $\xrightarrow{\overset{\ominus}{O}H}$ Aldehydes without α-H give cannizaro reaction
- (Clemmensen's reduction) $\xrightarrow[\text{Conc. HCl}]{\text{Zn-Hg}}$ Alkane
- $\xrightarrow[H^{\oplus}]{LiAlH_4}$ Alcohol
- $\xrightarrow{\text{Oxidation}}$ Acids
- $\xrightarrow{RMgX}$ Alcohols
- $\xrightarrow[\overset{\ominus}{O}H/\Delta]{NH_2-NH_2}$ Alkane (Wolf kishner reduction)

ALIPHATIC AMINES

Methods of preparation

All of the following give $R-NH_2$:

- $R-X \xrightarrow{NH_3}$ (mix. of 1°,2°,3° amine & quaternary salt is obtaind)
- $R-OH \xrightarrow{NH_3}$
- $R-NC \xrightarrow{H_3O^{\oplus}}$
- $R-NO_2 \xrightarrow{Sn/HCl}$
- $RCN \xrightarrow[H^{\oplus}]{LiAlH_4}$
- $RMgCl \xrightarrow{Cl-NH_2}$
- $RCONH_2 \xrightarrow{Br_2 + KOH}$ (Hoffmann Bromamide reaction)
- $RCOOH \xrightarrow[\text{Conc. } H_2SO_4]{N_3H}$ (Schmidt reaction)
- $RCOCl \xrightarrow[H_3O^{\oplus}]{NaN_3}$ (Curtius reaction)
- (Gabriel phthalimide reaction)



  $\xrightarrow[\text{(ii) } R-Br \text{ (iii) } H_3O^{\oplus}]{\text{(i) KOH}}$ (Only 1° aliphatic amine is prepared)
- $R-CH=O \xrightarrow[\text{(ii) } Ni/H_2]{\text{(i) } NH_3}$ (Reductive ammination)
- $R-\underset{\underset{NH_2}{|}}{CH}-COOH \xrightarrow[\Delta]{Ba(OH)_2}$

$$\textbf{R–NH}_2$$

Chemical properties

- $R-NH_2 \xrightarrow{HCl} R-\overset{\oplus}{N}H_3\overset{\ominus}{Cl}$
- $R-NH_2 \xrightarrow{Na} R-NHNa + \frac{1}{2} H_2$
- $R-NH_2 \xrightarrow{R-X} R_2NH$
- $R-NH_2 \xrightarrow{Cl-\underset{\underset{O}{||}}{C}-R} R-NH-\underset{\underset{O}{||}}{C}-R$
- $R-NH_2 \xrightarrow{Cl-\underset{\underset{O}{||}}{C}-Ph} R-NH-\underset{\underset{O}{||}}{C}-Ph$ (Schotten Baumann reaction)
- $R-NH_2 \xrightarrow{CHCl_3+KOH} R-NC$ (1° amine only) (Offensive smell) (Isocyanide test)
- $R-NH_2 \xrightarrow[\text{(ii) } HgCl_2]{\text{(i) } CS_2} R-N=C=S$ (Mustard oil smell) (test for 1° amine) (Hoffmann's mustard oil reaction)
- $R-NH_2 \xrightarrow{HNO_2} R-OH$
- $R-NH_2 \xrightarrow{RMgX} R-H$
- $R-NH_2 \xrightarrow{RCHO} R-NH=CHR$ (Schiff base)
- $R-NH_2 \xrightarrow{NOCl} R-Cl$

ANILINE

Methods of preparation

$$Ph\text{–}Cl + NH_3 \xrightarrow[\text{high T and P}]{Cu_2O} Ph\text{–}NH_2$$

$$Ph\text{–}OH + NH_3 \xrightarrow[300^\circ C]{ZnCl_2} Ph\text{–}NH_2$$

$$Ph\text{–}NC \xrightarrow{H_3O^{\oplus}} Ph\text{–}NH_2$$

$$Ph\text{–}NO_2 \xrightarrow{Sn/HCl} Ph\text{–}NH_2$$

$$PhCONH_2 \xrightarrow{Br_2/KOH} Ph\text{–}NH_2$$

$$PhCOOH \xrightarrow[\text{conc. } H_2SO_4]{N_3H} Ph\text{–}NH_2$$

$$PhCOCl + NaN_3 \xrightarrow{H^{\oplus}/\Delta} Ph\text{–}NH_2$$

$$Ph\text{–}Mg\text{–}Cl + Cl\text{–}NH_2 \longrightarrow Ph\text{–}NH_2$$

$$Ph\text{–}N{=}N\text{–}Ph \xrightarrow{\text{Reduction}} Ph\text{–}NH_2$$

Chemical properties

$$Ph\text{–}NH_2 \xrightarrow{HCl} Ph\overset{\oplus}{N}H_3\overset{\ominus}{Cl}$$

