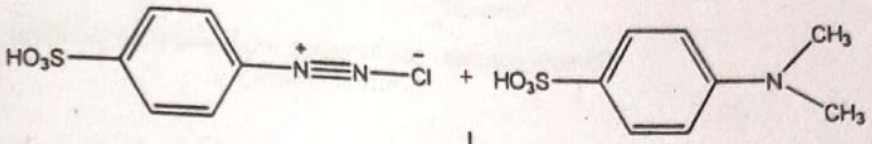
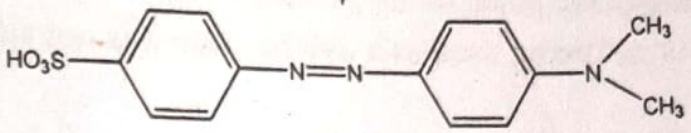
Methyl orange is an azo dye containing one azo (-N=N-) group. It contains sulphonic acid ($-SO_3H$) group and hence it is acidic. The $-SO_3H$ group acts as auxochrome. Due to the presence of $-SO_3H$ group it is more soluble and is also used as reactive point for fixing the dye.

**Preparation**

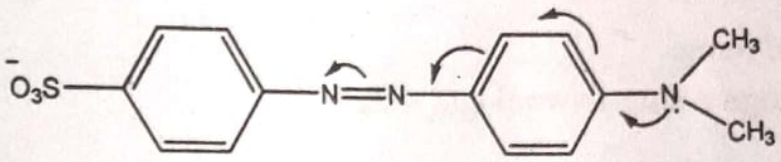
Methyl orange is an anionic dye which is prepared by coupling of diazotized sulphanilic acid with dimethylaniline.



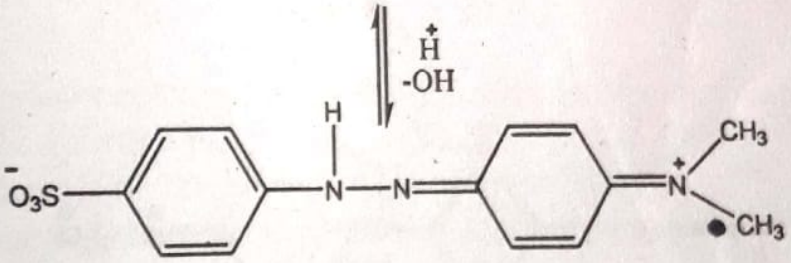
Diozotised sulphonilic acid + N,N - Dimethyl aniline



Methyl orange



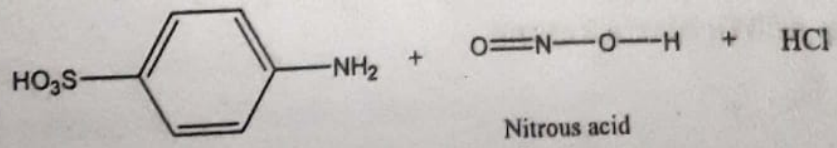
Methyl orange (alkaline medium)



Methyl orange (acidic medium)

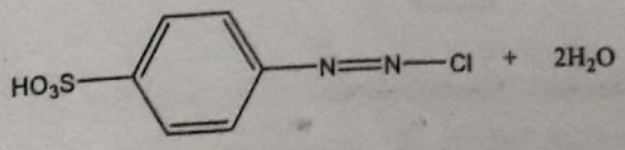
**Step 1: Diazotisation of sulphanilic Acid**

