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Chemical structures of α -D-glucopyranose and β -D-fructofuranose. The left structure is α -D-glucopyranose, a six-membered ring with an α -glycosidic bond to the anomeric carbon of D-glucose. The right structure is β -D-fructofuranose, a five-membered ring with a β -glycosidic bond to the anomeric carbon of D-fructose. Labels indicate the α -glycoside bond to the anomeric position of D-glucose and the β -glycoside bond to the anomeric position of D-fructose.

$$2(\text{C}_6\text{H}_{10}\text{O}_5)_n + n\text{H}_2\text{O} \xrightarrow{\text{Diastase}} n\text{C}_{12}\text{H}_{22}\text{O}_{11}$$

Starch Maltose

- 33

Polymer & POC

skm-nucleusacademy
(5070) mem

HW

Biomolecule sheet

EX-1

Aromatic sheet

EX-1

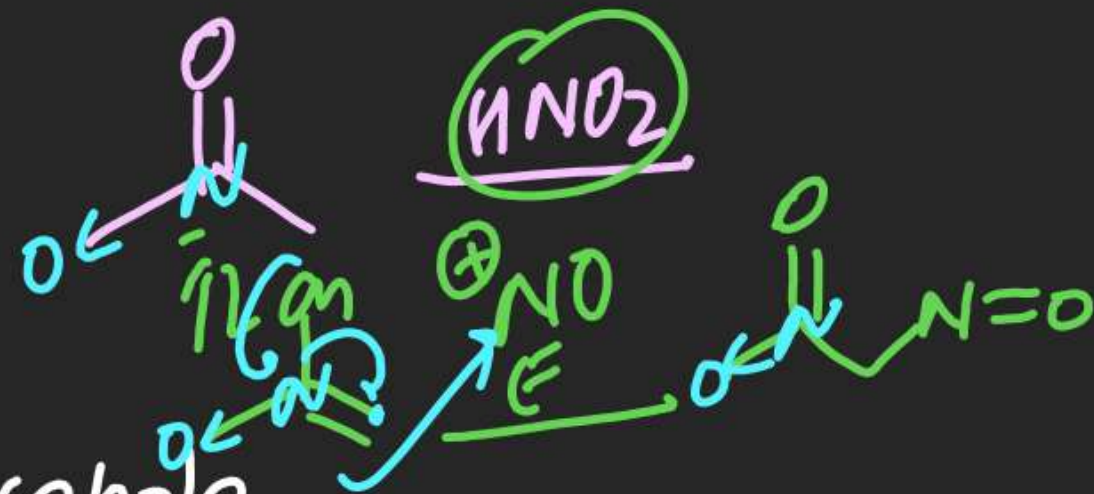
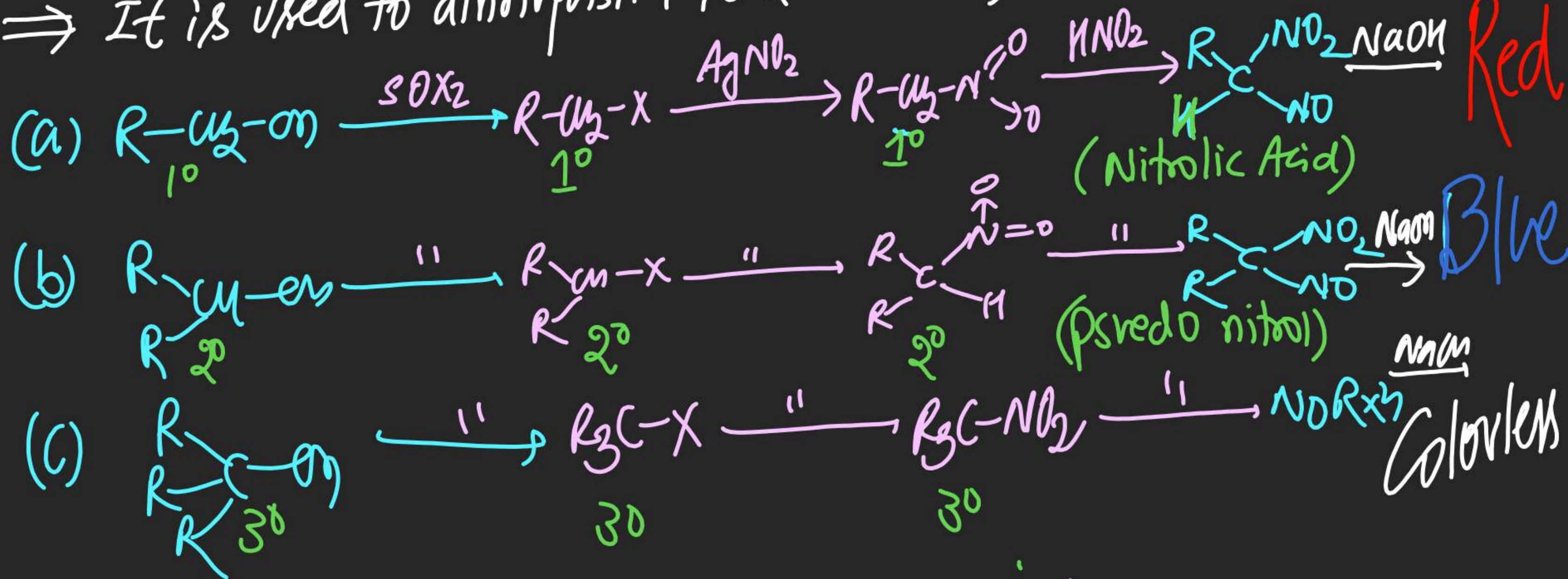
Carboxylic Acid
& Derivative

EX-1

Practical Organic Chemistry (POC)

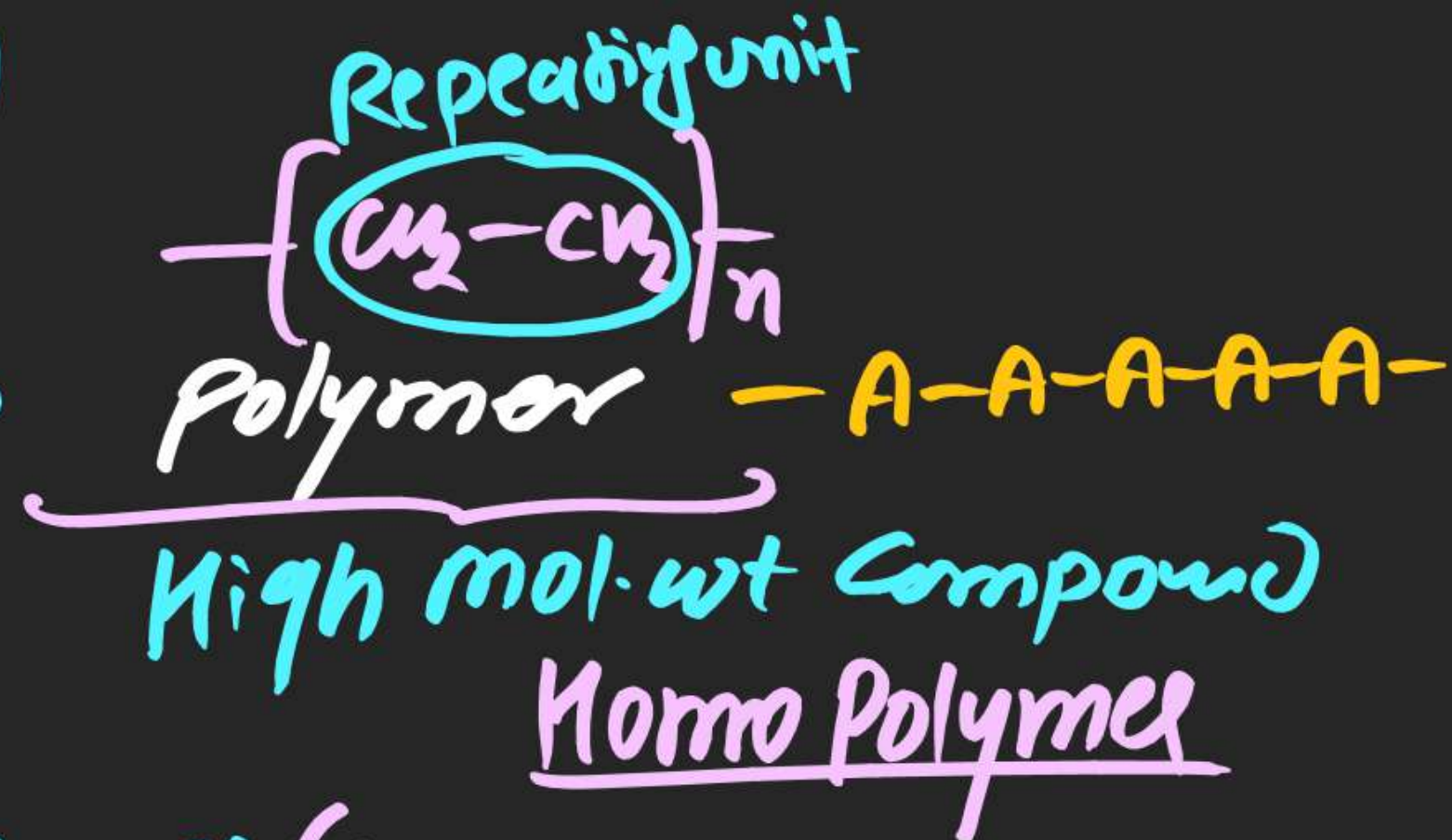
(*) Victor Mayer Test (RBC Test)

⇒ It is used to distinguish 1°, 2° & 3° alcohols.