$$Ph\text{–}NH_2 \xrightarrow{HAuCl_4} Ph\overset{\oplus}{N}H_3\,Au\overset{\ominus}{Cl_4}$$

$$Ph\text{–}NH_2 \xrightarrow{Na} PhNHNa + \frac{1}{2}H_2$$

$$Ph\text{–}NH_2 \xrightarrow{CH_3I} Ph\text{–}NH\text{–}CH_3$$

$$Ph\text{–}NH_2 \xrightarrow{Cl\text{–}COCH_3} Ph\text{–}NH\text{–}COCH_3$$

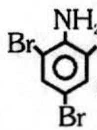
$$Ph\text{–}NH_2 \xrightarrow{CHCl_3+KOH} Ph\text{–}NC$$

$$Ph\text{–}NH_2 \xrightarrow{CH_3MgCl} CH_3\text{–}H$$

$$Ph\text{–}NH_2 \xrightarrow{O=CH\text{–}R} Ph\text{–}N{=}CH\text{–}R$$

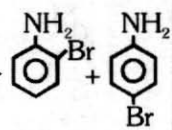
$$Ph\text{–}NH_2 \xrightarrow[\substack{[NaNO_2+HCl]\\ [5^\circ C]}]{HNO_2} Ph\overset{\oplus}{N_2}\overset{\ominus}{Cl}$$

$$Ph\text{–}NH_2 \xrightarrow{Br_2/H_2O}$$

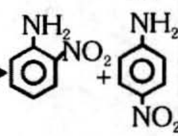


(wt. ppt)

$$Ph\text{–}NH_2 \xrightarrow[\text{(ii) } Br_2 \text{ (iii) } H_3O^{\oplus}]{\text{(i) } CH_3COCl}$$



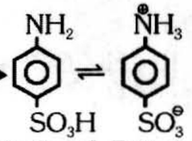
$$Ph\text{–}NH_2 \xrightarrow[\text{(ii) } \overset{\oplus}{N}O_2 \text{ (iii) } H_3\overset{\oplus}{O}]{\text{(i) } CH_3COCl}$$



$$Ph\text{–}NH_2 \xrightarrow[\substack{[NaNO_2+HCl]\\ 10^\circ C}]{HNO_2} \text{Phenol}$$

$$Ph\text{–}NH_2 \xrightarrow{CH_3Cl/AlCl_3} \text{No FCR}$$

$$Ph\text{–}NH_2 \xrightarrow[\Delta]{\text{conc. } H_2SO_4}$$



(Sulphanilic acid) (Zwitterion)

Comparison of S_N1 and S_N2

		S_N1	S_N2
A	Kinetics	1st order	2nd order
B	Rate	k[RX]	k[RX][Nu:$^-$]
C	Stereochemistry	Racemic Mixture	Inversion
D	Substrate	$3° > 2° > 1°$	$MeX > 1° > 2° > 3°$
E	Nucleophile	Rate independent to Nu^-	Needs Strong Nu
F	Solvent	Good ionizing	Faster in aprotic
G	Leaving Group	Needs Good LG	Needs Good LG
H	Rearrangement	Possible	Not Possible

Comparison of E_1 and E_2

		E_1	E_2
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 of base strength	Needs Strong bases
F	Solvent	Good ionizing	Polarity not important
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	Nu:$^-$/:B$^-$	Solvent	Temp.
1°	S_{N^2}	Better Nu:$^-$ HO:$^-$, $C_2H_5O:^-$	Polar aprotic	Low
	E_2	Strong & bulky base $(CH_3)_3CO:^-$		High
2°	S_{N^2}	HO:$^-$ $C_2H_5O:^-$	Polar aprotic	Low
	E_2	$(CH_3)_3CO:^-$		High
	S_{N^1}	Solvent	Polar protic	Low
	E_1	Solvent		High
3°	S_{N^1}	Solvent	Protic	Low
	E_1	Solvent	Protic	High

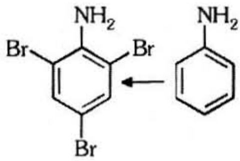
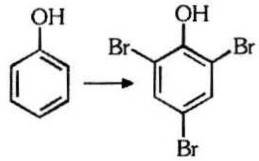
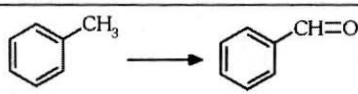
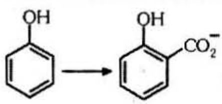
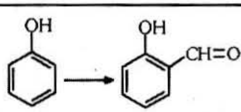
Darzan's process → ROH + $SOCl_2$ → RCl + SO_2

