* Introduction :→

A dye is a coloured organic compound or mixture that may be used for colouring the surface. The substances such as textile fibre and hence clothes, papers, plastics, leather, metal sheets etc. may be coloured with the help of dye. A dye may be defined as a coloured organic compound which is used to impart colour to a substrate. The substrate is the textile fibre or fabric.

* Importance :→

The non toxic dyes are used to colour the food stuffs and drugs. The dyes are also used to impart the colour to paper, leather, plastics, wax, cosmetic bases etc. In fact life would be dull without the colour

* Qualities of Good Dye :→

1. It must have an attractive and suitable colour.
2. It must be able to attach itself to the material like cloth from the solution.
3. Dye must be soluble in a suitable solvent and should form a stable dispersion in the solvent.
4. It should have fastness towards light, water, heat, perspiration, rubbing and bleaching agents.
5. Dye should be economically affordable.

* **Colour** :→ Colour is the physiological sensation which is produced when the light of certain wavelength reaches the eye.

When the white light (750 – 400 nm) falls on a substance, light may be totally reflected, the substance appears white, if the light is totally absorbed the substance appears black. If the selective band of visible light is absorbed while remaining part is reflected then the surface of the substance appears coloured.

* **Colour and Chemical constitution** :→ The ordinary light is composed of rays of many wavelengths. The human eye is sensitive to only a limited portion of electromagnetic radiations, producing light from violet to red called the visible region. (750 – 400 nm).

* **Complimentary colour** :→ The colour actually absorbed and colour seen are known as complimentary colour of each other.

Wavelength nm	Colour absorbed	Complimetary colour.
400 – 435	Violet	Yellow – green
435 – 480	Blue	Yellow
480 – 490	Green-blue	Orange
490 – 500	Blue – green	Red
500 – 560	Green	Purple
560 – 580	Yellow – green	Violet
580 – 595	Yellow	Blue
595 – 605	Orange	Green – blue
605 – 750	Red	Blue – green

The colour of a substance is a property which depends on the molecular structure of the substance.

several theories were put forward to explain the relation between colour and chemical constitution.

* Otto-Witt Theory of colour :→

Otto-Witt explained the colour in relation to structure that colour compound must contain certain unsaturated group to which he called chromophores. A compound containing chromophore is called as chromogen.

* Chromophore :→ (Chroma means colour, phores means bearing group)

Chromophores are a groups which is responsible for absorbing the radiation and imparting colour to the substance.

e.g.

$-N=O$ Nitroso, $-N(=O)\rightarrow O$ Nitro

$-N=N-$ Azo, $-CH=N-$ Azomethane

$>C=S$ Thiocarbonyl, $-N=N-NH$ Azoamine

$-N=N-O$ Azoxy, $>C=O$ Carbonyl.

* Auxochrome :→ (Auxein means to increase, Chroma means colour)

Witt also pointed out that certain group present in chromogen, do not impart colour, but deepen intensity of the colour such group are known as auxochrome.

Auxochromes are the saturated groups which do not produce colour but deepens the colour of the chromogen.

e.g. Benzene is colourless while aniline is yellow in colour.

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Some important auxochrome are as fallows.
$-OH$ hydroxyl, $-COCH_3$ acetyl, $-Cl$ Chloro, $-CONH_2$ acetamide, $-OCH_3$ methoxy, $-NH_2$ amine, $-CN$ cyano and $-COOH$ carboxylic etc.

*** Main Functions of Auxochromes :→**

1. Auxochrome deepens or increases the intensity of the colours.
2. Auxochrome converts the chromogen into a dye.
3. The sulphonic acid group increases the solubility of dye in water.
4. The carboxylic group enables the dye to form lakes.

*** Bathochromic shift or Red shift :→**

Any change in the dye molecule which causes the absorption of light from shorter wavelength to a longer wavelength. This is known as bathochromic shift. As it brings about the deepening of the colour, the shift is also called as Red shift. When hydrogen atom of amino is replaced by alkyl group, red shift or bathochromic shift is produced..

*** Hypsochromic shift or Blue shift :→**

Any change in the dye molecule which causes the absorption of light from longer to a shorter wavelength. This is termed as hypsochromic effect. As it brings about fading of the colour, the shift is called as blue shift. When hydrogen atom of the hydroxyl or amino group is replaced by acetyl group, blue shift is produced.

* Molecular orbital Approach to colour :→

In a molecule the electrons are present in sigma (σ), Pi (π) or nonbonding molecular orbital (n) in a ground state. When it absorbs radiations there is electronic excitation i.e. from bonding molecular orbital to antibonding molecular orbital (σ*, π*). The electronic transitions possible are

More energy, U.V. region	①	$\sigma - \sigma^*$	methane, ethane, n-hexane
	②	$n - \sigma^*$	Alkohols, alkyl halide, amine, thiols.
less energy, visible region	③	$\pi - \pi^*$	alkenes, alkynes, carbonyl comp.
	④	$n - \pi^*$	compound containg = bond and heteroatoms

Out of these transitions $\sigma - \sigma^*$ and $n - \sigma^*$ transitions are difficult and require more energy and take place only by absorption of U.V. radiations. Hence saturated compounds are colourless. But the $\pi - \pi^*$ and $n - \pi^*$ transition require less energy and transition takes place in U.V. region. This is seen in the molecules having unsaturated groups like $-C=C-$, $-C=O$, $-C\equiv N$, $-N=O$, $-N=N-$ etc. When the conjugation is extended in molecule transition requires less energy and absorption shifts towards longer wavelength i.e. absorption shifts to visible region and compound becomes coloured.

① $\sigma - \sigma^*$ transition :→ The electrons from the sigma bond are tightly held and hence $\sigma - \sigma^*$ transition require high energy and absorption takes place at very shorter wavelength. (150 nm). e.g. Saturated hydrocarbons like methane, ethane, n-hexane etc.

② $n-\sigma^*$ transition:→ The electrons from the compound containing non bonding or unshared pair of electrons present on heteroatoms such as O, N, S and halogens give $n-\sigma^*$ transition. Transition takes place from non-bonding (n) orbital to σ^* antibonding orbital.

e.g. Alkohols, alkyl halides, amines and thiols.