$$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$$



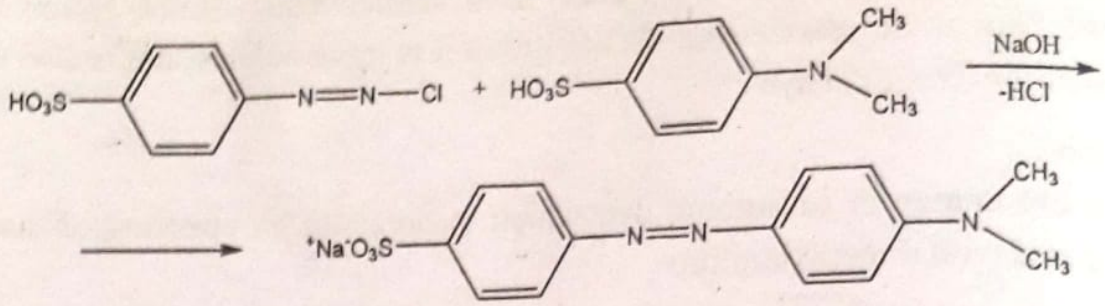
Sulphanilic acid + Nitrous acid

0-5 $^0$C
Diazotization



Diazotized Sulphanilic acid

Step 2: Coupling of diazo compound with dimethyl aniline




Dimethylamine - azobenzene sulphonic acid [Sodium salt]
(Methyl orange)

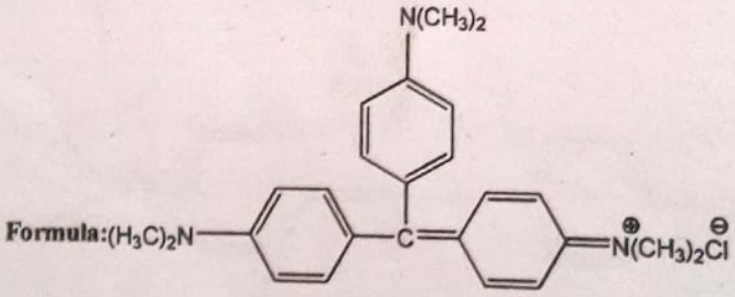
**Properties:**

1) It is used as an indicator being orange in alkaline solution and red in acid solution. This colour change take place in the pH range 3.1 – 4.5
2) Methyl orange is not being used as a dye because it is not sufficiently stable to soap and light.
3) It acts as a good acid-base indicator.

**Uses:**

1) It is used for dyeing.
2) It imparts orange colour to wool and silk.

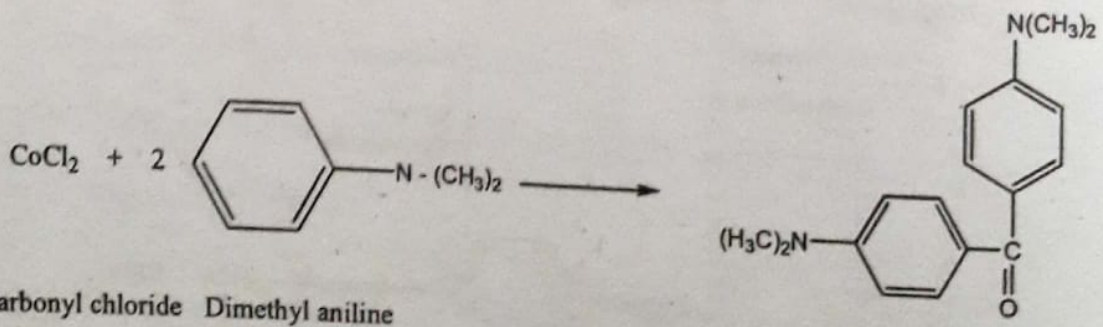
**1) Crystal Violet**




**Preparation:**

Crystal Violet may be prepared by Michler's ketone with dimethylaniline in presence of phosphoryl chloride or carbonyl chloride. It involves two steps

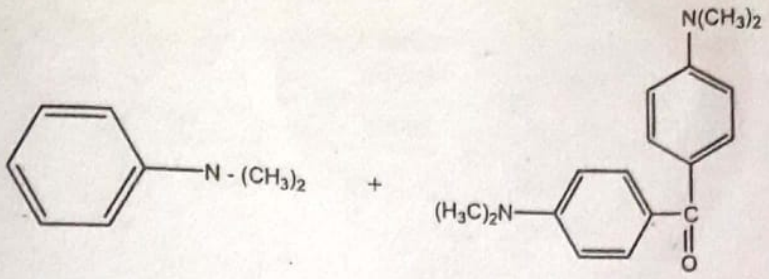
**Step 1:- Preparation of Michler's ketone**