Polymer

(a) " n " A
monomer



(b) " n_1 " A + " n_2 " B → Polymer (Copolymer)

Alternate Copolymer



Random Copolymer

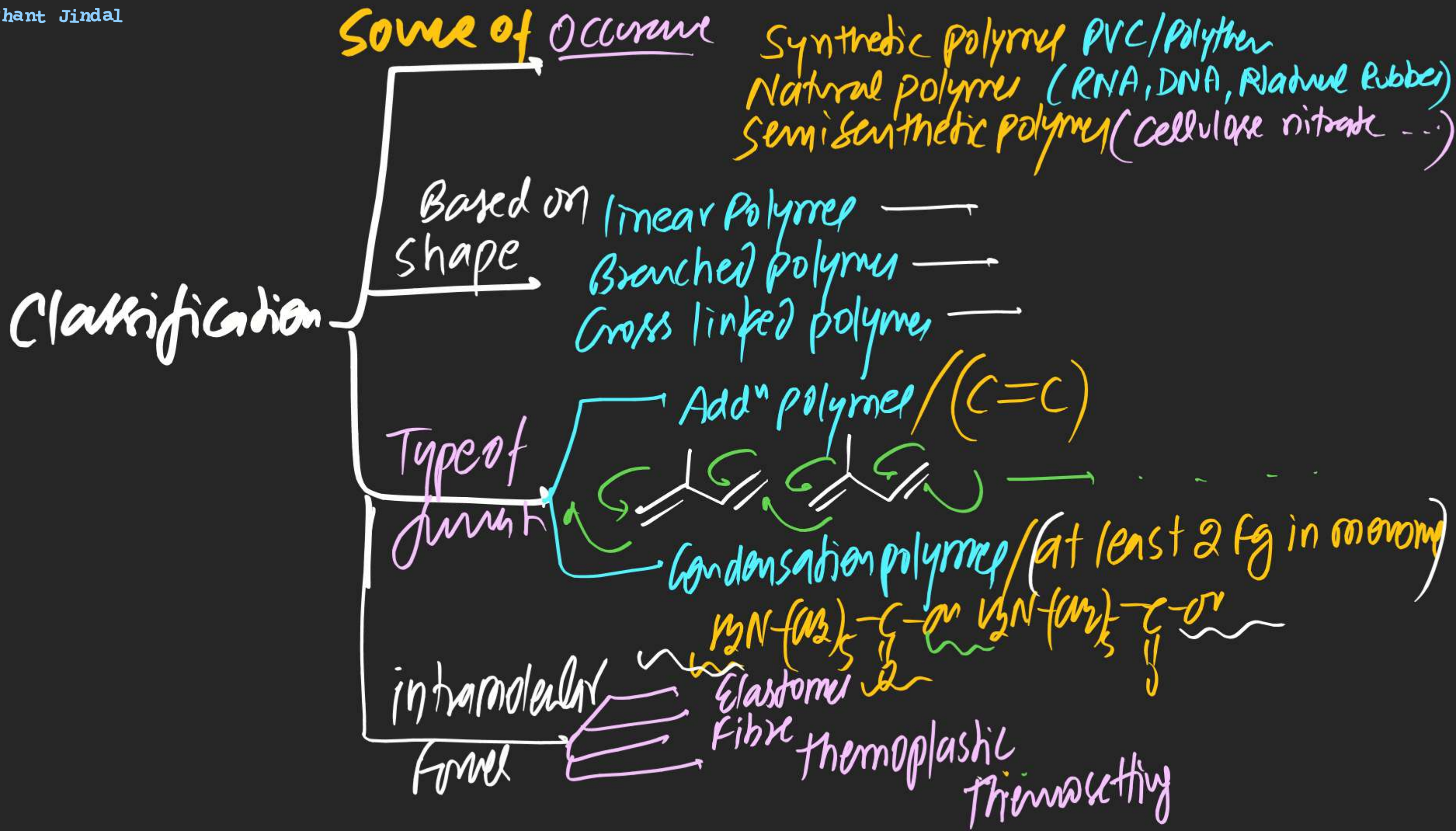


Block Copolymer



Graft Copolymer





POLYMERS AND PRACTICAL ORGANIC CHEMISTRY NOTES

- The term polymer is used to describe a very large molecule that is made up of many small repeating molecular units. These small molecular units from which the polymer is formed are called monomers.
- The chemical reaction that joins the monomers together is called polymerisation.
- Starting from n molecules of a compound M , linking in a linear manner will form polymer $x - M - (M)_{n-2} - M - y$. The nature of linkages at the terminal units i.e. $M - x$ and $M - y$ depends upon the mode of reaction used in making the polymers.

Homopolymers and Copolymers

Polymers which are formed by only one type of monomer are called homopolymers. Some examples of homopolymers and their monomers are given below :

Homopolymer	Monomer
Starch	Glucose
Cellulose	Glucose
Glycogen	Glucose
Dextrin	Glucose
Inulin	Fructose
Polyethylene	Ethylene
Polyvinyl chloride	Vinyl chloride
Teflon	Tetrafluoro ethylene
Nylon-6	Caprolactam
Polystyrene	Styrene
Orlon (Acrilan)	Acrylonitrile
Plexiglas (Lucite)	Methyl methacrylate
Polyvinyl acetate	Vinyl acetate

Polymers, which are formed by more than one type of monomers are known as copolymers. Some examples are given below in the table :

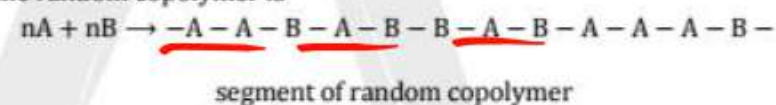
Copolymer	Monomers
Saran	<u>Vinyl chloride and vinylidene chloride</u>
SAN	<u>Styrene and acrylonitrile</u>
ABS	<u>Acrylonitrile, butadiene and styrene</u>
Butyl rubber	<u>Isobutylene and Isoprene</u>
Buna-S, SBR	Styrene and Butadiene
Buna-N, NBR	Acrylonitrile and Butadiene
Nylon-66	Hexamethylenediamine and Adipic acid
Terylene	Terephthalic acid and ethylene glycol

Types of copolymers

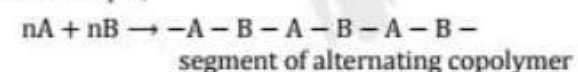
Depending upon the distribution of monomer units, the following types of copolymers are possible.

(1) Random Copolymer

If the monomer units have random distribution throughout the chain, it is called random copolymer. For example, if the monomer A and monomer B undergo copolymerisation then the structure of the random copolymer is

**(2) Alternating Copolymer**

If the two monomer units present alternatively throughout the polymer chain, it is said to be alternating copolymer. For example,

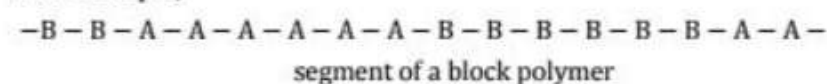


The exact distribution depends upon the proportion of the two reactant monomers and their relative reactivities. In practice neither perfectly random nor perfectly alternating copolymers are usually formed. However, most copolymers tend more towards alternating type but have many random imperfections.

(3) Block copolymer

Polymers in which different blocks of identical monomer units alternate with each other are called block copolymers.

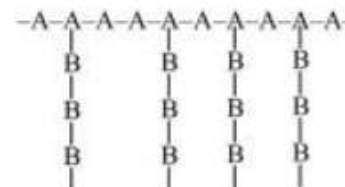
For example,



Block copolymer can be prepared by initiating the radical polymerisation of one monomer to grow homopolymer chains, followed by addition of an excess of the second monomer.

(4) **Graft copolymer**

Polymers in which homopolymer branches of one monomer unit are grafted onto a homopolymer chain of another monomer unit are called graft co-polymers. For example:



(Segment of a graft copolymer)

Graft copolymers are prepared by γ -irradiation of a homopolymer chain in the presence of a second monomer. the high energy radiation knock out H-atoms from the homopolymer chain at random points thus generating radical sites that can initiate polymerisation of the second monomer.

CLASSIFICATION OF POLYMERS

Polymers are classified in following ways :

(I) **CLASSIFICATION BASED UPON SOURCE**

(1) **Natural polymers**

Polymers which are obtained from animals and plants are known as natural polymers.

Examples of natural polymers are given below.