③ $\pi-\pi^*$ transition:→ In this type of transition the electrons bonding π orbital takes place to π^* antibonding orbital. Compounds having multiple bonds undergoes $\pi-\pi^*$ transition.

e.g. alkenes, alkynes, carbonyl compound etc.

④ $n-\pi^*$ transition:→ Compounds containing double bonds involving heteroatoms like $-C=O$, $-C=S$, $-C=N$, $-N=O$, etc. The transitions may be arranged in decreasing order of energy as $\sigma-\sigma^* > n-\sigma^* > \pi-\pi^* > n-\pi^*$

On the basis of molecular orbital theory the relation between colour and chemical constitution is as fallows. e.g. in ethane $\pi-\pi^*$ transition takes place in the region 165 - 205 nm. but in 1-3 butadiene the two double bonds are conjugated and absorption takes place at longer wavelength 220 nm. Further increase in conjugation shift the absorption to longer wavelength. α- carotene has 10 conjugated double bonds it absorbs radiation in visible region at 445 nm and it is coloured.

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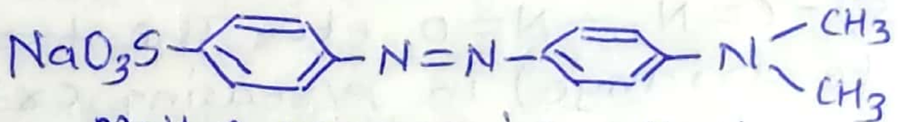
* Resonance Theory :→

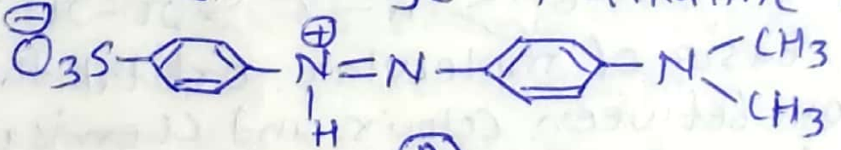
The process by which electrons are stimulated by radiation is called resonance. In resonance theory the chromophore is considered as electron withdrawing group and auxochrome as an electron donating group. When they are conjugated through double bonds then electrons move from auxochrome to chromophore. This increases the resonance and causes the change in dipole moment, hence intensity of colour is increased.

* Relation of colour to Resonance :→

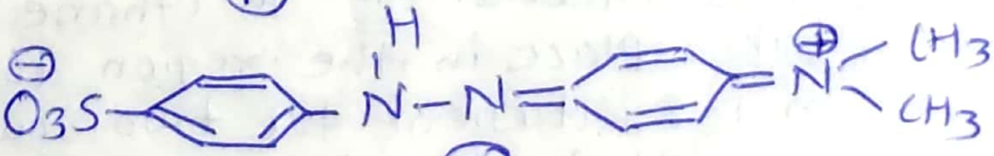
(I) Azo class :→ Methyl orange is a mono azo dye and used as an indicator for acidimetry and alkalimetry. In alkaline medium methyl orange is in azo form and solution is yellow in colour. In acidic medium the colour deepens to red. As azo nitrogen atom takes on a proton and then gives resonance hybrid (A) and (B)



Methyl orange in alkaline medium (yellow)



(A)

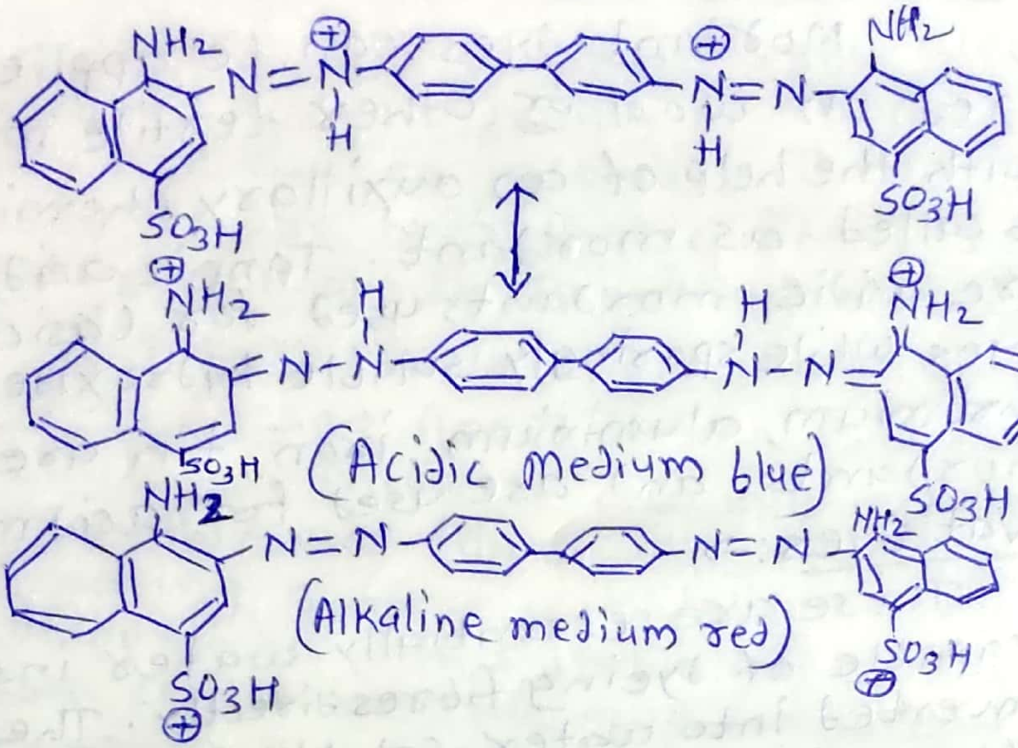


(B)

Methyl orange in acidic medium (Red)

(II) Congo red :→

Congo red is a diazo dye and used as an indicator. In acidic medium congo red is in diazo form and the solution is blue - violet in colour but in alkaline medium, it turns red.



* Classification of Dyes Based on Application:

The dyes are classified according to their mode of application as fallows.