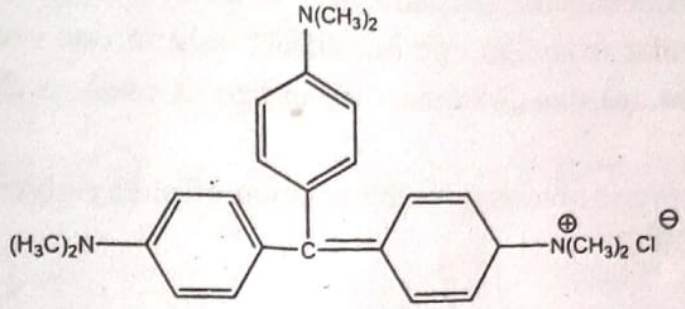

Carbonyl chloride Dimethyl aniline

Michler's ketone

Step 2: Condensation of Michler's ketone with dimethyl aniline




Dimethyl aniline Michler's ketone


Crystal violet

**Properties:**

1) This dye forms violet colour crystals hence it is called as crystal violet.
2) A weakely acidic solution of crystal violet gives a purpal colour.
3) The colour changes with the acid strength of the solution.
4) It gives deep blue colour when dissolve in water and.

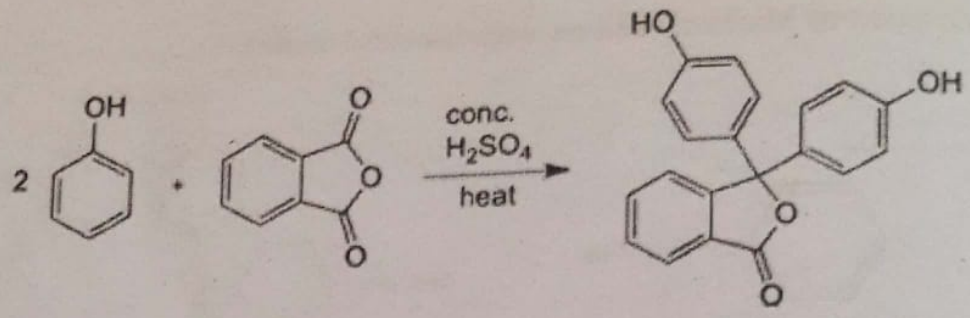
**Uses**

1) They are mostly used for colouring papers, inks, stamping pads and type -writer ribbons etc.
2) It dyes wool, silk and tannin mordanted cotton fibre.
3) It is used as an indicator to find out $H^+$ ion concentration of solution.
4) Gentian violet (a combination of crystal violet and methyl violet) is used as an antiseptic for certain skin diseases like burn, ulcers and also used for washing the wounds.
5) Used as biological stain and for making pencils.

**d)Phenolphthalein Dyes:**

**Preparation :**

Pthalein dyes are prepared from phthalic anhydride and phenols; in presence of dehydrating agents like fused $ZnCl_2$ or conc. $H_2SO_4$. In this dye triphenyl-methane structure is act as chromophoric group.




**Uses :**

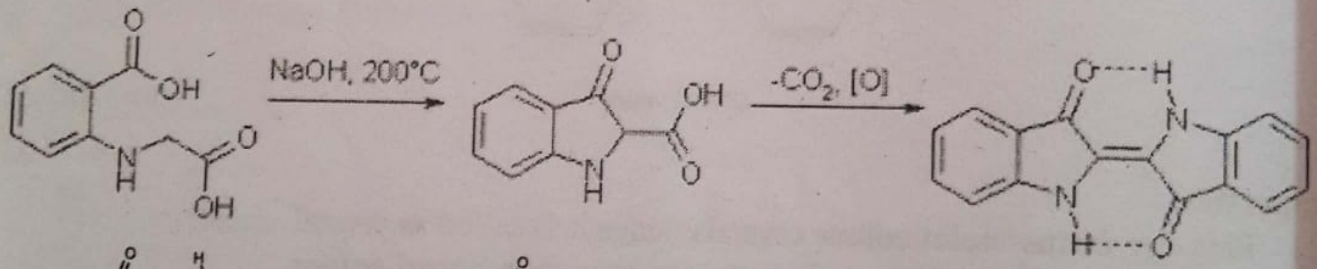
1)Phenolphthalein's most common use is as an indicator in acid-base titrations

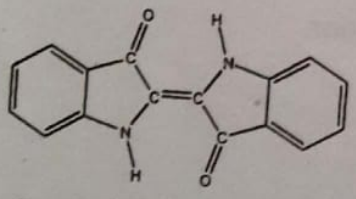
2) Phenolphthalein is used in a test to identify substances thought to contain blood, commonly known as the Kastle-Meyer test.