Natural polymer

1. Polysaccharide ✓
2. Proteins ✓
3. Nucleic acid ✓
4. Silk ✓
5. Natural Rubber (cis polyisoprene) ✓
6. Gutta purcha (trans polyisoprene) ✓

Monomers

- Monosaccharide
- α -L-Amino acids
- Nucleotide
- Amino acids
- Isoprene (2-Methyl-1,3-butadiene)
- Isoprene

Natural polymers which take part in metabolic processes are known as biopolymers. Examples are polysaccharides, proteins, RNA and DNA.

(2) **Semisynthetic polymers**

Polymers which are prepared from natural polymers are known as semisynthetic polymers. Most of the semisynthetic polymers are prepared from cellulose. Examples are: cellulose acetate, cellulose nitrate, cellulose xanthate and Rayon.

(3) **Synthetic polymers**

Man-made polymers, i.e. polymers prepared in laboratory are known as synthetic polymers.

Example are : PVC, polyethylene, polystyrene, nylon-6, nylon-66, nylon-610, terylene, synthetic rubbers etc.

(II) CLASSIFICATION BASED UPON SHAPE

(1) Linear polymers

Polymer whose structure is linear is known as linear polymer. The various linear polymeric chains are stacked over one another to give a well packed structure.



The chains are highly ordered with respect to one another. The structure is close packed in nature, due to which they have high densities, high melting point and high tensile (pulling) strength. Linear polymers can be converted into fibres.

Note :

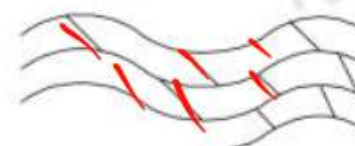
- (i) All fibers are linear polymers. Examples are cellulose, silk, nylon, terylene etc.
- (ii) Linear polymers may be condensation as well as addition polymers. Examples are cellulose, polypeptide, nucleic acid, nylon, terylene etc.

(2) Branched chain polymers

Branched chain polymers are those in which the monomeric units constitute a branched chain. Due to the presence of branches, these polymers do not pack well. As a result branched chain polymers have lower melting points, low densities and tensile strength as compared to linear polymers. Branched chain polymers may be formed due to addition as well as condensation polymerisation. Examples are amylopectin, glycogen, low density polyethylene and all vulcanised rubbers.

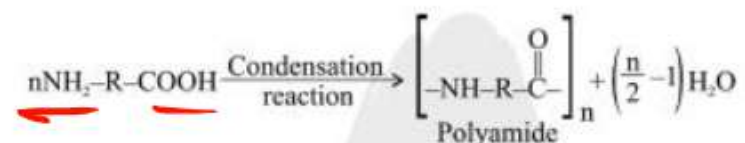
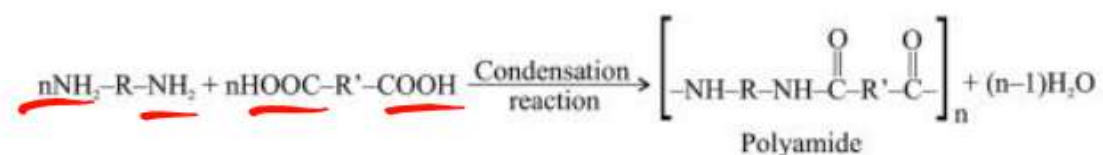
(3) Cross-linked or Three Dimensional network polymers

In these polymers the initially formed linear polymeric chains are joined together to form a three dimensional network structure. These polymers are hard, rigid and brittle. Cross-linked polymers are always condensation polymers. Resins are cross linked polymers.

CLASSIFICATION BASED UPON SYNTHESIS(1) Condensation polymerisation

They are formed due to condensation reactions. Condensation polymerisation is also known as step growth polymerisation. For condensation polymerisation, monomers should have at least two functional groups. Both functional groups may be same or different. Monomers having only two functional group always give linear polymer.

For example,

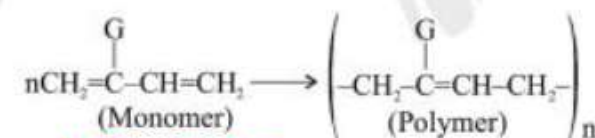


Condensation polymers do not contain all atoms initially present in the monomers. Some atoms are lost in the form of small molecules. Monomer having three functional groups always gives crosslinked polymer.

Examples are : Urea-formaldehyde resin, phenol-formaldehyde resin.

(3) Addition polymerisation

Polymers which are formed by addition reaction are known as addition polymers. If monomer is ethylene or its derivative, then addition polymer is either linear polymer or branch-chain polymer. Examples are : polystyrene, polytetrafluoroethylene, polyacrylonitrile etc. If monomer is 1, 3-butadiene or 2-substituted-1, 3-butadiene $\left(\text{CH}_2 = \underset{\text{G}}{\text{C}} - \text{CH} = \text{CH}_2 \right)$, then polymer is always branched chain polymer.



(Monomer)

(i) G = H: 1,3 - Butadiene

(ii) G = CH₃; 2 - Methyl-1,3-butadiene or isoprene

(iii) G = Cl; 2 -Chloro-1,3-butadiene or chloroprene

(Polymer)

(i) Polybutadiene

(ii) Polyisoprene

(iii) Polychloroprene (Neoprene)

Addition polymers retain all the atoms of the monomer units in the polymer. Addition polymerisation takes place in three steps. Initiation, chain propagation and chain termination.

Addition polymers are called as chain growth polymers.

(D) Ziegler- Natta polymerisation :

Addition polymerisation which takes place in the presence of Ziegler- Natta catalyst $[(C_2H_5)_3Al \text{ and } TiCl_4]$ is known as Ziegler- Natta polymerisation or coordination polymerisation. Ziegler- Natta polymerisation always gives linear, stereo-regular polymers. Ziegler- Natta catalyst revolutionised the field of polymer chemistry because they allow the synthesis of stronger and stiffer polymers (due to linear geometry) that have greater resistance to cracking and heat. High density polyethylene is prepared using a Ziegler- Natta catalyst.

CLASSIFICATION BASED ON INTERMOLECULAR FORCES**(SECONDARY FORCES)**

Intermolecular forces present between polymeric chains are (a) Van der Waals forces (b) Hydrogen bonds and (c) Dipole - dipole attractions. Mechanical properties such as tensile strength, elasticity, toughness etc. depend upon the secondary forces present between the polymeric chains. Magnitude of secondary forces depends upon the size of the molecule and the number of functional groups along the polymeric chains. Magnitude of secondary forces is directly proportional to the length of the polymeric chain. On the basis of magnitude of secondary forces, polymers can be divided into the following following categories.

(1) Elastomes

An elastomer is a plastic that stretches and then reverts back to its original shape. It is randomly oriented amorphous polymer. It must have some cross-links so that the chains do not slip over one another. Very weak Vander Waal forces are present in between polymeric chains.

When elastomers are stretched, the random chains stretch out, but there are insufficient Vander Waal forces to maintain them in that configuration and position. When the stretching force is removed, they go back to their random shape. Elastomers have the ability to stretch out over ten times their normal length. Important examples are vulcanized rubbers.

Note : Addition polymers obtained from butadiene and its derivatives are elastomers.

(2) Fibres

Fibres are linear polymers in which the individual chains of a polymer are held together by hydrogen bonds and / or dipole-dipole attraction. In the fibres, the polymeric chains are highly ordered with respect to one another. Due to strong intermolecular forces of attraction and highly ordered geometry, fibres have high tensile strength and least elasticity. They have crystalline character and have high melting points and low solubility. Examples are cellulose, nylon, terylene, wool, silk etc.

Note :

(i) Condensation polymers formed from bifunctional monomers are fibres in character.

(ii) Addition polymers of alkene derivatives having strong- I group are fibres in character.

(3) Thermoplastic Polymers

Thermoplastic polymers are polymers that have both ordered crystalline regions (the regions of the polymer in which the chains are highly ordered with respect to one another) and amorphous, non crystalline regions (the regions of the polymer in which the chains are randomly oriented). The intermolecular forces of attraction are in between elastomers and fibres. There are no cross links between the polymeric chains. Thermoplastic polymers are hard at room temperature, but when they are heated, the individual chains can slip past one another and the polymer become soft and viscus. this soft and viscous material become rigid on cooling. The process of heating softening and cooling can be repeated as many times as desired without any change in chemical composition and mechanical properties of the plastic. As a result, these plastics can be moulded into toys, buckets, telephone and television cases. Some common examples are : polyethene polypropylene, polystyrene, polyvinyl chloride, teflon etc.

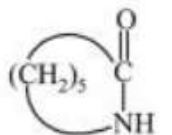
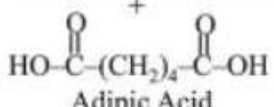
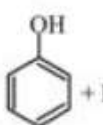
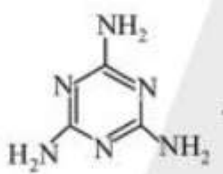
Note : Addition polymers obtained from ethylene and ethylene derivatives are thermoplastic polymers.