(I) Acid dyes:→ These are water soluble anionic dyes that are applied to fibres such as silk, wool, nylon and modified acrylic fibres using neutral acid dye baths. e.g. orange II, alizarin.

(II) Basic dyes:→ These are water soluble cationic dyes that are mainly applied to acrylic fibres but find some use for wool and silk. It is also used in colouration of paper. e.g. crystal violet and Rhodamine B.

(III) Direct dyes:→ Direct dyes are used on cotton paper, leather, wool, silk and nylon. They are also used as biological stains. These dyes are easily applied from aqueous solution so they are called as direct dye. These dyes are also called as salt dyes.

e.g. chrysophenine G.

④ Mordant dyes:→

Mordant dyes can be applied or fixed on wool or other textile materials with the help of an auxillary chemical which is called as mordant. Tannic acid, tannin are acidic mordants used for basic mordant dyes while sparingly soluble hydroxides of Chromium, aluminium, iron, tin are basic mordants and are used for acid mordant dyes.

⑤ Vat dyes:→

These are essentially water insoluble and incapable of dyeing fibres directly. These are converted into water soluble leuco form by action of caustic soda and reducing agent such as sodium hyposulphite. During dyeing process this leuco form of the dye is applied to cotton and then allowed to oxidise in air. Then the original insoluble dye molecules are fixed on the fibre. e.g. Indigo.

⑥ Reactive dyes:→

It utilise a chromophore attached to a substituent that is capable of directly reacting with the fibre substrate. The bonds that attach reactive dyes to natural fibres make them among the most permanent dyes. Cold reactive dyes such as procion MX are very easy to use because the dye can be applied at room temperature. Hot reactive dye such as Procion blue is applied at elevated temp. in alkaline medium.

(7) Disperse dyes:→ These dyes were originally developed for the dyeing of cellulose acetate. They are water insoluble. These dyes are used to dye hydrophobic fibres such as Polyester, Polyamide, Polyethylene and Polyacrylonitrile e.g. Dispersol blue and Celliton scarlet.

(8) Azoic dyes:→ Azoic dyeing is a technique in which an insoluble azo dye is produced on or within the fibres. This is achieved by treating a fibre with both diazoic and coupling components with suitable adjustment of dye bath conditions, the two components react to produce the required insoluble dye. This type of dyeing is unique, in that the final colour is controlled by the choice of the diazoic and components. These dyes are also called as Ingrain dyes. e.g. Naphthol AS and Napthol ASG.

(9) Sulphur dyes:→ These are water insoluble compounds and are highly coloured. They form water soluble sodium salts by treating them with aqueous sodium sulphide solution. This is a substantive form of dye which has affinity to cellulosic fibre. e.g. sulphur black.

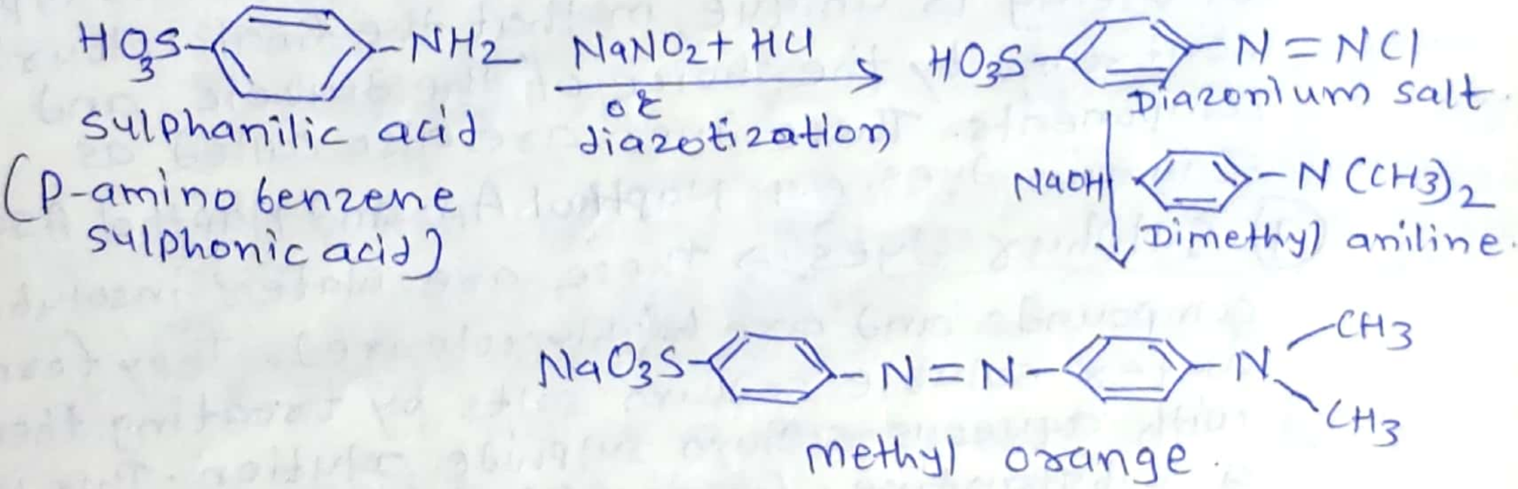
(10) Fluorescent dyes:→ These dyes are used for dyeing and printing fabrics, carpets in cinemas and other purposes where luminescence in the dark is desired. Fluorescein dye was used for detection of leaks in drains. e.g. Rhodamine B gives bluish pink fluorescent shade on the animal fibres.

(11) **Pigments** :→ Pigments are discrete particles which give colour to substrate. Pigments are organic or inorganic compounds which are insoluble in medium. Pigments are used for printing, colouring, paints, Varnishes.
e.g. Indigo, copper Phthalocyanine.

✱ Synthesis and uses of the following Dyes:

(1) **Methyl orange** :→ It is an acidic azo dye and characterized by a acidic sulphonic group as an auxochrome.