**e) Indigo Dyes:**

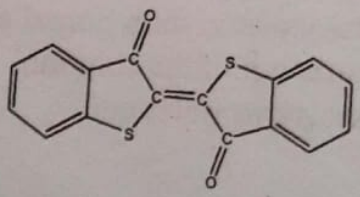
Indigoid dye is obtained from plant. It is used for dyeing cotton by vat process. Thioindigo dye is similar to indigo dye but differs only in one respect that in place of two -NH groups there are two S-atoms. Thioindigo is used to dye cotton, wool and polyester.

**Preparation:** Indigo dye is obtained by the reaction of phenylglycine-o-carboxylic acid react with alkali At $200^0$C.



Indigo



Thioindigo

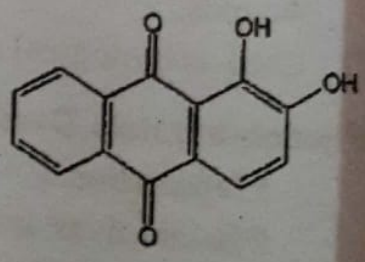
**Uses :**

1) The primary use for indigo is as a dye for cotton yarn, which is mainly for the production of denim cloth for blue jeans. 2) It is also used as a food colorant,

**f) Anthraqumone Dyes:**

**Alizarin**

Alizarin is one of the most important anthraquinoid dyes. It is splendid colour dye. Alizarin is the constituent of madder root wherein it is present as the glucoside, ruberythric acid.



Alizarin

**Preparation:**

It can be prepared by following methods:

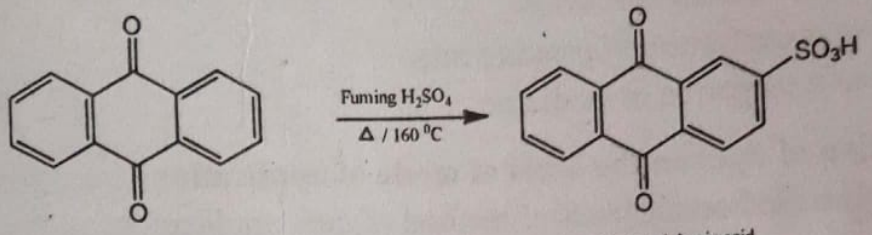
1. **From madder root:** Alizarin is extracted from the root of madder plant.

$$C_{26}H_{28}O_{14} + 2\,H_2O \xrightarrow[(\text{ or Enzyme})]{H^+} 2\,C_6H_{12}O_6 + C_{14}H_6O_2(OH)_2$$

Ruberythric acid — Glucose — Alizarine

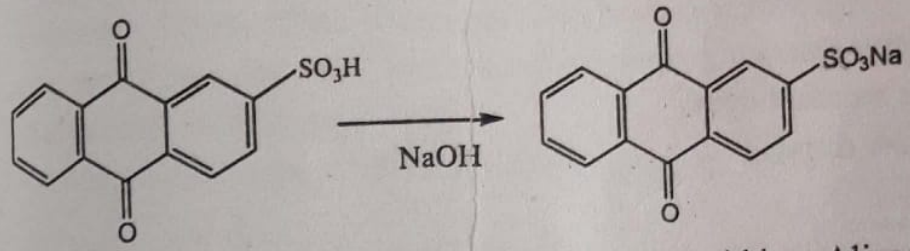
**From anthraquinone:** It involves following following steps

