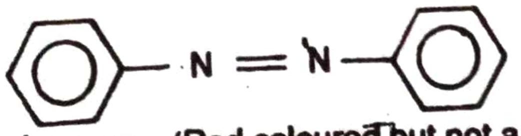
1

Introduction

1.1 Definitions

Dye or Dyestuff. A *dye or a dyestuff is usually a coloured organic compound or mixture that may be used for imparting colour to a substrate such as cloth, paper, plastic or leather in a reasonably permanent fashion.* In other words, a dyed substrate should be resistant to a normal laundry or cleansing procedures (*wash fast*) and stable to light (*light fast*). All the dyes may not necessarily be coloured substances. Therefore, optical brighteners or whiteners which may be called **white dyes** may be included in the term dye.

A dye is a coloured substance but all coloured substances are not dyes. Thus a dye should fix itself on the substrate to give it a permanent coloured appearance. Thus, azobenzene is not a dye even though it has red colour, as it cannot be attached to substrate. However, congo red is a dye as it can be applied on cotton and retained by it. Thus, the dyes should have certain groups which help the attachment to the fibre.



Azobenzene (Red coloured but not a dye)

White Dye. Some colourless compounds are used as the optical brightners. They may also be called as the *white dyes.* They have the special property of absorbing ultraviolet light and re-emiting the visible light so that the fabric appears bright.

Pigment. The coloured substance which is insoluble in water or other solvents is called a pigment. Thus the application of dye and pigment will be different. A dye is applied in the form of a solution, 2

Colour and Chemical Constitution

2.1. Bathochromic and Hypsochromic Effects

If a structure change in a dye molecule shifts the absorption towards higher wavelengths, it will deepen the colour of the dye in accordance to the following sequence :

yellow → *orange* → *red* → *purple* → *violet* → *blue* → *green*

Any group or a factor that produces the deepening of the colour in accordance to the above sequence is known as *bathochrome* and the effect, *i.e.*, the deepening of colour, is known as *bathochromic* effect.

When a bathochromic group is introduced into a dye, it will increase the resonance which in turn deereases the energy gap of the *ground state-excited state transitions* with visible colour production. The shifting of the absorption towards higher wavelengths with the introduction of bathochromes has been illustrated in Fig. 2.1.

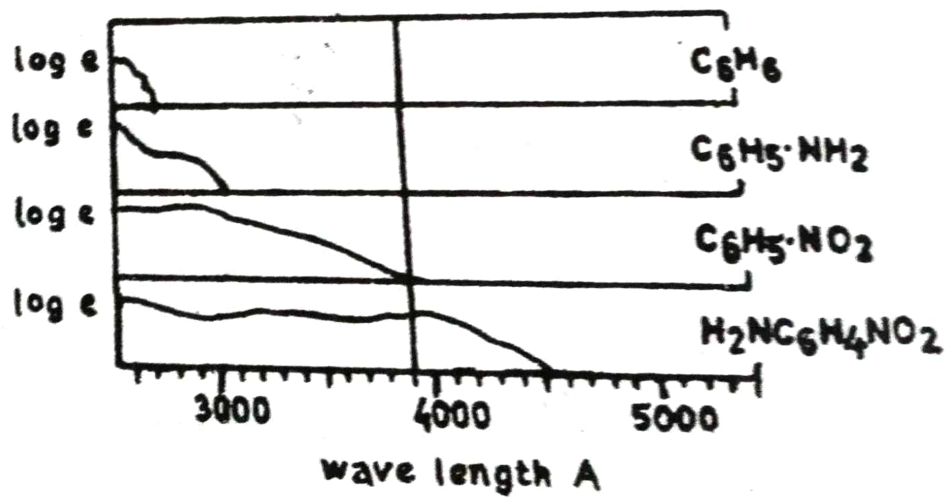


Fig. 2.1. Absorption spectra of benzene, aniline, nitrobenzene, and *p*-nitroaniline.

If a structural change in a dye molecule shifts the absorption from higher to lower wavengths, it will lighten the colour of the dye in accordance to the following sequence :

green → blue → violet → purple → red → orange → yellow

Any group or a factor that will lighten the colour of the dye in accordance to the above sequence is known as *hypsochrome* and its effect produced is known as *hypsochromic effect*. The hypsochrome group diminishes resonance, often by forcing π-orbitals out of coplanarity.