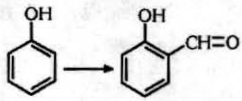
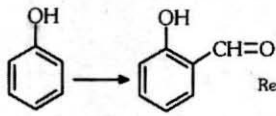
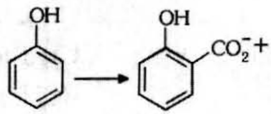
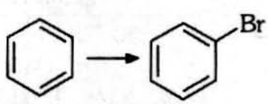
	Primary (1°)	Secondary (2°)	Tertiary (3°)
Strong nucleophile	$S_{N^2} >> E_2$	$S_{N^2} + E_2$ (if weak base, S_{N^2} favoured)	100% E_2
Weak nucleophile weak base	Mostly S_{N^2}	Mostly S_{N^2}/S_{N^1} (Aq. increases S_{N^1})	Mostly S_{N^1} at low T mostly E_1 at high T
Weak nucleophile strong base	Mostly E_2	Mostly E_2	100% E_2

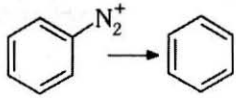
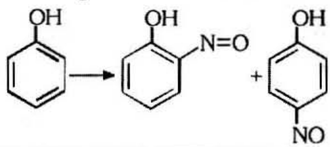
Nutshell Review and Preview of

ORGANIC REAGENTS

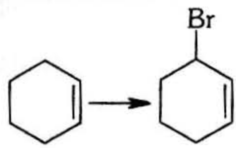
1.	Alcoholic KOH	R—X → Alkene ; Elimination
2.	Aluminium Ethoxide	$RCH{=}O \longrightarrow R{-}\underset{\underset{O}{\parallel}}{C}{-}O{-}CH_2R$ Aldehyde → Ester (Tischenko Reaction)
3.	Aqueous KOH/NaOH	R—X → ROH Nucleophilic substitution reaction also used for Cannizzaro reaction
4.	Baeyer's Reagent (Alkaline cold dilute $KMnO_4$)	$RCH{=}CHR' \longrightarrow R\underset{\mid \atop OH}{C}H{-}\underset{\mid \atop OH}{C}HR'$ (Syn) alkene ⟶ 1, 2 diol (used to detect unsaturation)

5.	Bromine water	(i) used to detect unsaturation; (ii)  **2,4,6-tribromoaniline** (iii)  **2,4,6-tribromophenol**
6.	Benedict's solution	Used to detect aldehyde group $RCHO \rightarrow RCO_2^-$ [ketone gives -ve test]
7.	$Cu_2Cl_2 + NH_4OH$ (Fehling solution))	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) $R_3COH \rightarrow$ no reaction
10.	$CCl_4 + \overline{O}H$ (Reimer Tiemann)	 + p-product
11.	$CO + HCl + AlCl_3$	 + p-product Gatterman koch reaction

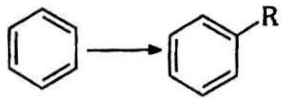
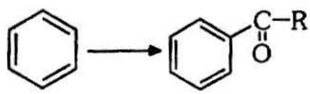
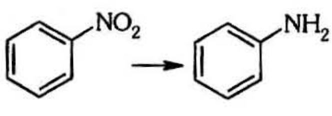
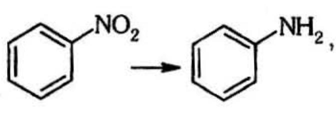
12.	HCN + HCl + $AlCl_3$	 Gatterman Aldehyde Synthesis
13.	$CHCl_3$ + KOH	(i)  Reimer Tiemann reaction (ii) $RNH_2 \rightarrow RNC$ **(Carbyl amine reaction)** (used to detect 1° Amine) (Isocyanide test)
14.	$CO_2 + OH^-$ (high temp. + pressure)	 + p–product Kolbes reaction
15.	Cu/Δ	(i) $RCH_2OH \rightarrow RCHO$, (ii) $R_2CHOH \rightarrow R_2C{=}O$ (iii) $H_3C-\underset{CH_3}{\overset{CH_3}{\mid}}{C}-OH \longrightarrow H_2C{=}C\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$
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