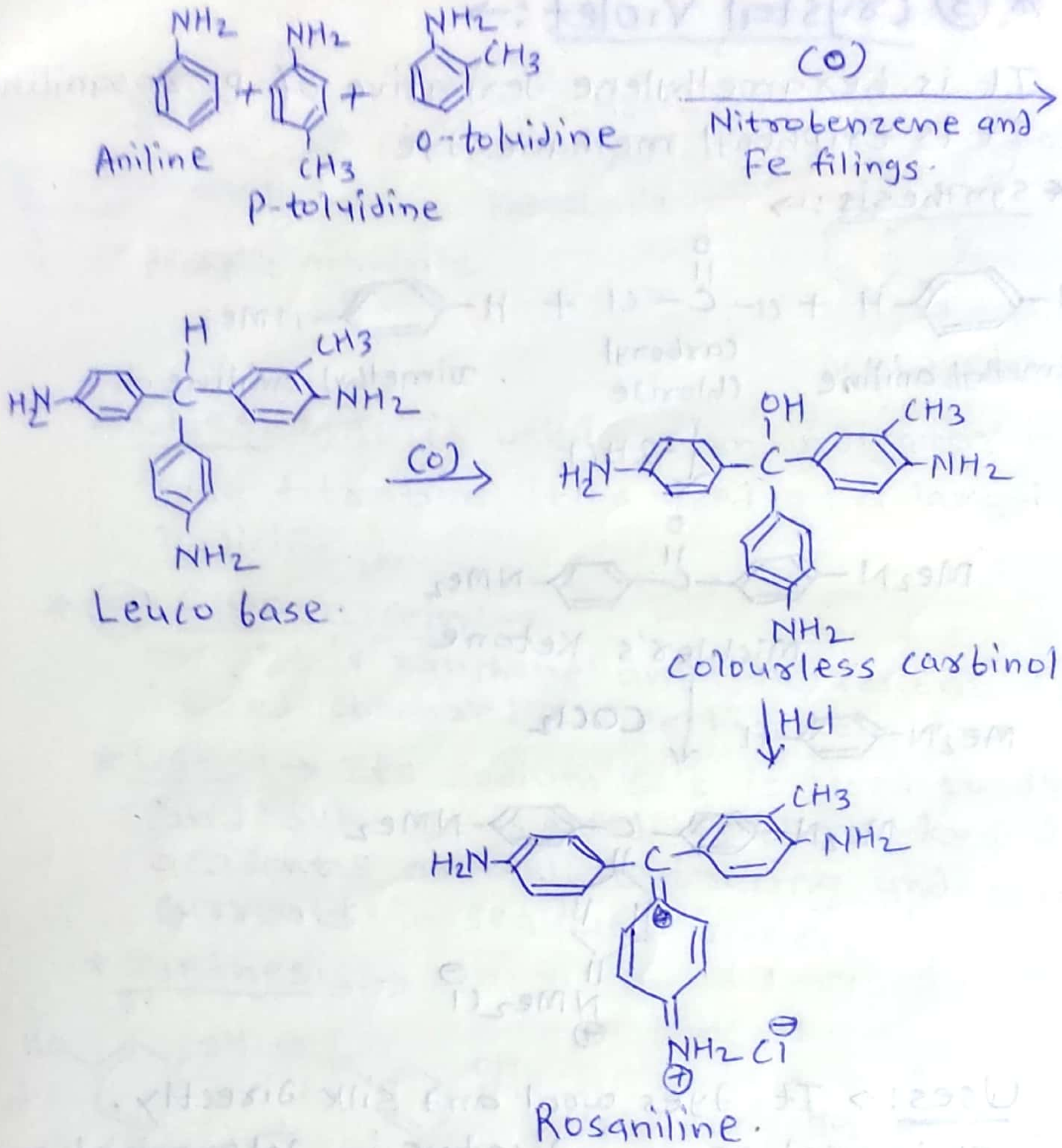
★ **Synthesis**:



★ **Uses** :→ (1) Sodium salt of methyl orange used as an indicator in acid-base titration
(2) Methyl orange imparts orange colour to silk and wool.

(2) **Rosaniline** : (Magenta of fuchsine).
It is triphenyl methane dye. Its crystals are green but solution in water is deep red.

★ **Synthesis** :→



* **Uses:**

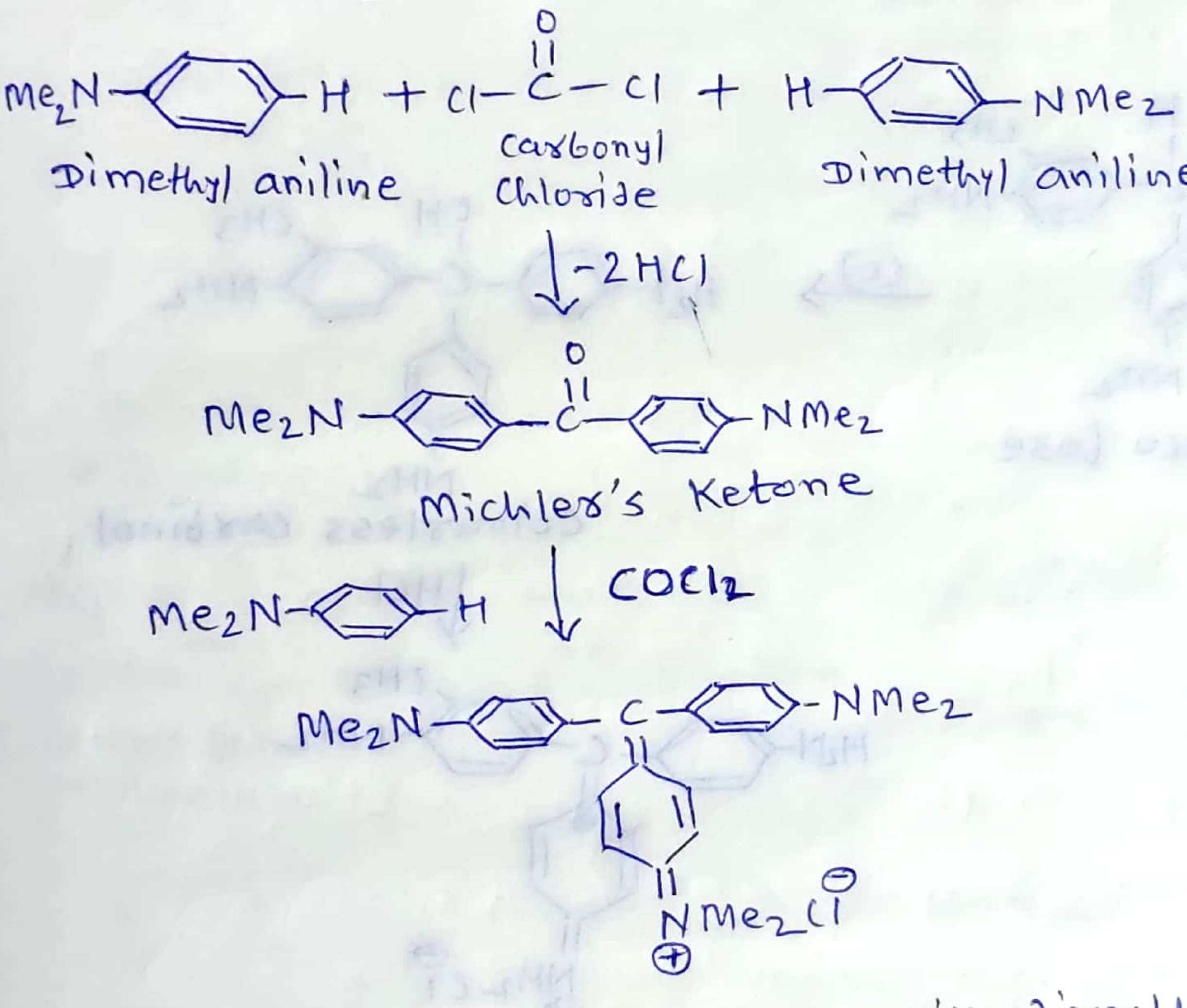
① It is used as a direct dye for wool and silk.