Changes in the structure of a dye due to which the intensity of absorption increases are said to be *hyperchromic*. On the other hand, structural changes which decrease the intensity of absorption are termed as *hypochromic*.

Bathochromic, hypsochromic, hypochromic and hyperchromic effects are represented by the absorption spectra (Fig. 2·2) which are obtained by plotting the intensity of absorption against wavelength (λ).

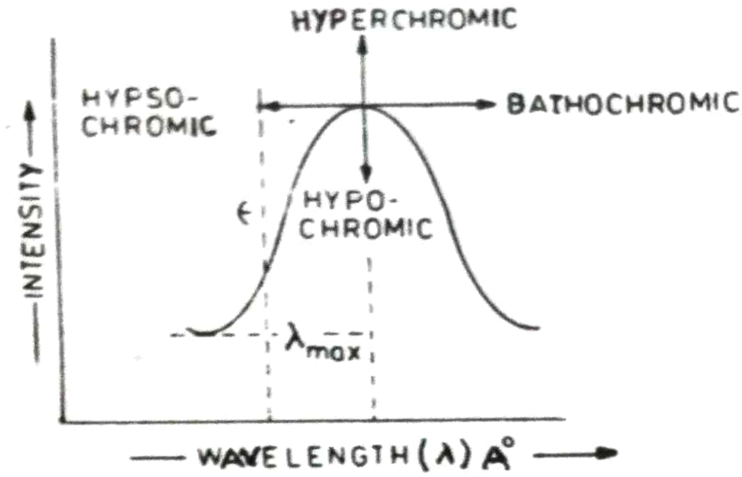
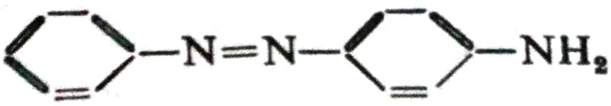


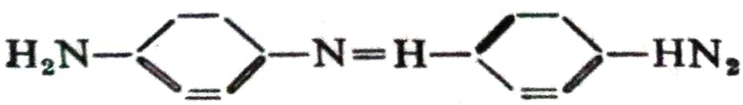
Fig. 2.2. Absorption spectrum of a particular dye.

The introduction of certain groups in a dye molecule causes the bathochromic and hypsochromic effects. This is summarised in the following facts :

(*i*) The bathochromic effect is produced by the introduction of additional auxochromes such as —OH and —NH_2 groups in a dye molecule. For example, when an additional —NH_2 group comes in the aniline yellow, chrysodine is produced which is an orange coloured dye.



aniline yellow



chrysodine (orange)

(*ii*) In addition to the auxochromes, the *o*- and *p*- directing groups, when present on the aromatic ring, also deepen the colour. For example, alkyl, aryl and halogens deepen the colour and are therefore known as bathochromes.

(*iii*) When the alkylation of amino group is done, it produces the bathochromic effect. On the other hand, when the alkylation as well as acylation of phenolic groups are done, these will produce hypsochromic effect. A good example of illustrating the bathochromic effect is to introduce six methyl groups in pararosaniline (red dye) nucleus to give crystal violet (violet colour).

$-NH_2 \longrightarrow -N(CH_3)_2$ *bathochromic effect.*

$-OH \longrightarrow OCH_3$ or $-OCOCH_3$ *hypsochromic effect.*

(*iv*) The bathochromic effect is also produced by salt formation because it increases the possibility of resonance which is again due to the formation of dye ions :

$-NH_2 \longrightarrow NH_3^+Cl^-$
$-OH \longrightarrow O^-Na^+$ *bathochromic effects.*

2.2. Colour and Chemical Constitution

Colour. *The psychological sensation which is produced when the light of certain wavelength reaches the eye is known as the colour.* Thus, colour is dependent on and varies with the nature of the light illuminating the colourled substance.

The ordinary light consists of electromagnetic radiations of varying wavelengths which can be categorised in three headings :

Part of light	Range of wavelength of light
Ultraviolet light	1000—4000 Å
Visible part (white light)	4000—7500 Å
Infrared	7500—100,000,0 Å

The range of wavelength visible to human eyes is consisting of electromagnetic radiations covering rays of wavelength in the region 4000 to 8000 Å. Radiations below 4000 Å and above 8000 Å in the near vicinity are invisible and lie in ultraviolet (U.V.) and infrared (I.R.) regions respectively. Thus, the visible region is responsible for producing a definite colour to a particular substance. In the visible range of wavelength, light is composed of seven different colours namely, violet, indigo, blue, green, yellow, orange and red (VIBGYOR). The sequence of ultraviolet, visible (with spectral colours) and infrared regions is shown in Fig. 2.3.