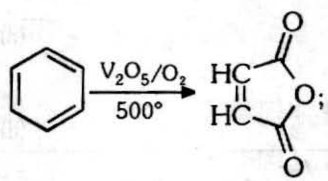
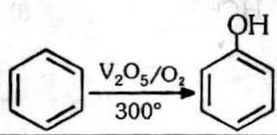
21.	$H_2(Pd/CaCO_3)$ Quinoline	Lindlar catalyst : $R—C\equiv C—R \rightarrow R—CH=CH—R$ (cis)
22.	H_3PO_2	 (Sodium stannite also can be used for this purpose)
23.	$HN_3 + H_2SO_4$	$R-\underset{\underset{O}{\Vert}}{C}-OH \longrightarrow RNH_2$ (Schmidt Reaction)
24.	H_3PO_4/Δ	$H_3PO_4 \Rightarrow$ Same as H_2SO_4/Δ
25.	H_2SO_4/Δ	$R\underset{\underset{OH}{\vert}}{C}H-CH_3 \longrightarrow RCH=CH_2$ 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)	$R\underset{\underset{OH}{\vert}}{C}H—\underset{\underset{OH}{\vert}}{C}H—R' \longrightarrow RCH=O + R'CH=O$ Oxidative cleavage of diol
28.	$H_2(Ni)$	$H_2(Ni)$ can reduce) (i) $R-\underset{\underset{O}{\Vert}}{C}-R \longrightarrow R_2CHOH$; (ii) $R-\underset{\underset{O}{\Vert}}{C}-H \longrightarrow RCH_2OH$ (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	$R-\underset{\underset{O}{\Vert}}{C}-Cl \longrightarrow RCH=O$ (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 $\underset{\underset{OH}{\vert}}{CH_2}-\underset{\underset{OH}{\vert}}{CH}-CH_2-OH \longrightarrow CH_2=CH-CH=O$
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.	$NaHSO_3$	$R-\underset{\underset{O}{\Vert}}{C}-R \longrightarrow R\underset{\underset{R}{\vert}}{C}\genfrac{}{}{0pt}{}{OH}{SO_3^-Na^+}$ [White crystals, soluble in water used to separate carbonyl from noncarbonyl compound]
36.	NaOH(aq)	(i) $R-X \rightarrow R-OH$; (ii) $R-\underset{\underset{O}{\Vert}}{C}-OR' \xrightarrow[(H_2O)]{NaOH} R-\underset{\underset{O}{\Vert}}{C}-O^- + R'OH$ 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) $H_3C-C(=O)-OEt \longrightarrow H_3C-C(=O)-CH_2-C(=O)-OEt$ (claisen condensation) (β keto ester)
39.	$NaOH + X_2$	(i) $RC(=O)-CH_3 \xrightarrow[-CHI_3]{} RCO_2^-$; (Haloform reaction) (ii) $R-C(=O)-NH_2 \longrightarrow RNH_2$ (Hoffman Degradation)
40.	NaOH + CaO	$RCO_2H \rightarrow RH$
41.	NaOX	Same as $NaOH + X_2$
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 →	$R-\underset{\underset{O}{\Vert}}{C}-R \rightarrow R-CH_2-R$ Clemmensen's reduction
47.	$NH_2 - NH_2/OH^-$	$R-CO-R \rightarrow R-CH_2-R$ Wolf Kishner
48.	Na in Liq. NH_3	$R-C\equiv CR \rightarrow \underset{H}{\overset{R}{\diagdown}}C=C\underset{R}{\overset{H}{\diagup}}$ (Birch reduction) (trans alkene)
49.	$OsO_4 + H_2O$ →	$RCH=CHR \rightarrow R\underset{OH}{\underset{\vert}{C}}H-\underset{OH}{\underset{\vert}{C}}H-R$ (syn addition)
50.	O_3	$R-CH=CH-R \xrightarrow[H_2O\backslash Zn]{O_3} R-CHO+R-CHO$ (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 → no reaction (Mild oxidizing reagent)
53.	P(red) + Br_2	(i) $CH_3CO_2H \rightarrow H_2\underset{Br}{\underset{\vert}{C}}-CO_2H$ (HVZ reaction) (ii) $ROH \rightarrow R-Br$
54.	P (red) + HI (strong reducing agent can reduce any oxygen or halogen containing compound to alkane)	$CH_3CO_2H \rightarrow CH_3-CH_3$ $CH_3CH=O \rightarrow CH_3-CH_3$ $CH_3CH_2OH \rightarrow CH_3-CH_3$

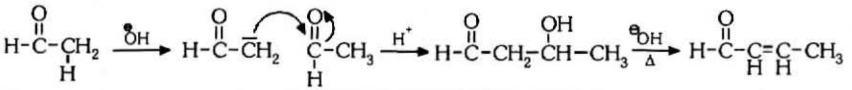
55.	Perbenzoic acid	$R-\underset{\underset{O}{\|}}{C}-R' \longrightarrow R-\underset{\underset{O}{\|}}{C}-OR'$ R' having more migrating tendency than R (Baeyer Villiger Oxidation)
56.	$RCl + AlCl_3$	 Friedel craft alkylation
57.	$RCOCl + AlCl_3$	 Friedel craft acylation
58.	$ROH+R-\underset{\underset{O}{\|}}{C}-OH$	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) $RCN \rightarrow R{-}CH_2NH_2$