**Step: 1 Sulphonation of anthraquinone**

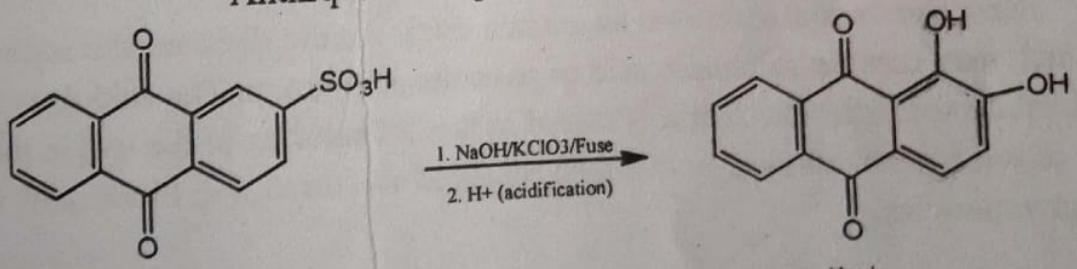



anthraquinone — anthraquinone sulphonic acid

**Step 2: Formation of sodium salt of anthraquinone Sulphonic acid**



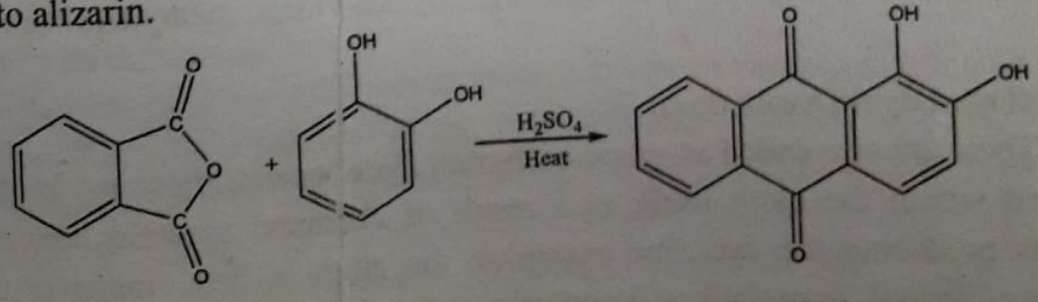

Step 3: Conversion of 2-Anthrquione sulphonic acid into Alizarin




anthraquinone sulphonic acid — Alzarin

2. **From phthalic anhydride:**

Phthalic anhydride on condensation with catechol in presence of $H_2SO_4$ at $180^0$ C gives rise to alizarin.




Phthalic anhydride — Alizarin

**Properties:**

1) It melts at 290° C.
2) It sublimes on heating.
3) Alizarin from ruby red crystals.
4) Alizarin is insoluble in water and sparingly soluble in alcohol.
5) It dissolves in alkalies to give violet or purple coloured salt called alizarete.

**Uses:**

1) It is used as a mordant dye.
2) It is used in the preparation of anthrarobin.
3) It is used to dye cotton and wool.
4) It is used in manufacture of printing inks.
5) It is used as a purgative in medicine.

**2. Classification of dyes on the basis of mode of application**

Dyes can be classified on the basis of method of their application,

1) Acidic dye
2) Basic dyes
3) Developed dyes.
4) Direct dyes (substantive dyes)
5) Indirect (adjective or mordant dyes)
6) Disperse dyes (reactive dyes)
7) Vat dyes.

**1. Acidic dyes:**

These dyes are also known as anionic dyes. Acidic dyes are the sodium salts of acid which may contain sulphonic acid or phenolic acid group. The acid dyes are always used in acidic solution. The fabric is stirred in the hot solution of the dye in the presence of acid or salt till it is easily dye. It is then removed and dried, e.g. Picric acid, Orange-II, naphthol yellow etc.

**2. Basic dyes:**

These are called as cationic dyes. Those dyes contain a basic amino group and it is protonated under the acid condition of fibres by formation of salt linkages with anionic or acid group in the fibre are basic dye, e.g. Crystal violet, methylene blue and methyl violet.

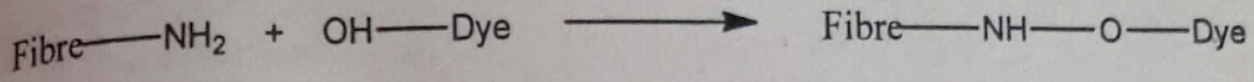
**3. Developed dyes (Azoic dyes)**

These are also called as azotic or ingrain dyes because these are the dye which is produced within the cloth itself as a result of chemical reaction between the two reactants producing the dye. For examples, the cloth is first dipped in the alkaline solution of phenol, resorcinol or β-naphthol and then immersed in the alkaline solution

of diazo compounds. The coupling reaction takes place between the phenol and diazo compounds withintextile fibres giving rise to the formation of dyes.