(4) Thermosetting Polymers

Polymers which become hard on heating are called thermosetting polymers. thermosetting polymers can be heated only once when it permanently sets into a solid, which cannot be remelted by heating. Thermosetting polymers are cross- linked polymers . Greater the degree of cross - linking that exist, the more rigid is the polymer. Cross-linking reduces the mobility of the polymer chains, causing them to be relatively brittle materials. the hardening on heating is due to the extensive cross-linking between different polymer chains to give a three dimensional network solid. Examples are : phenol formaldehyde resin, urea-formaldehyde resin ,melamine - formaldehyde resin.

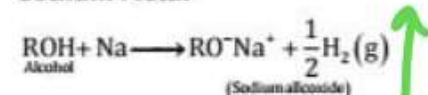
DIFFERENCE BETWEEN THERMOPLASTIC AND THERMOSETTING POLYMERS

S.NO.	Thermoplastic polymers	Thermosetting polymers
1.	Soften and melt on heating and become hard on cooling i.e. process is reversible	Become hard on heating and process is irreversible.
2.	Can be moulded and remoulded and reshaped.	They can be moulded once and cannot be remoulded or reshaped. They are addition polymers
3.	They are addition polymers	They are condensation polymers.
4.	Structure is generally linear	Structure is cross-linked.

20.  Caprolactam	$\text{—NH(CH}_2)_5\text{—C(=O)—}$	Nylon-6
21. $\text{NH}_2(\text{CH}_2)_6\text{—NH}_2$ Hexamethylenediamine +  Adipic Acid	$\text{—NH—(CH}_2)_6\text{—NH—C(=O)—(CH}_2)_4\text{—C(=O)—}$	Nylon - 66
22.  + HCHO	—	Bakelite or resol
23. $\text{NH}_2\text{—C(=O)—NH}_2$ + HCHO	—	Urea- formaldehyde resin
24.  + HCHO Melamine	— (POC)	Melamine formaldehyde resin

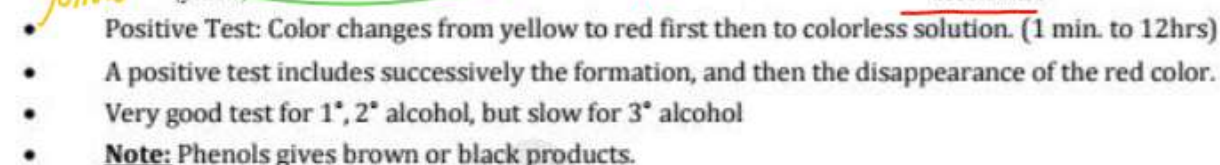
CHEMICAL TESTS FOR FUNCTIONAL GROUPS

- Elemental analysis, physical, spectral and solubility test give a reasonable idea regarding the identity of unknown compound.
- Despite the tremendous importance and ease of spectral analysis, chemical tests are indispensable to complete characterization.

✓ 1. **Test For Alcohols :**(i) **Sodium Metal**

- When Na-metal reacted with alcohol $\text{H}_2(\text{g})$ evolve
- It occurs in 1°, 2° & 3°

- (ii) **Ceric Ammonium Nitrate Oxidation (CAN Test)** (CAN Test for Alcohol)



(iii) **Jones Oxidation:** Chromic anhydride or Chromium Trioxide (CrO_3)

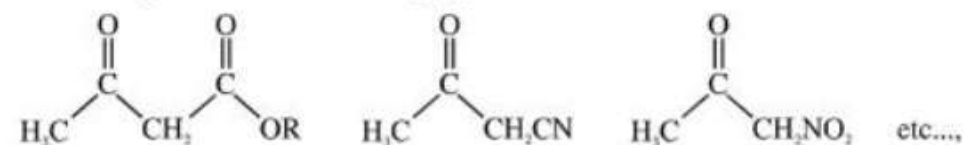
- $$\begin{array}{l}
 \text{1}^\circ \text{ alcohol} \quad 3\text{RCH}_2\text{OH} + 4\text{CrO}_3 + 6\text{H}_2\text{SO}_4 \xrightarrow{+6} 3\text{R}-\text{C}(=\text{O})\text{OH} + 9\text{H}_2\text{O} + 2\text{Cr}_2(\text{SO}_4)_3 \\
 \text{(orange-red)} \qquad \qquad \qquad \text{carboxylic acid} \qquad \qquad \qquad \text{(intense blue to green)}
 \end{array}$$
- $$\begin{array}{l}
 \text{2}^\circ \text{ alcohol} \quad 3\text{R}_2\text{CHOH} + 2\text{CrO}_3 + 3\text{H}_2\text{SO}_4 \xrightarrow{+6} 3\text{R}_2\text{C}=\text{O} + 6\text{H}_2\text{O} + 2\text{Cr}_2(\text{SO}_4)_3 \\
 \text{(orange-red)} \qquad \qquad \qquad \text{ketone} \qquad \qquad \qquad \text{(intense blue to green)}
 \end{array}$$
- $$\begin{array}{l}
 \text{aldehyde} \quad 3\text{R}-\text{C}(=\text{O})\text{H} + 2\text{CrO}_3 + 3\text{H}_2\text{SO}_4 \xrightarrow{+6} 3\text{R}-\text{C}(=\text{O})\text{OH} + 3\text{H}_2\text{O} + \text{Cr}_2(\text{SO}_4)_3 \\
 \text{(orange-red)} \qquad \qquad \qquad \text{carboxylic acid} \qquad \qquad \qquad \text{(blue to green)}
 \end{array}$$

(iv) **Lucas Test**

- This test distinguishes 1°, 2° & 3° alcohol from each other
 - It uses, anhydrous ZnCl_2 in conc. HCl (lucas reagent)
- $$\text{R}-\text{OH} \xrightarrow{(\text{HCl}+\text{ZnCl}_2)} \text{R}-\text{Cl} + \text{H}_2\text{O}$$
- 3° alcohols give white turbidity solution immediately
 - 2° alcohols give white turbidity solution within 5 to 10 minutes
 - 1° alcohols does not give white turbidity at normal temperature

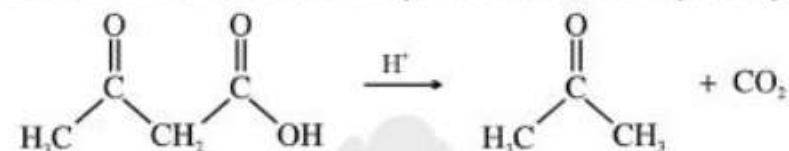
Note : Benzyl alcohol also react immediately

- The test is negative for the following type:



In such compounds the reagent removes the acetyl group and converts it to acetic acid, which resists iodination.

Acetoacetic acid is unstable, acidic aqueous solutions decompose to give CO_2 and acetone.

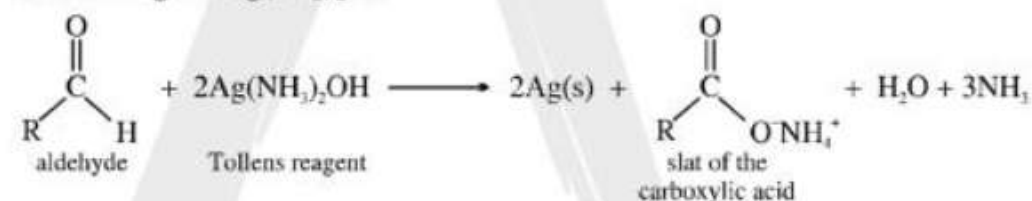


3. Tests that give positive results with aldehydes and negative results with Ketones

(i) Jones Oxidation: Chromic anhydride or Chromium Trioxide (CrO_3)

(Refer Jones Oxidation for alcohols at Page No. 22)

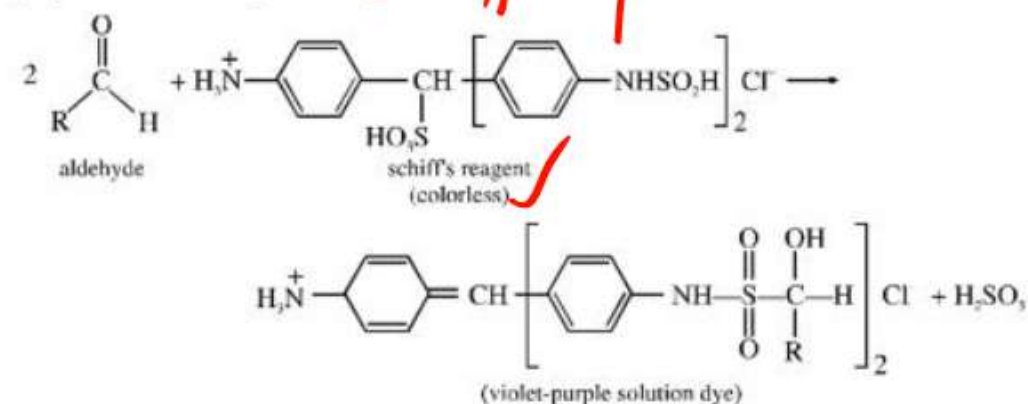
(ii) Tollens Reagents $\text{Ag}(\text{NH}_3)_2\text{OH}$



- Positive Test:** Formation of silver mirror (Ag(s)) or colloidal (granular) gray or black Ag precipitate.