61.	Silver salt RCOOAg	$Br_2/CCl_4/\Delta \rightarrow RBr + CO_2 + AgBr$ Hunsdiecker reaction
62.	(i) AgOH/moist Ag_2O	$R_4\overset{+}{N}\bar{X} \rightarrow R_4\overset{+}{N}\bar{O}H$;
63.	$SOCl_2$	$R-\underset{\underset{O}{\\|}}{C}-OH/R-OH \longrightarrow R-\underset{\underset{O}{\\|}}{C}-Cl/R-Cl$
64.	Tollens Reagent	$-CH=O \rightarrow -CO_2^- + Ag$ (Shining silver mirror) (I) α- hydroxy ketone, Ph–NH–OH, HCO_2H gives positive test (II) Reagent also used to distinguish (i) $-\overset{\overset{H}{\|}}{C}=O$ Vs $-\underset{\underset{O}{\\|}}{C}-R$ (ii) HCOOH Vs other acid (III) ketone gives -ve test;
65.	Benzene sulphonyl chloride (Hinsberg reagent)	It is used to distinguish and separate 1°, 2° and 3° amines.
66.	Tetra ethyl lead	Used as antiknock compound
67.	V_2O_5	(I)  (II) 

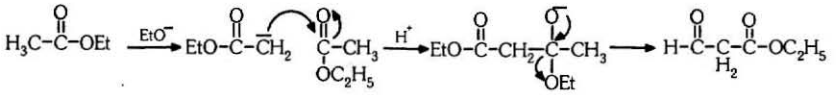
NUTSHELL REVIEW & PREVIEW OF

ORGANIC NAME REACTIONS

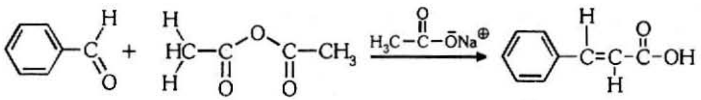
- **Aldol Condensation**



- **Claisen Condensation**

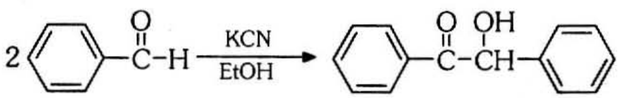


- **Perkin Condensation**



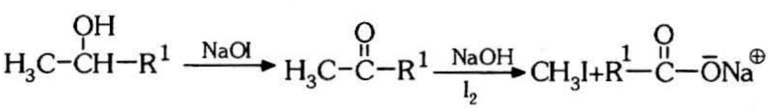
Cinnamic acid

- **Benzoin Condensation**

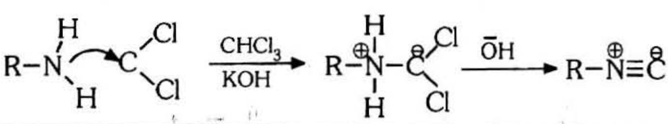


Benzoin

- **Haloform Reaction**

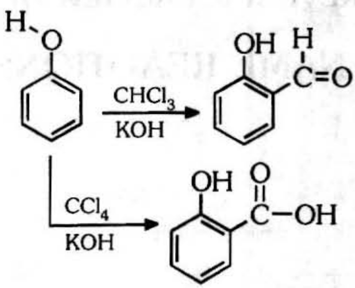


- **Carbylamine Test**



Isocyanide

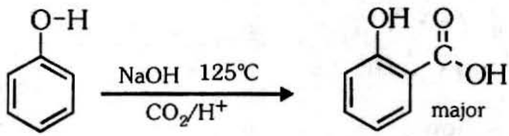
- **Reimer Tiemman Reaction**



(Salicylaldehyde)

(Salicylic acid)

- **Kolbe's Schimdt Reaction**



(Salicylic acid)

- **Hoffmann Bromamide Degradation**

$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[KOH]{Br_2} R-NH_2 + K_2CO_3$$

- **Curtius Reaction**

$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[\Delta, H_3O^+]{NaN_3} R-NH_2$$

- **Schimdt Reaction**

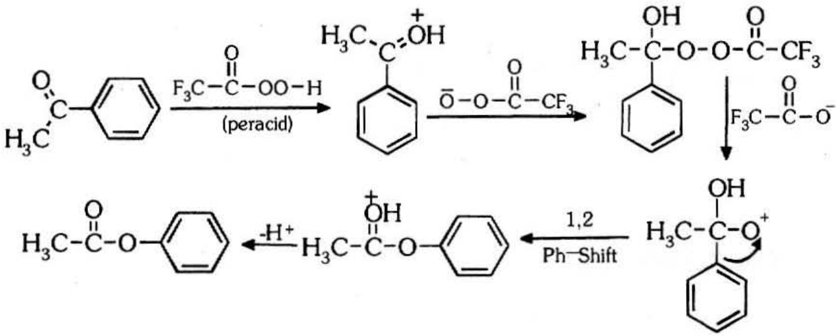
$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[H_2SO_4]{HN_3} R-N=C=O \xrightarrow{H_3O^{\oplus}} R-NH_2$$