② The solution of rosaniline is decolourised by passing SO_2 gas and then solution is used as Schiff's reagent which is used for testing aldehyde.

* ③ Crystal Violet :→

It is hexamethylene derivative of p- rosaniline
It is triphenyl methane dye.

* Synthesis :→

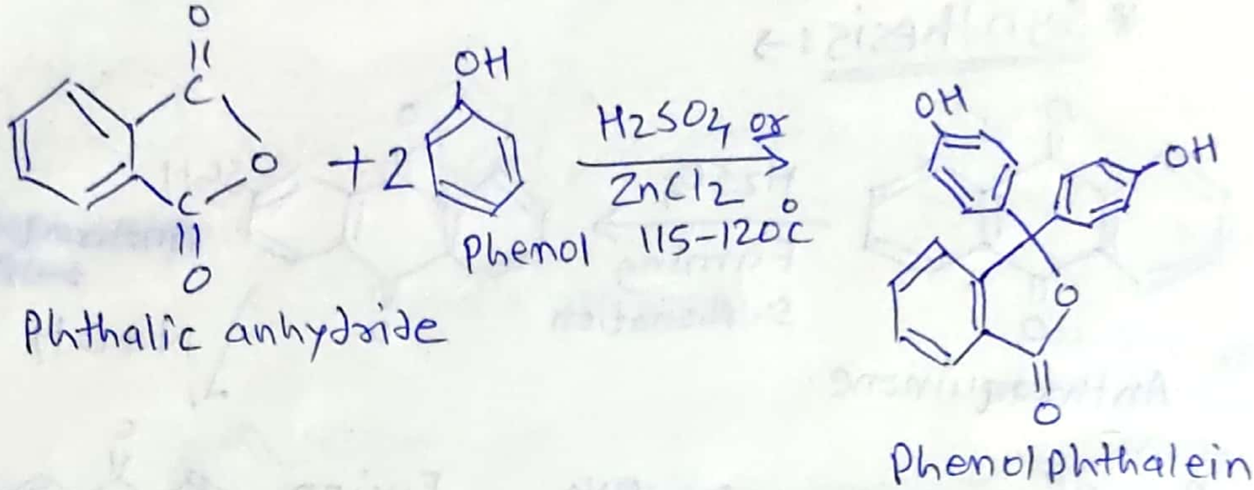


Uses :→ It dyes wool and silk directly.
It is used as an indicator in determination of $H^{\oplus}$ ion concentration of the solution.
It is also used in stamping pads.

* ④ Phenolphthalein :→

It is phthalein dye.

* Synthesis :→



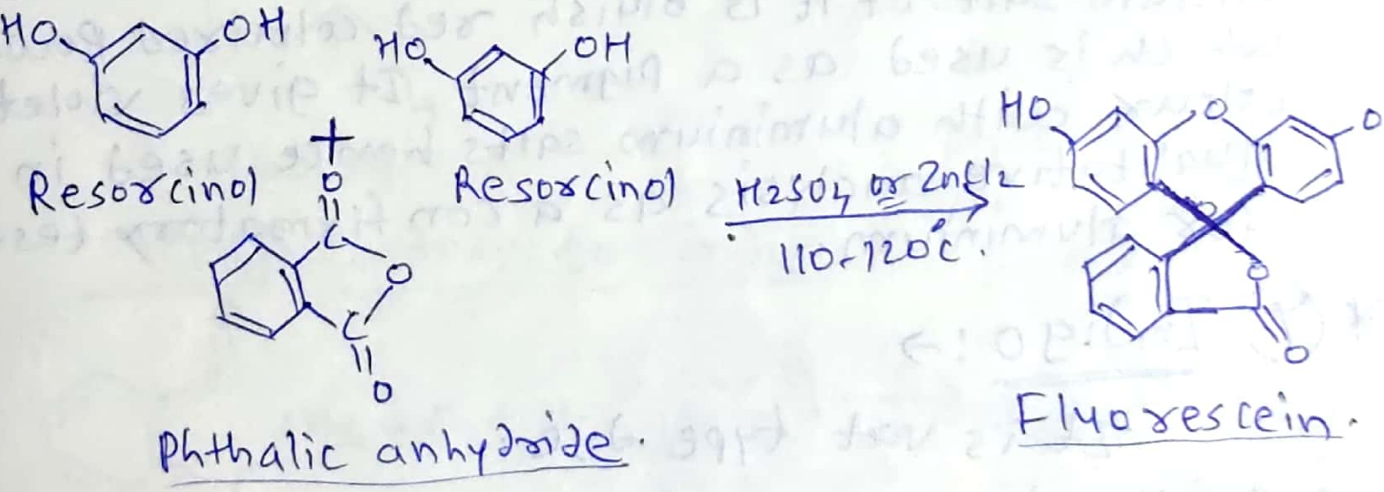
* **Uses:→** It is used as an indicator in acid-base titration. It is used as a laxative in medicine.