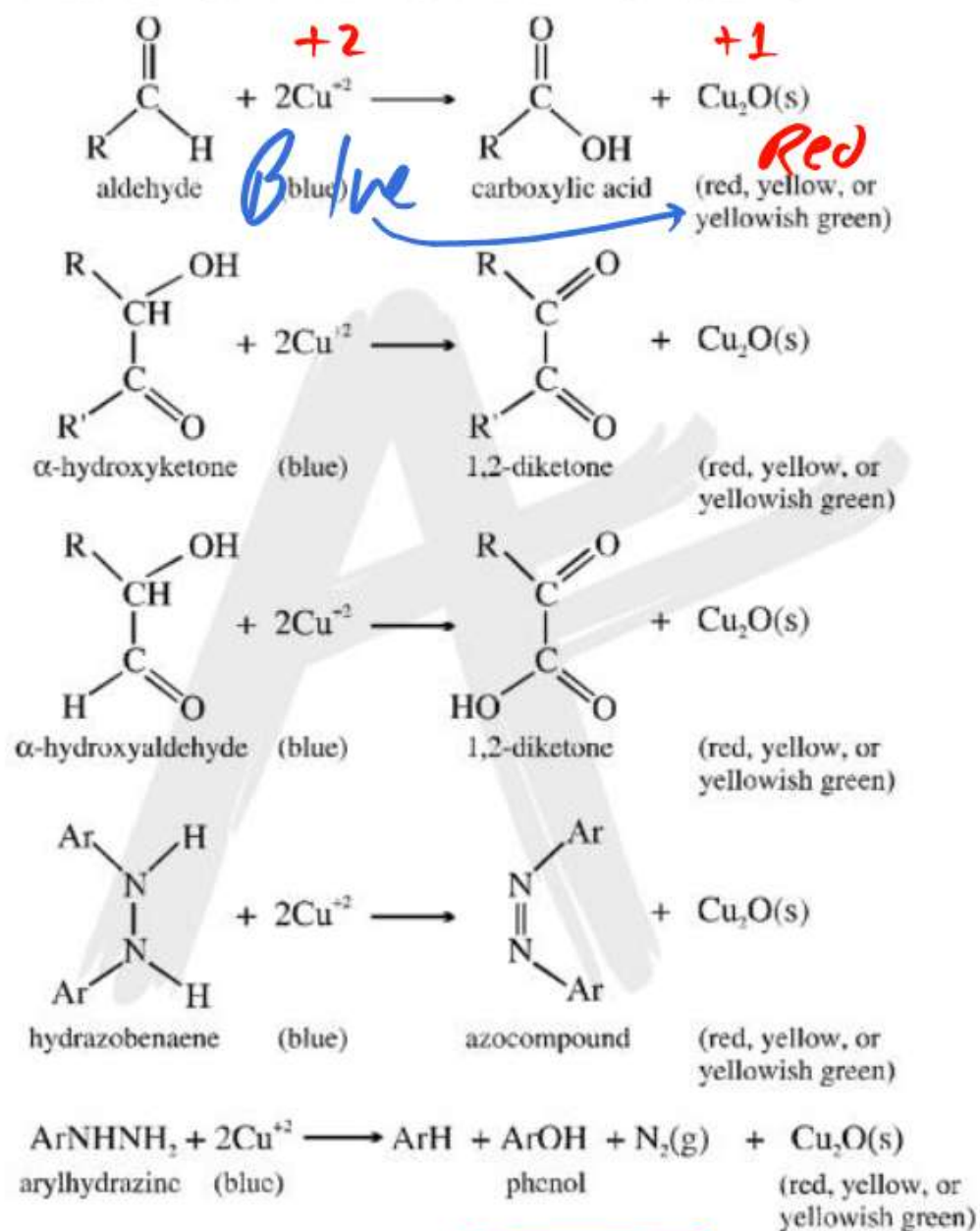
(iii) Fuchsin Reagent

Schiff's Reagent



(iv) Benedict's solution and Fehling's Solution

- Positive Test: yellow or yellowish green ppt.
- All aldehydes give positive result except aromatic aldehydes (negative)

4. Classification Tests for Unsaturation "alkenes & alkynes"

- Alkanes are not usually characterized chemically because they are quite inert to most classification reactions

$\text{C}=\text{C} + \text{Br}_2 \longrightarrow \begin{array}{c} \text{Br} \quad | \\ | \quad | \\ -\text{C}-\text{C}- \\ | \quad | \\ \text{Br} \end{array}$
 alkene (red-brown) 1,2-dibromoalkane (colourless)

$\text{C}\equiv\text{C} \xrightarrow[\text{(brown)}]{\text{Br}_2} \begin{array}{c} \text{Br} \quad | \\ | \quad | \\ -\text{C}=\text{C}- \\ | \quad | \\ \text{Br} \end{array} \xrightarrow[\text{(brown)}]{\text{Br}_2} \begin{array}{c} \text{Br} \quad \text{Br} \\ | \quad | \\ -\text{C}-\text{C}- \\ | \quad | \\ \text{Br} \quad \text{Br} \end{array}$
 alkene 1,2-dibromoalkane (colourless) 1,1,2,2-tetrabromoalkane (colourless)

- **Positive Test:** Bromine color discharged without evolution of gas (HBr)
- Alkenes & alkynes give positive results
- If HBr is evolved, it indicates phenols, enols & enolizable compounds, -
- Bromine color is discharged by amines to produce a salt, which could be mistaken for addition.

Imp

$$3 \begin{array}{c} \diagup \quad \diagdown \\ \text{C} = \text{C} \\ \diagdown \quad \diagup \end{array} + 2\text{KMnO}_4 + 4\text{H}_2\text{O} \longrightarrow 3 \begin{array}{c} | \quad | \\ -\text{C} - \text{C}- \\ | \quad | \\ \text{OH} \quad \text{OH} \\ \text{1,2-diol} \end{array} + 2\text{KOH} + 2\text{MnO}_2(\text{s})$$

alkene (purple) manganese dioxide (brown)

$$\text{R} - \text{C} \equiv \text{C} - \text{R}' + 2\text{KMnO}_4 + 2\text{H}_2\text{O} \longrightarrow$$

alkene potassium permanganate (purple)

$$\text{R} - \text{C}(=\text{O})\text{O}^-\text{K}^+ + \text{R}' - \text{C}(=\text{O})\text{O}^-\text{K}^+ + 2\text{H}_2\text{O} + 2\text{MnO}_2(\text{s})$$

salts of carboxylic acids manganese dioxide (brown)

- **Positive Test:** Purple color discharges, and brown color ppt (MnO_2) appears
- **Note :** Aldehydes and alcohols also give positive result
- Since the ionic characters of the Br_2 and KMnO_4 reactions are very different, there is some complementary character between the two tests.
- For example, some alkenes bearing electron-withdrawing groups undergo rapid reaction with KMnO_4 but often slow or negligible reaction with Br_2 .



- A few tetrasubstituted olefins such as $\text{C}_6\text{H}_5\text{CBr}=\text{CBrC}_6\text{H}_5$ and $(\text{C}_6\text{H}_5)_2\text{C}=\text{C}(\text{C}_6\text{H}_5)_2$ fail to give positive tests with Br_2 in CCl_4 or KMnO_4 solution.

5. Tests for Alkyl Halides

- Aliphatic halides are often detected initially by qualitative by halogen analysis halogen analysis.

(i) Ethanolic Silver Nitrate & (ii) Sodium Iodide in Acetone

- Both tests involve displacement of halogen:
- AgNO_3 / ethanol test proceeds by a carbocation ($\text{S}_\text{N}1$) process & NaI / acetone test proceeds by a direct displacement ($\text{S}_\text{N}2$)

AgNO_3 / ethanol test: $\text{R}_3\text{CX} > \text{R}_2\text{CHX} > \text{RCH}_2\text{X}$ $3^\circ > 2^\circ > 1^\circ$

NaI / acetone test: $\text{R}_3\text{CX} < \text{R}_2\text{CHX} < \text{RCH}_2\text{X}$ $3^\circ < 2^\circ < 1^\circ$

(i) Ethanolic Silver Nitrate Solution

- The reaction of alkyl halide with silver nitrate yields a silver halide precipitate



- Positive Test: formation of ppt. indicates 2° and 3°RX
- 1°RX , $\text{Ar}\cdot\text{X}$, and vinyl halides give negative Result.
- Note:** allylic and benzylic RX give positive result
- The identity of the halogen can sometimes be determined from the color of the silver halide: AgCl (white); AgBr (pale yellow); AgI (yellow)

(ii) Sodium Iodide in Acetone Test

- The NaI test can be used to test for the presence of bromine or chlorine.
- Sodium halide (NaX) precipitates from the solution.



- Positive Test:** precipitate forms
- Indications:** 1° , 2°RX , allylic and benzylic halides. Not good for ArX , vinyl halides, HCCl_3 , and 3°RX .

- Since reactivity toward alcoholic silver nitrate is often very different from reactivity toward sodium iodide in acetone, both tests should be used with any halogen compound.