- **Cannizzaro reaction**

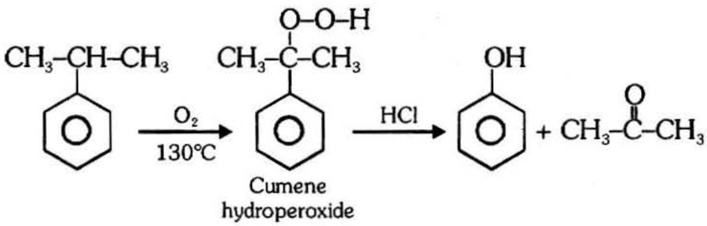
$$H-\overset{O}{\overset{\|}{C}}-H \xrightarrow[NaOH]{50\%} H_3C-\overset{\bar{O}}{\overset{|}{\underset{H-O}{\underset{|}{C}}}}-H \quad \overset{O}{\overset{\|}{\underset{H}{\underset{|}{C}}}}-H \xrightarrow[RDS]{slow}$$

$$H-\overset{O}{\overset{\|}{C}}-OH + H-\overset{O^-}{\overset{|}{\underset{H}{\underset{|}{C}}}}-H \longrightarrow H-\overset{O}{\overset{\|}{C}}-\bar{O}Na^+ + CH_3-OH$$

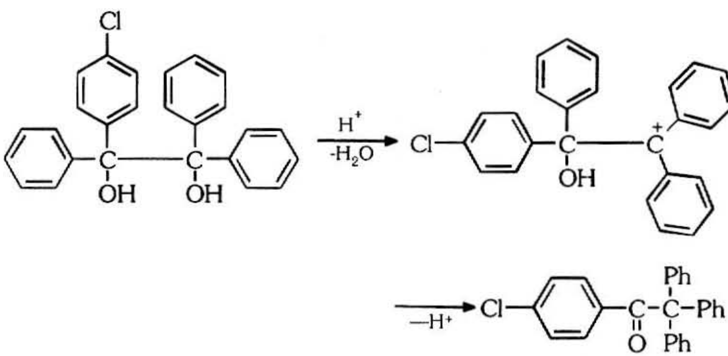
- **Bayer villiger oxidation**



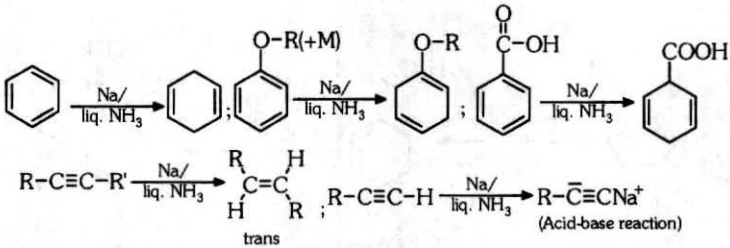
- **Cumene**



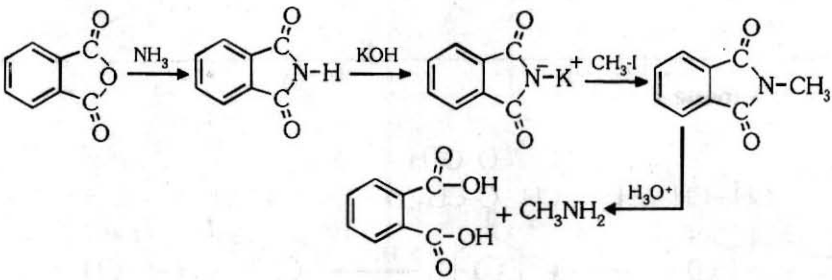
- **Pinacol-Pincolone rearrangement**



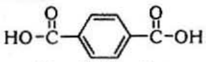
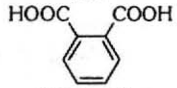
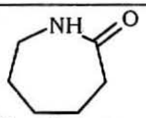
- **Birch Reduction**



- **Gabriel Synthesis**



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	$HO-\overset{O}{\overset{\parallel}{C}}(CH_2)_4-\overset{O}{\overset{\parallel}{C}}-OH$ 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

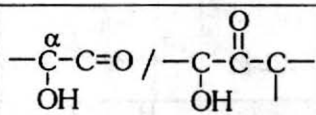
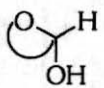
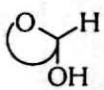
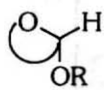
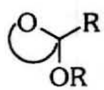
CARBOHYDRATES

- 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)

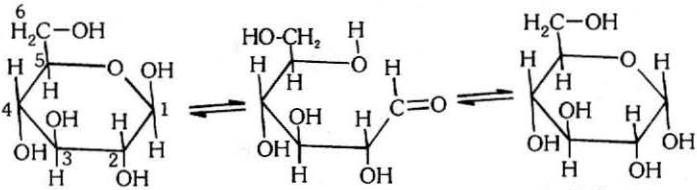
  Sucrose $\xrightarrow{H_3O^+}$ α–D. Glucose + β–D. Fructose;

  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.