* (5) Fluorescein:→

It is xanthene and fluorescent dye. It is red coloured water insoluble dye.

* **Uses:→** Its sodium salt is used to dye wool and silk. It is used as a marker during accidents as well as tracing underground currents in sea and rivers.

* **Synthesis:→**



* (6) Alizarin:→

It is an anthroquinone mordant type dye. chemically it is 1,2 dihydroxy anthraquinone.

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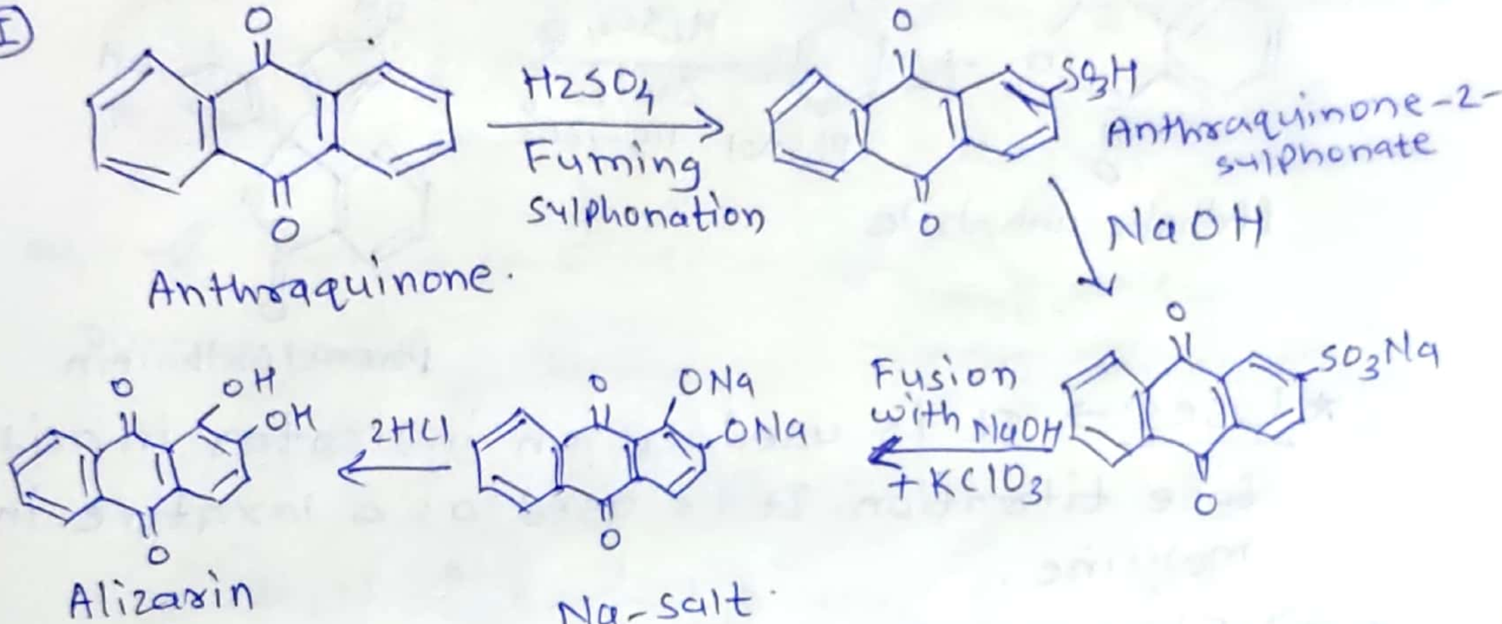
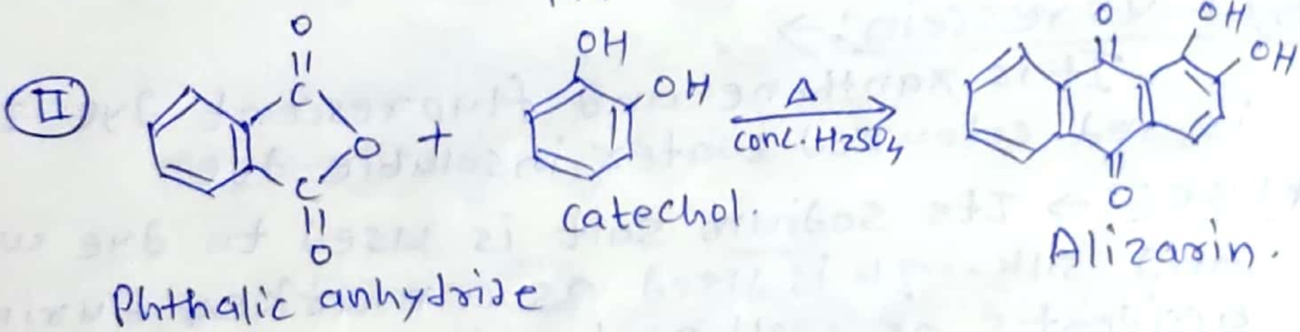
* Synthesis :→

(I)



(II)