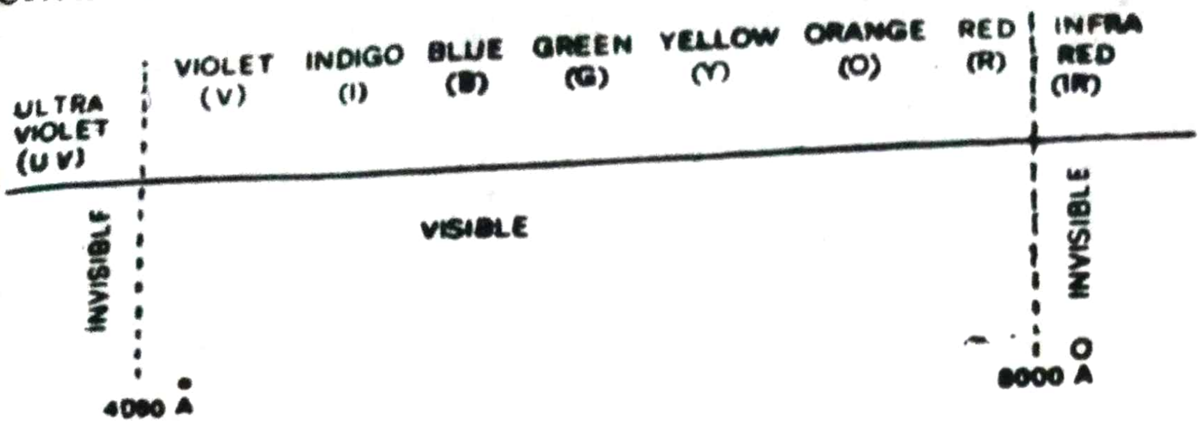


Fig. 2.3. Sequence of U.V., visible with spectral colours and I.R.

When white light is incident on a substance, colour is obtained in the following different ways :

(*i*) If the white light is reflected completely, the substance will appear light.

(*ii*) If the white light is absorbed completely, the substance will appear black.

(*iii*) If all the wavelengths of white light are absorbed except a single narrow band which is reflected, the colour of the substance will be the colour of the reflected band. For example, if the substance absorbs all wavelengths except one single band say the blue (4500 Å) which is reflected, the substance will appear blue.

(*iv*) If only a single band of white light is absorbed, the substance will have the complementary colour of the absorbed band. For instance, blue colour is produced if light of 5900 Å (region of yellow colour) is absorbed because the composite of the remaining wavelengths which are reflected gives the psychological sensation of blue colour. Thus, blue and orange are said to be complementary colours because the absorption of one from white light gives the other. The relation of colour absorbed and colour visualised with respect to a given range of wavelength is given in Table 2.1.

TABLE 2.1

Colour absorbed and colour visualised with respect to wavelength regions

Wavelength Å	Colour absorbed	Colour visualised
4000—4350	Violet	Yellow-green
4350—4800	Blue	Yellow
4800—4900	Green-blue	Orange
4900—5000	Blue-green	Red
5000—5600	Green	Purple
5600—5800	Yellow-green	Violet
5800—5950	Yellow	Blue
5950—6050	Orange	Green-blue
6050—7500	Red	Blue-green

2.3. Relation Between Colour and Chemical Constitution

The colour of a compound is related to its chemical constitution. It is evident from the following examples.

(*i*) Benzene is colourless while its isomer fulvene is coloured.

(*ii*) Reduction of coloured organic compounds results in the loss of colour and oxidation of the reduced compounds regenerates the original colour (Graebe and Libermann 1868)

$$\text{colourled organic compound} \underset{\text{oxidation}}{\overset{\text{reduction}}{\rightleftharpoons}} \text{colourless compound}$$

From this example, Graebe and Libermann concluded that unsaturation was responsible for the development of colour.

The relation between colour and chemical constitution of a substance has been explained by different theories which are described as follows :

1. Witt's theory (Chromophore-auxochrome theory). According to this theory (1876), there existed a relationship between colour and chemical constitution of a compound and further a dye is made up of two parts, *chromophores* and *auxochromes*.