Give Test	Reducing	Non Reducing
1. Tollen's Reagent	+ve test	–ve test
2. Fehling Reagent	+ve test	–ve test
3. Benedict Test	+ve test	–ve test
4. Mutarotation	Yes	No
5. Functional Unit	  Hemiacetal  Hemiketal	 Acetal  Ketal
6. Example	All monosaccharides Glucose; fructose, mannose, galactose, Disaccharide : maltose; lactose	Disaccharide:Sucrose Polysaccharide:Starch, cellulose

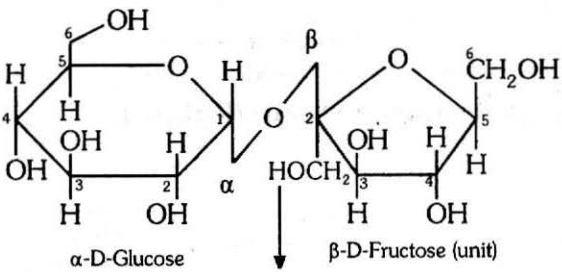
- **Mutarotation:** When either form of D-glucose is placed in aq. solution it slowly form the other via open chain aldehyde and gradual change in specific rotation until specific rotation (± 52.5°) is reached.



β-D-Glucose $[\alpha]_D = +19°$ | $[\alpha]_D = 52.5$ | α-D-Glucose $[\alpha]_D = +112°$

- **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

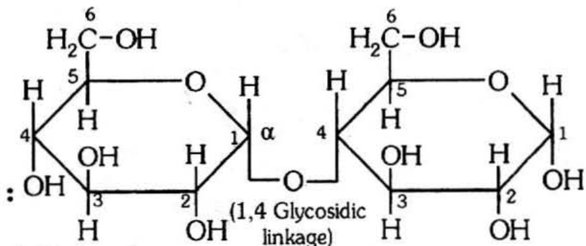
  eg. D-Glucose & D-monnose
  D-Glucose & D-Galactose
- **Sucrose :**



α-D-Glucose β-D-Fructose (unit)

(1,2 Glycosidic linkage)

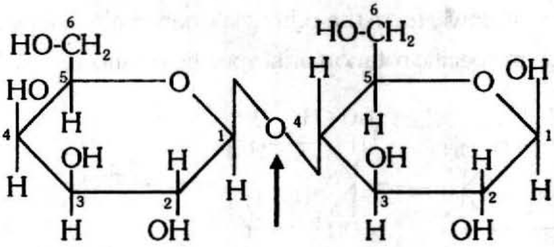
- **Maltose**



(α-D-glucose)

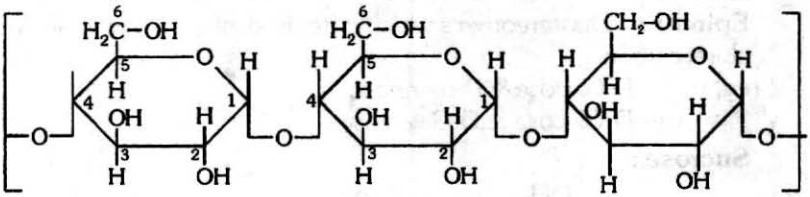
Two α-D-Glucose unit

- **Lactose :**



(1,4 Glycosidic linkage)

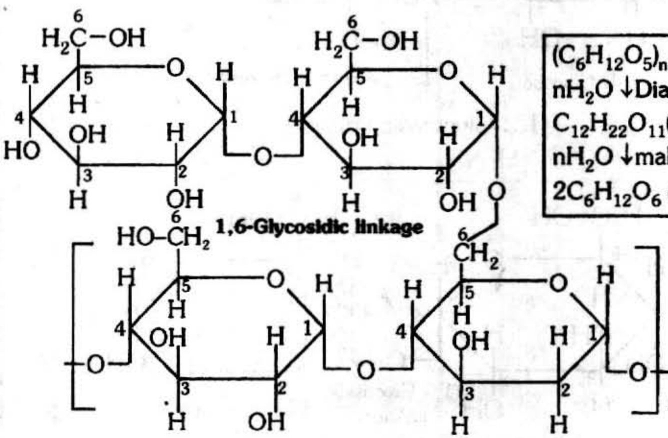
- **Starch** : (Amylose & Amylopectin)
- **Amylose : (Straight Chain) :**



(α-1,4 Glycosidic linkage)

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

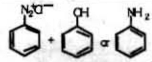
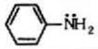
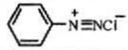
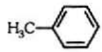
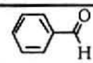
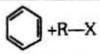
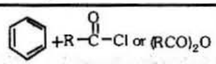
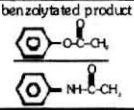
- **Amylopectin (Branch chain) : $(C_6H_{12}O_5)_n$**