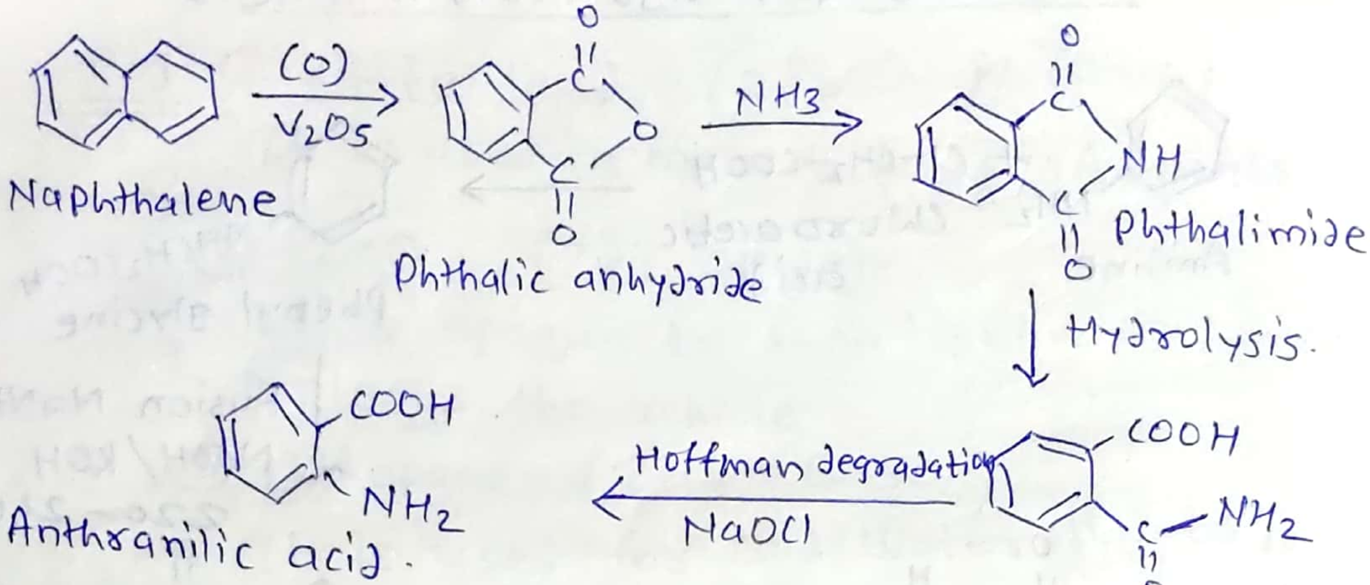
*** Uses :→** It produces turky red colour to wool when applied with aluminium hydroxide mordant. Calcium salt of it is bluish red coloured powder which is used as a pigment. It gives violet colour with aluminium salts hence used in the qualitative analysis as a confirmatory test for aluminium.

* (7) Indigo :→

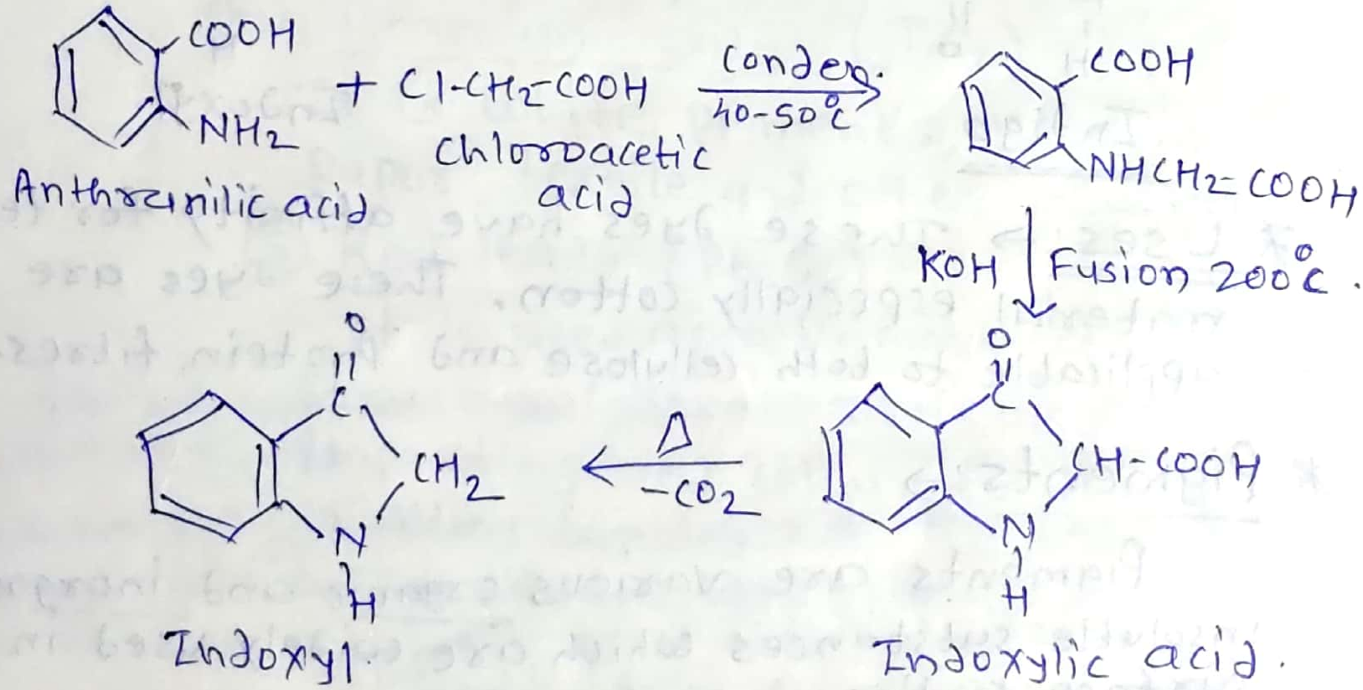
It is vat type dye.