(*a*) **Chromphores.** The colour usually appears in an organic compound if it contains certain unsaturated groups. Witt called these groups as the chromophores (Greek *chroma*-colour, and *phoros*, bearing). For example, diazomethane contains the unsaturated group, azo group, and is, therefore, yellow in colour. On reduction, the azo group is reduced and methlyhydrazine is produced which is colourless because it does not contain unsaturated group. Some important chromophores are listed in Table 2.2

Table 2.2
Some Typical Chromophores

$-N=O$	nitroso		*o*-quinonoid
$>C=S$	thiocarbonyl	$-\overset{H}{C}=N-$	azomethine
$-N=N$	azo	$-N(=O)\rightarrow O$	nitro
$-N=N\rightarrow O$	azoxy		
$-N=N-NH$	azoamino	$>C=O$	carbonyl
	*p*-quinonoid	$>C=C<$	ethylenic

The chromophores listed in the above Table are of two types :

(a) *Independent chromophores.* This type includes such chromophores when a single chromophore is sufficient to impart colour to the compound. Examples of such chromophores are $-N=O$, $-NO_2$, $-N=N$, $-N=N\rightarrow O$, $-N=N-NH$, $-N=N\rightarrow O$, *p*-quinonoid, etc.

(b) *Dependent Chromophores.* This type includes such chromophores when more than one chromophore is required to impart colour. Examples of such chromophores are $>C=O$, $>C=C<$, etc. This type is exemplified by various examples. For example, acetone, containing one carbonyl group, is colourless while biacetyl, containing two carbonyl groups, is yellow. A single C=C group does not produce colour in the compound but if a number of them are present in conjugation, the colour usually appears. For example, ethylene, $CH_2=CH_2$ is colourless while $CH_3(CH_2)_6CH_3$ is yellow.

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$
acetone

$$CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3$$
biacetyl

Diphenylpolyenes provide another example. The formula of these is $Ph(CH=CH)_nPh$. When $n=0$, 1 or 2, the compound is colourless. However, when n is 3, the compound becomes yellow and when n is further increased, the colour gets deepened, *i.e.*, when n is 5, the colour is orange, when n is 7, the colour is copper-bronze and when n is 11, the colour is violet-black.

The shade of the colour is also influenced by the proximity of the chromophores. If these are separated by other groups, the compound becomes colourless. For example,

$CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3$ is yellow in colour while

$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$ is a colourless compound.

Compounds containing a chromophoric group were called as **chromogens** by Witt.

(b) **Auxochromes.** A chromogen may be coloured but it does not represent a dye. Witt pointed out that the presence of certain groups in a chromogen leads to a deepening of the colour although these groups are not chromophores themselves and do not impart colour to the compound when present without the chromophore. Witt called these groups as **auxochromes** (Greek *auxein*-to increase, and *chroma*-colour).

Witt had listed a number of auxochromes which are given in Table 2.3.

Table 2.3

Some Typical Auxochromes

Name	Group	Name	Group
Amino	$-NH_2$	Chloro	$-Cl$
Methylamino	$-NHCH_3$	Methyl	$-CH_3$
Dimethyl amino	$-N(CH_3)_2$	Methoxy	$-OCH_3$
Sulphonic acid	$-SO_3H$	Cyano	$-CN$
Hydroxy	$-OH$	Acetyl	$-COCH_3$
Carboxylic acid	$-COOH$	Acetamido	$-CONH_2$

The auxochromes serve two functions, namely.

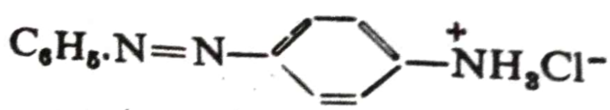
(*a*) *They increase the intensity of the colour.* This is illustrated by the following example :

(*i*) Benzene (no chromophore) is colourless.

(*ii*) Nitrobenzene ($-NO_2$ as a chromophore) is pale yellow.

(*iii*) *p*—Nitroaniline (NO_2 as a chromophore and $-NH_2$ as an auxochrome) is dark yellow.

(*b*) *They make the chromogen a dye by fixing it to the fabric or the material to be dyed either by associatian or by salt formation.* The fixing of the dye to the fibre is generally due to the formation of chemical bond between the fibre and the auxochrome. This is best illustrated by the following example :

C_6H_6 $C_6H_5.N{=}N.C_6H_5$ 

benzene — azobenezene (coloured but not a dye) — p-aminoazobenzene hydrochloride (a dye, aniline yellow)

Auxochromes are mainly of two types :

(*a*) **Bathochromic auxochromes.** These are the groups which increase the depth of the colour. These shift the absorption maxima from the violet towards the red and thereby bring about the deepening of the colour. It is called *red shift.* When the hydrogen atoms in an amino group $-NH_2$ are replaced by R, a bathochromic effect is produced.