6. Tests for Amines and Amine Salts

(i) Diethyl oxalate test: (DEO Test)

- This method helps in the separation of primary, secondary and tertiary amines.
- Primary amines on reaction with diethyl oxalate gives solid oxamide, secondary amine gives liquid oxamic ester and tertiary amine remains unreacted in gaseous form.

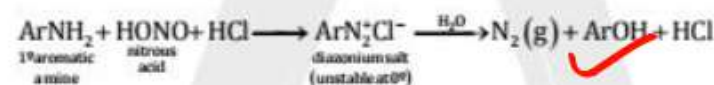
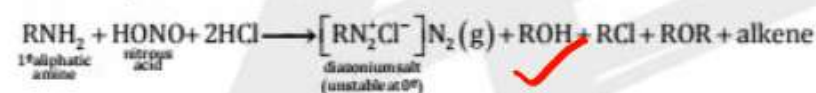


1. The gaseous tertiary amine is separated out.
2. The solid oxamide is filtered out of the liquid oxamic ester.
3. These products are added to the alkaline solution of NaOH.

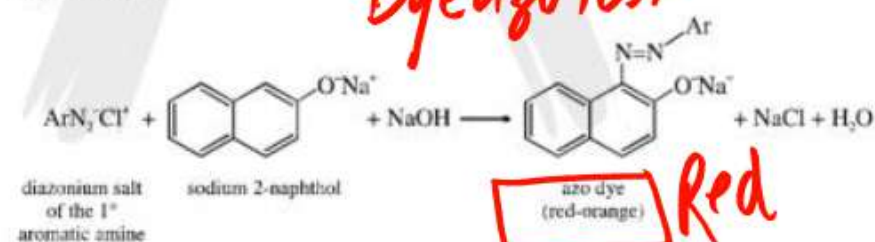
In this way, Primary, secondary and tertiary amines are separated by Hoffmann's Method

(ii) Nitrous Acid

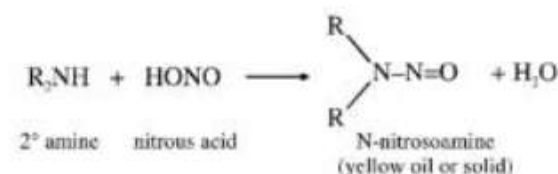
- Reaction of amines with nitrous acid (HONO) classifies the amine not only as 1°, 2°, or 3°, but also as aliphatic or aromatic.



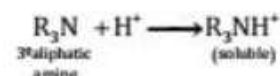
- The diazonium salt of the primary aromatic amine reacts with sodium 2-naphthol to produce a red-orange azo dye.



- 2° amines undergo a reaction with nitrous acid to form N-nitrosoamine, which are usually yellow solids.

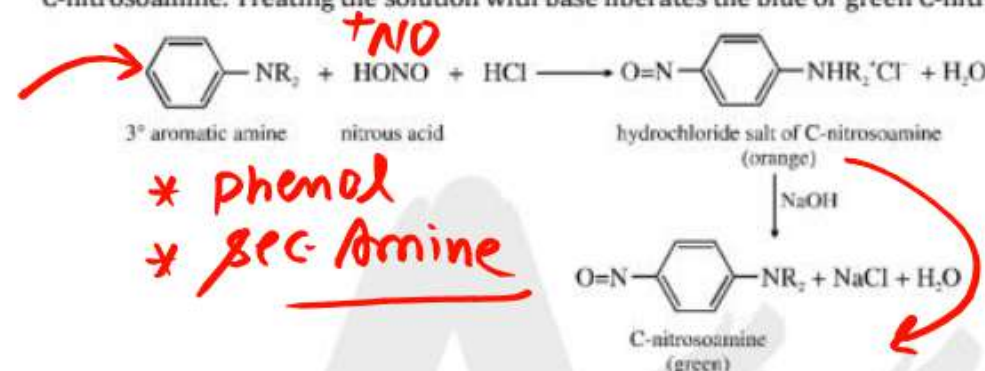


- 3° aliphatic amines do not react with nitrous acid, but they form a soluble salt. The reaction mixture gives an immediate positive test on the starch-iodide paper for nitrous acid.

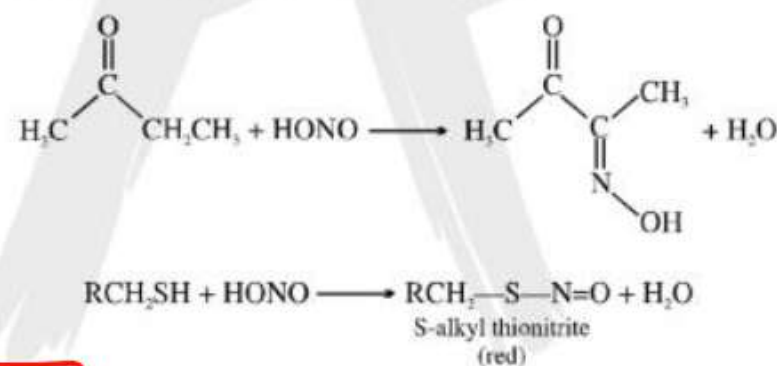


Libermann nitroso Test

- 3° aromatic amines react with nitrous acid to form the orange-colored hydrochloride salt of the C-nitrosoamine. Treating the solution with base liberates the blue or green C-nitrosoamine.



- Although nitrous acid is useful for characterizing amines, other functional groups also react.
- A methylene group adjacent to a keto group is converted to an oximino group and alkyl mercaptans yield red S-alkyl thionitrites.

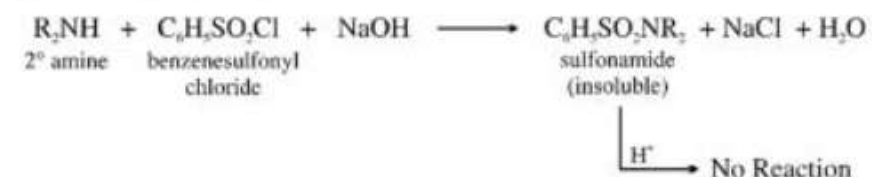


(iii) Hinsberg Test

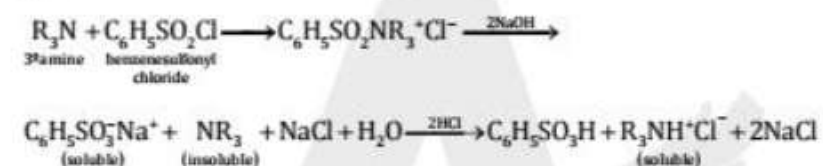
- Based on the reaction of the amine with benzenesulfonyl chloride (Hinsberg reagent), it can be used to separate 1°, 2°, and 3° amines.
- 1° amines: give solution that produce ppt after addition of HCl



2° amines: give ppt - acidification of the solution does not dissolve the sulfonamide (i.e., the PPT is not soluble in NaOH or HCl)



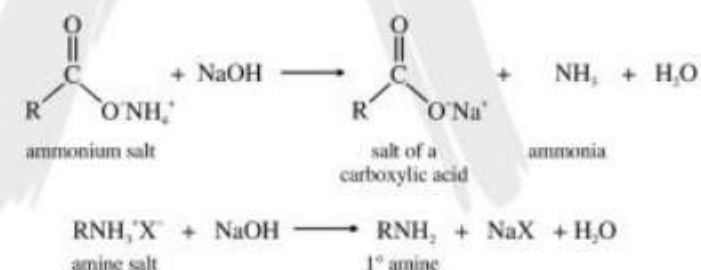
- 3° amines: undergo reaction with benzenesulfonyl chloride to produce quaternary ammonium sulfonate salts, which yield sodium sulfonate and insoluble 3° amines in basic solution.
- Acidification of the reaction mixture results in the formation of sulfonic acids and soluble amine salts



- The results of the Hinsberg test must not be used alone in classifying amines. The solubility of the original compounds must also be considered.
- If the original compound is amphoteric, which means that it is soluble in both acids and alkalis, the Hinsberg method fails to distinguish among the types of amines.

(iv) Sodium Hydroxide Treatment of Ammonium Salt and Amine Salts

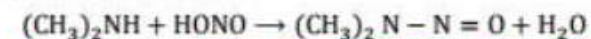
- Amine salts can be detected by treating the salt with NaOH to liberate ammonia or amine.



Moistened pink litmus paper placed in the vapor above the solution will turn blue if ammonia or a volatile amine is present.

(v) Libermann's nitroso test :

It is used as a test for secondary amines. Secondary amines (aliphatic as well as aromatic) reacts with nitrous acid to form N-nitrosoamines.

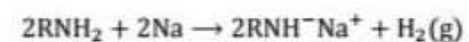


- Nitrosoamines are water soluble yellow oils and when warmed with phenol and few drops of conc. H_2SO_4 produce a green colour solution which turns blue on adding alkali. This reaction is called Libermann's nitroso reaction.

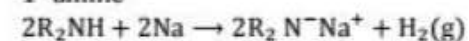
- Tertiary amine do not react with nitrous acid.