*** Synthesis :→**

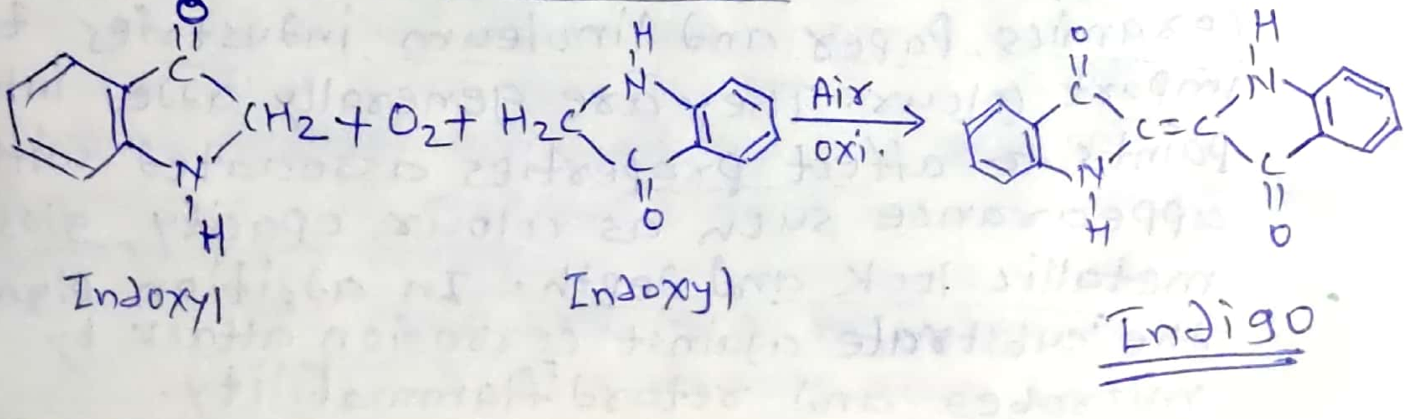
Step (1) Naphthalene to anthranilic acid.



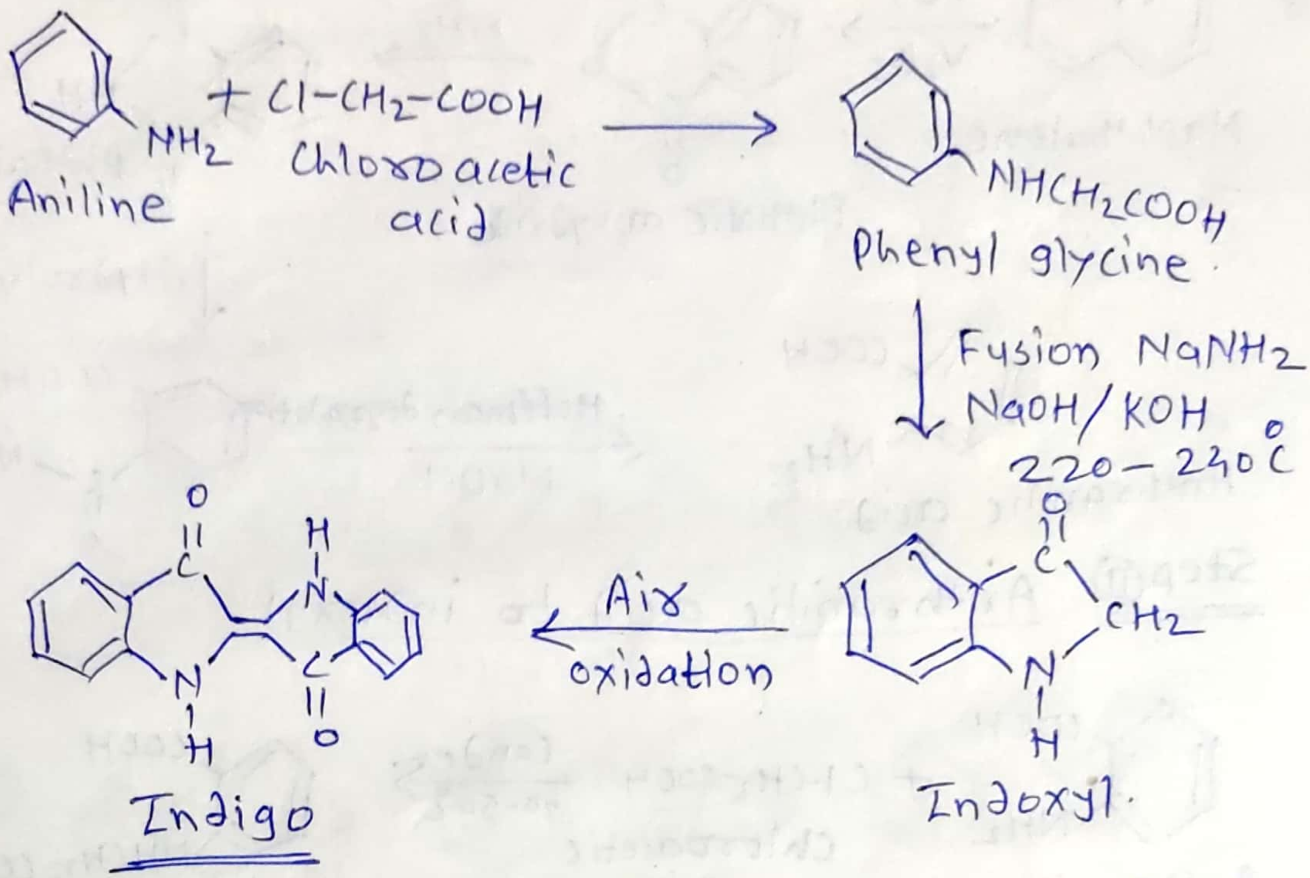
Step (II) Anthranilic acid to indoxyl.



Step (III) Indoxyl to Indigo.



* Synthesis of Indigo from Aniline:→



* **Uses:→** These dyes have affinity for textile material especially cotton. These dyes are applicable to both cellulose and Protein fibres.

* Pigments:→

Pigments are various organic and inorganic insoluble substances which are widely used in surface coating.

They are also used in ink, plastic, rubber, ceramics, Paper and linoleum industries to impart colour. They are generally added into paints to affect properties associated with a appearance such as colour, opacity, glass, metallic look and depth. In addition pigment the substrate against corrosion attack by microbes and retard flammability.

e.g. ① White lead : ($2PbCO_3 \cdot Pb(OH)_2$)
It is used in manufacture of paints.

② ZnO : (Zinc oxide).
It is opaque to U.V. light and hence protects the vehicle.

③ Lithopone : ($ZnS + BaSO_4$)
It is used for cold water paints, traffic paints, floor coverings, oil cloth industries.

④ Titanium dioxide : (TiO_2)
It is white pigments, used in paints, paper, textile and other industries.

⑤ Red lead : (Pb_3O_4) :
It is used as a primary coat for structural steel. It is also used for imparting red colour to the glass for making bangles.

⑥ Chromium oxide : (Cr_2O_3) :
It is used as a green pigment called Chrome green.

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