**4. Direct dyes (substantive dyes)**

Direct dyes can dye cotton as well as wool and silk. The dye is applied to the fabric by immersing it its hot boiling solution, removing and then drying the fabric. Some typical members of direct dyes are congo red, naphthol yellow S and martius yellow is a direct dye contain acidic –OH group which reacts basic $-NH_2$ group of wool or silk.

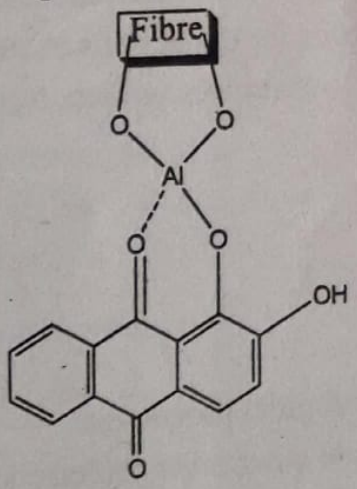



wool or silk

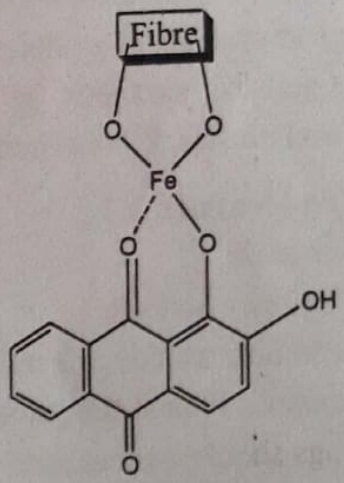
**5. Indirect (Mordant dyes)**

These dyes are also called adjective dyes. They can not directly dye cotton, silk or wool but require the help of a mordant. A fibre is first treated with the mordant and then with the dye solution. Salt of oxides of aluminium or chromium are called mordants. The mordant forms an insoluble co-ordination complex between the fibre and dye, and binds the two. The insoluble complex compound appears in the form of lakes that are fast to light and washing.

Alizarin is an example of a mordant dye




Red coloured lake of Alizarin on fibre

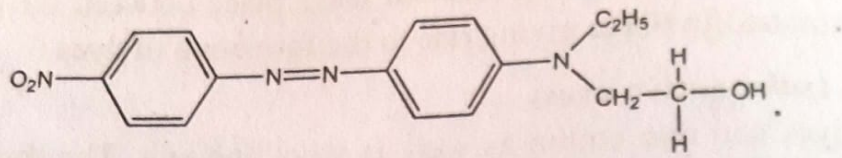


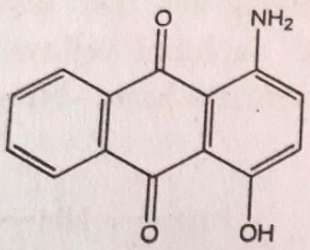

Black-violet coloured lake of Alizarin on fibre

**5. Disperse dyes (reactive dyes)**

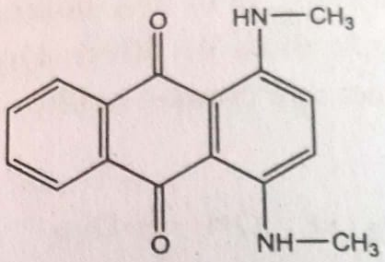
Disperse dyes are insoluble in water but can be dispersed in a colloidal form in water. The fabric is dispersed in the colloidal dispersion of the dye. The fine dye particles are absorbed into the crystal structure of the fabric. Disperse dyes are used with modern synthetic fibres such as nylon, orlon, polyesters and cellulose acetate. The nitro, azo and anthraquinone dyes are used as dispersed dyes.

Examples of dispersed dyes:




Cellinton fast




Cellinton fast blue-B

**4) Vat dyes**

These dyes are insoluble in water but on reduction with alkaline sodium bisulphide the vat dye are converted into water soluble compounds called *leuco compounds*. They dye both vegetable and animal fibres directly. It is mostly used to dye cotton. Some typical examples of vat dye are indigo and anthraquinone dyes.