Sodium Metal :

- The active hydrogen on 1° and 2° amines undergo reaction with sodium to form salt and liberate hydrogen gas



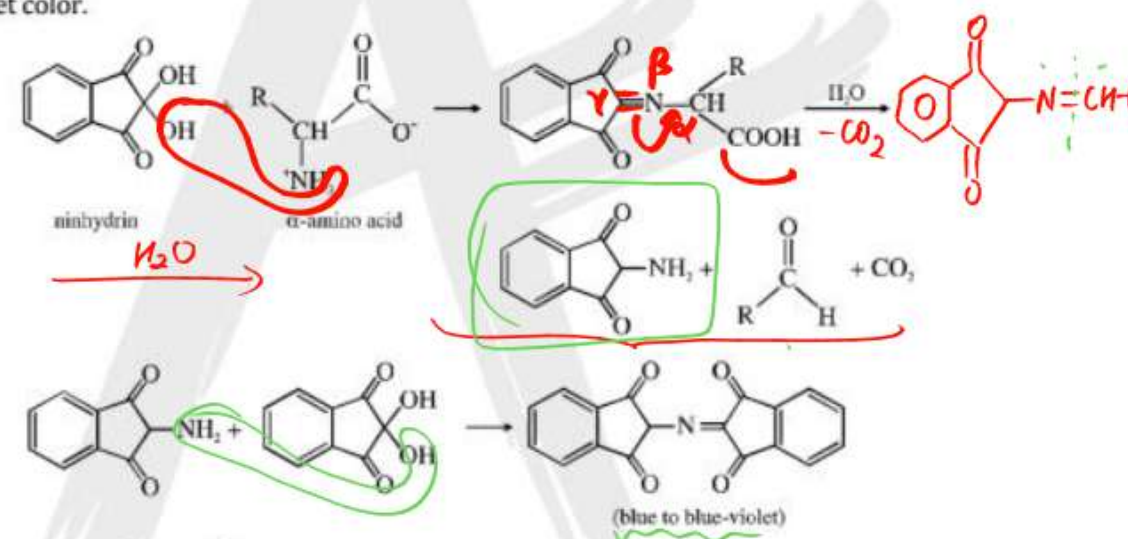
1° amine



2° amine

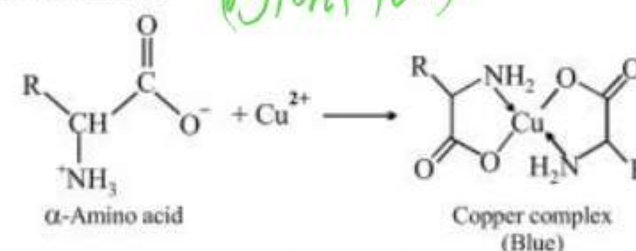
7. Tests for Amino Acids**(i) Ninhydrin Test :**

- Amino acids and α -amino acids react with ninhydrin to give a positive test which is blue or blue-violet color.



- Ammonium salts (NH_4^+Cl^-) give a positive test.
- Some amines, such as aniline, yield orange to red colors, which is considered a negative test.
- Proline, hydroxyproline, and 2-, 3-, and 4-aminobenzoic acids fail to give

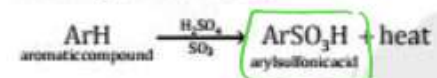
Blue colour but produce a yellow color instead.

(ii) Copper Complex Formation*(Biom Test)*

- Reaction with copper(II) sulfate solution yields a moderate-to deep-blue liquid or a dark-blue solid.
- 8. **Tests for Aromatics**
- If the molecule already contains reactive chemical substituents (acids, amines, ethers, carbonyl compounds, etc.,) use the corresponding classification test for that particular group.
- New substituents can be added onto the aromatic ring or existing substituents can be modified, such that the new

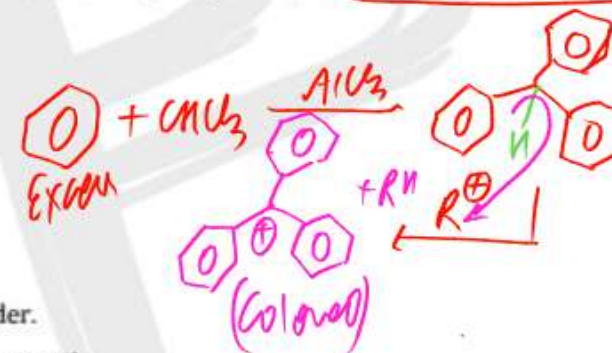
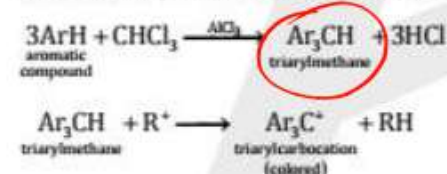
Compound May be More Readily Characterized.

(i) **Fuming Sulfuric Acid**



- This test is good for aromatics with no other functional groups.
- Positive Test: the aromatic compound dissolves completely in H_2SO_4 with the evolution of heat (Fuming)

(ii) **Chloroform and Aluminum Chloride**

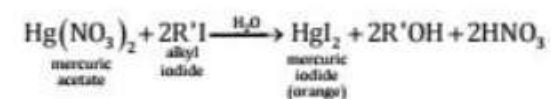
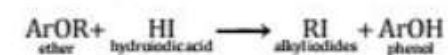


- Aromatics give colored solution or powder.
- Positive Test: (Orange, red, blue, purple, green)
- Non aromatics give yellow color (Negative result)

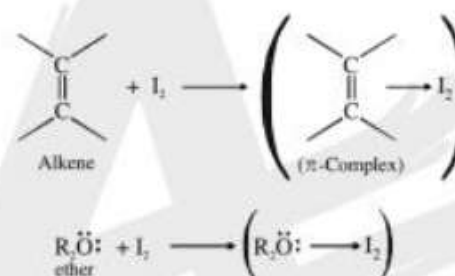
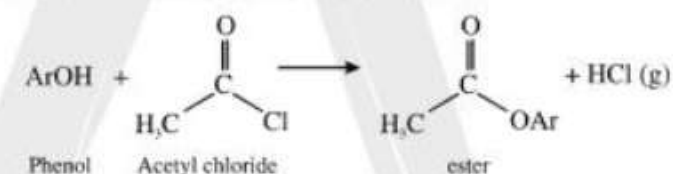
(iii) **Azoxybenzene and Aluminum Chloride**

- The color of the solution or precipitate is dependent on the functional groups present on the aryl group.
- Aromatic hydrocarbons and their halogen derivatives produce a deep-orange to dark-red color in solution or give a precipitate.
- Fused aromatic ring (such as naphthalene, anthracene, and phenanthrene) produce brown color.
- Aliphatic hydrocarbons give no color or, at most, a pale yellow.
- 9. **Tests for Ethers**
- Ethers are only a little more polar and slightly more reactive than either saturated hydrocarbons or alkyl halides

- Ethers form extremely explosive peroxides upon standing, specially when exposed to air and/or light. Liquid ethers that shows solid precipitates should not be handled.

(i) **Hydroiodic Acid (Zeisel's, Alkoxy method)**

- Positive Test:** Orange or Orange-red color indicating.
- Note:** Ethyl and methyl esters give also positive result.

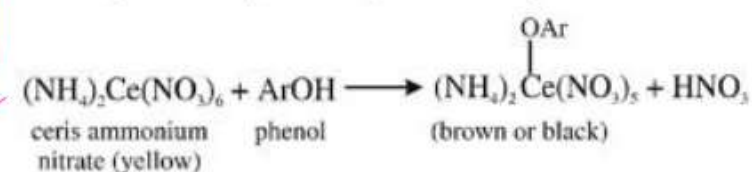
(ii) **Iodine Test for Ethers and Unsaturated Hydrocarbons**

- Positive test: the color of the solution changes from purple to tan.
- Aromatic hydrocarbons, saturated hydrocarbons, fluorinated hydrocarbons and chlorinated hydrocarbons do not react.
- Unsaturated hydrocarbons produce a light-tan solid, while retaining the purple color of the iodine solution.

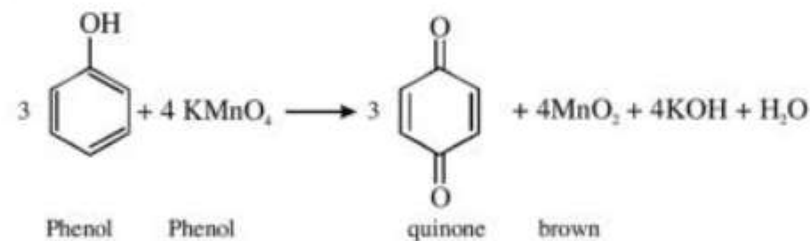
10. Tests for Phenols

- As with alcohols, the acidic hydrogen in phenol can be detected with sodium (hydrogen gas is evolved) or with acetyl chloride (an ester layer is formed).