1,4-Glycosidic linkage

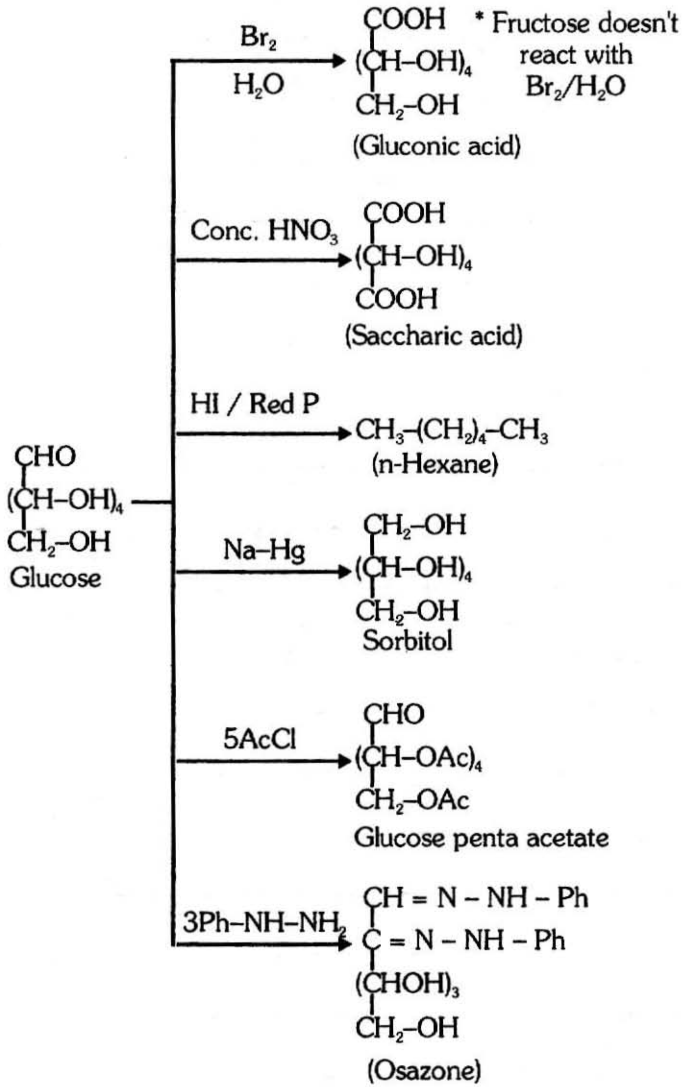
$(C_6H_{12}O_5)_n$
$nH_2O \downarrow$ Diastase
$C_{12}H_{22}O_{11}$(maltose)
$nH_2O \downarrow$ maltase
$2C_6H_{12}O_6$ α-D-Glucose

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

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-Zelinksy 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, $Pd/BaSO_4$, S, 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	benzolytated product 
Stephen reaction	alkyl cyanide	$SnCl_2$/HCl	Aldehyde
Williamson synthesis	alkyl halide	sodium alkoxide or sodium phenoxide	Ether
Wurtz-Fittig reaction	alkyl halide + aryl halide	Na/dry ether	alkyl benzene

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 or	$CH_3CH=CH_2$	Homopolymer, linear, chain growth
3.	Polystyrene	$C_6H_5CH=CH_2$	Homopolymer, linear, chain growth
II. Polydiences			
1.	Neoprene	$H_2C=CH-\overset{Cl}{\overset{\vert}{C}}=CH_2$ Chloroprene or 2-Chloro-1,3-butadiene	Homopolymer, chain growth
2	Buna S (Styrene-Butadiene, Rubber) SBR or GRS	$H_2C=CH-CH=CH_2$ 1,3-butadiene and $C_6H_5CH=CH_2$ Styrene	Copolymer, chain growth
III. Polyacrylates			
1.	Polymethylmethacrylate (Flexiglass Lucite, Acrylite or Perspex PMMA	$H_2C=\overset{CH_3}{\overset{\vert}{C}}-COOCH_3$	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


Br2
H2O
COOH
(CH–OH)4
CH2–OH
(Gluconic acid)
* Fructose doesn't react with Br2/H2O
Conc. HNO3
COOH
(CH–OH)4
COOH
(Saccharic acid)
HI / Red P
CH3–(CH2)4–CH3
(n-Hexane)
CHO
(CH–OH)4
CH2–OH
Glucose
Na–Hg
CH2–OH
(CH–OH)4
CH2–OH
Sorbitol
5AcCl
CHO
(CH–OAc)4
CH2–OAc
Glucose penta acetate
3Ph–NH–NH2
CH = N – NH – Ph
C = N – NH – Ph
(CHOH)3
CH2–OH
(Osazone)

IMPORTANT NOTES