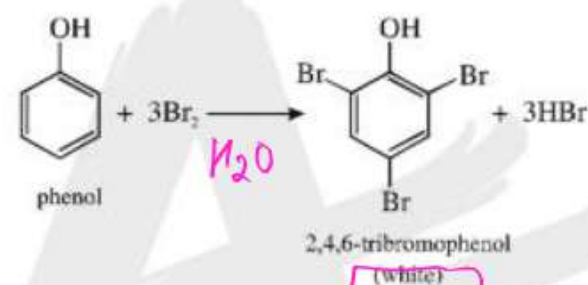
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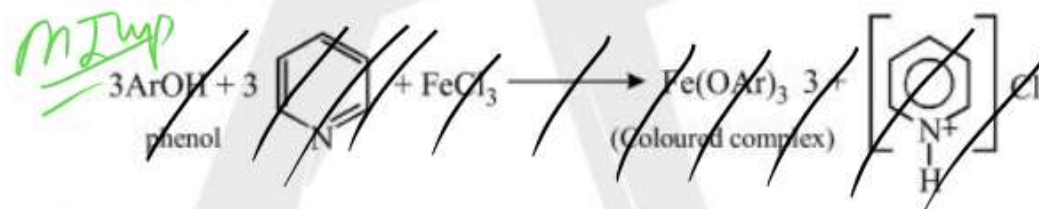
- Phenols undergo reaction with yellow ceric ammonium nitrate to produce brown or black products.



- Phenols reduce potassium permanganate solution and undergo oxidation to quinones.
- The manganese is reduced from +7 which gives a purple solution to +4 which is brown.

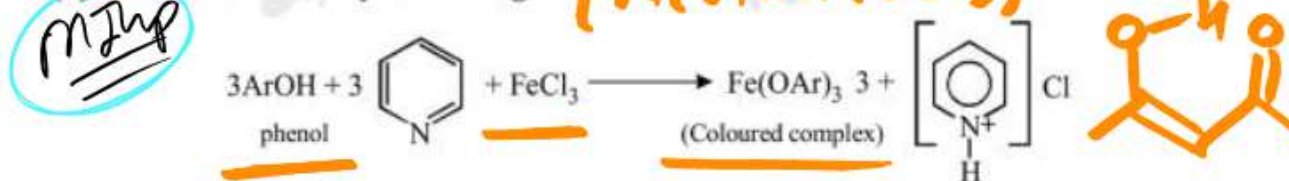


(i) Bromine water



- Positive Test: decolorization of bromine.
- This is good for water soluble phenols

(ii) Ferric Chloride - Pyridene Reagent

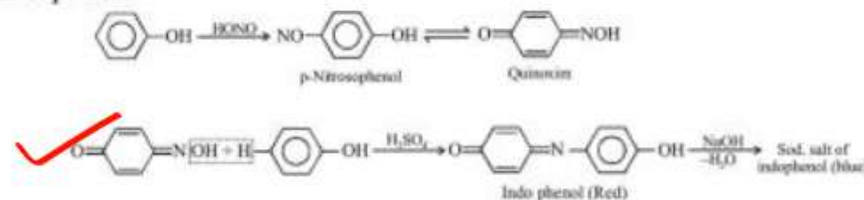
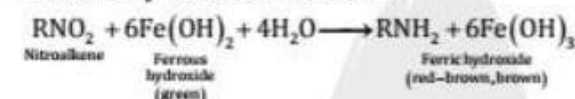


- Positive Test:** Production of blue, violet, purple, green, or red-brown colors
- Good for all types of Ar-OH.
- Positive test for enols. $\text{CH}_3\text{C(OH)=CHCOCH}_3$

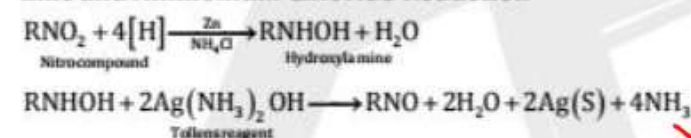
- Carboxylic acid with FeCl₃ gives red colour only when saturating with NH₃.

(iii) **Liebermann's nitroso test :**

While phenol is reacted with NaNO_2 and concentrated H_2SO_4 , it provides a deep green colour which changes to red on dilution with water. while generated alkaline along with NaOH , blue colour is restored. This reaction is termed as Liebermann's nitroso reaction and is employed as a test of phenol.

**11. Test For Nitro Compounds****(i) Ferrous Hydroxide Reduction**

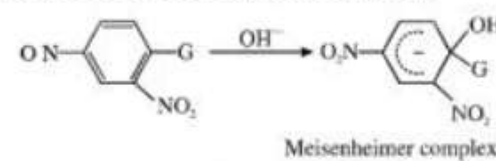
- **Positive Test:** indicated by the change in color from green to red-brown or brown due to the oxidation of iron from +2 to +3.
- A negative test is indicated by a greenish precipitate.
- **Note:** Nitroso compounds, quinones, hydroxylamines alkyl nitrates give also positive results

(ii) Zinc and Ammonium Chloride Reduction

- ✗ Test the solution with Tollens Reagent
- Positive Test: formation of metallic silver
- Only 3° aliphatic nitro compounds and aromatic nitro compounds are reduced by $\text{Zn}/\text{NH}_4\text{Cl}$ to the hydroxylamine.
- The hydroxylamine is then detected by the formation of metallic silver in the Tollens test (or formation of a black or grey precipitate). This is known as Mulliken-baker test.

(iii) Treatment of Aromatic Compounds with Sodium Hydroxide

- The number of nitro groups on an aromatic ring can be determined by the reaction with NaOH
- In the reaction with NaOH :
- Mononitro aromatic compounds yield no color change or a very light yellow
- Dinitro aromatic compounds produce a bluish-purple color
- Trinitro aromatic compounds give a red color
- The color of the solution is due to a Meisenheimer complex



Organic Compound Sample

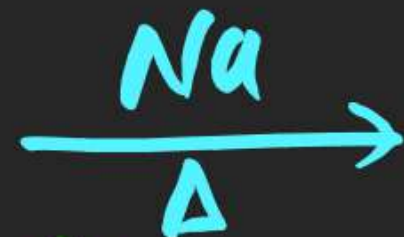
Carbon present

Elemental analysis
N present

Sulphur present

X present

N & S present



Soda Extract
Inorganic

(Prussian Blue)



PbS

(Black ppt)



AgX

(white ppt)



(Blood Red color)

<u>(A) ELEMENTAL ANALYSIS</u> <i>Lassaigne method (Detection of elements)</i>			
Element	Sodium Extract (S.E.)	Confirmed Test	Reactions
Nitrogen	$\text{Na} + \text{C} + \text{N} \xrightarrow{\Delta} \text{NaCN}$ (S.E.)	S.E. + $\text{FeSO}_4 + \text{NaOH}$, boil and cool, + FeCl_3 + conc. HCl Blue or green colour (i) S.E. + sodium nitro prusside (A) A deep violet colour, (ii) S.E. + CH_3COOH + $(\text{CH}_3\text{COO})_2 \text{Pb}$ A black ppt. S.E. + $\text{HNO}_3 + \text{AgNO}_3$ (i) White ppt. soluble in aq NH_3 confirms Cl (ii) Yellow ppt partially soluble in aq. NH_3 confirm Br (iii) Yellow ppt insoluble in aq NH_3 confirms I As in test for nitrogen; instead of green or blue colour, blood red coloration confirms presence of N and S both	$\text{FeSO}_4 + 2\text{NaOH} \longrightarrow \text{Fe}(\text{OH})_2 + \text{Na}_2\text{SO}_4$ $\text{Fe}(\text{OH})_2 + 6\text{NaCN} \longrightarrow \text{Na}_4[\text{Fe}(\text{CN})_6] + 2\text{NaOH}$ $3\text{Na}_4[\text{Fe}(\text{CN})_6] + 4\text{FeCl}_3 \xrightarrow{\text{HCl}} \text{Fe}_4[\text{Fe}(\text{CN})_6]_3 + 12\text{NaCl}$ Prussian blue (i) $\text{Na}_2\text{S} + \text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \longrightarrow \text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$ (A) deep violet (ii) $\text{Na}_2\text{S} + (\text{CH}_3\text{COO})_2\text{Pb} \xrightarrow{\text{CH}_3\text{COOH}} \text{PbS} \downarrow + 2\text{CH}_3\text{COONa}$ black ppt. $\text{NaX} + \text{AgNO}_3 \xrightarrow{\text{HNO}_3} \text{AgX} \downarrow$ ppt $\text{AgCl} + 2\text{NH}_3(\text{aq}) \longrightarrow [\text{Ag}(\text{NH}_3)_2]\text{Cl}$ white ppt soluble $\text{NaCNS} + \text{FeCl}_3 \longrightarrow [\text{Fe}(\text{CNS})]\text{Cl}_2 + \text{NaCl}$ blood red colour
Sulphur	$2\text{Na} + \text{S} \xrightarrow{\Delta} \text{Na}_2\text{S}$ (S.E.)		
Halogen	$\text{Na} + \text{Cl} \xrightarrow{\Delta} \text{NaCl}$ (S.E.)		
Nitrogen and Sulphur together	$\text{Na} + \text{C} + \text{N} + \text{S} \xrightarrow{\Delta} \text{NaCNS}$ (S.E.)		