(*b*) **Hypsochromic auxochromes.** These are the groups which decrease the depth of the colour. These shift the absorption maxima from the red to violet and this results in the fading of the colour. It is called *blue shift*. When the hydrogen atom in a hydroxyl group $-OH$ or in an amino group, $-NH_2$ by an acetyl group produces hypsochromic effect.

Witt's theory has proved to extremely useful empirical guide in developing many of the dyes.

4

Classification of Dyes

4.1. Introduction

Dyes are classified in various ways according to (*a*) the chemical constitution, (*b*) their methods of application to the fibre, (*c*) the types of materials to be dyed, and (*d*) the intermediates from which they are prepared. Neither system of classification is satisfactory by itself. However, the first two types of classification of dyes are very important and they have been discussed here.

1. Classification of dyes according to application. Dyes are classified according to application method, for the convenience of the dyer. The best classification method available is that used in the Colour Index, a publication sponsored by the Society of Dyers and Colourists (England) and the American Association of Textile Chemists and Colourists. This classification of dyes also gives the various different methods of dyeing of the various fabrics with the different dyes.

(*a*) **Acid dyes.** These dyes are usually the sodium salts of the colour acids which may contain sulphonic acid or phenolic group. These dyes give very bright hues and have a wide range of fastness properties from very poor to very good.

Acid dyes are used to dye fibres having basic groups, such as wool, silk and polyamides. Application is generally made under acidic conditions which cause protonation of the basic groups. The dyeing process may be represented as follows :

$$\text{Dye}^- + \text{H}^+ + \text{Fibre} \rightarrow \text{Dye}^-\ \text{H}^+ \text{—Fibre}$$

This is the reversible process. Generally, acid dyes can be removed from fibres by washing. The rate of removal depends on the rate at which the dye can diffuse through the fibre under the conditions of washing. For a given fibre, the diffusion rate depends upon temperature, size and shape of the dye molecules, and the number and kind of linkages formed with the fibre.

Some important examples of acid dyes are picric acid, metanil yellow, naphthol yellow, orange II, etc.

(*b*) **Basic or cationic dyes.** These are those dyes which have a basic amino group which is protonated under the acid conditions of the fibres by formation of salt linkages with anionic or acidic groups in the fibres. They generally give intense and brilliant shades but have poor light fastness.

Like the acid dyes, these are used for dyeing silk and wool directly but not unmordanted cotton (vegetable fibres). For dyeing cotton the basic dyes need a mordant like tannic acid and tartar emetic or some synthetic organic substances.

Examples of basic dyes are methyl violet, crystal violet, methylene blue, magneta, rhodamine, etc.

(*c*) **Direct dyes.** These are a class of dyes that become strongly adsorbed on cellulose. These usually bear sulphonic acid groups. However, these are not considered acid dyes because these groups are not used as a means of attachment to the fibre.

Direct dyes are large, flat, linear molecules which can enter the water-swollen amorphous of cellulose and orient themselves along the crystalline regions. Common salt or Glauber's salt is often used to promote dyeing because the presence of excess sodium ions favours establishment of equilibrium with a minimum of dye remaining in the dye bath.

The dyeing process with direct dyes is reversible because these dyes are held in cellulosic fibres by adsorption. Unless after-treated with resins and dye-fixing agents, direct dyes, as a class, have poor, fastness to washing. They are used mainly because these are economical and easy to apply. The direct dyes dye wool and silk from a neutral or nearly neutral bath. A typical direct dye is congo red.

A special type of direct dye having free amino groups is designed to be diazotised and coupled (developed) in the fibre. This improves the fastness of direct dyes to washing. An evample of this type is direct black 17 (zambesi black D). This dye is used primarily to colour plain grounds which are later to be printed in a pattern with vat dyes.

(*d*) **Mordant or adjective dyes.** These dyes by themselves have poor affinity for the fibre. However, these dyes require a pretreatment of the fibre with a mordant material designed to bind the dye. The mordant gets attached to the fibre and then combines with the dye to form an insoluble complex called a *lake*. Dyes with mordant dyeing properties must contain groups which can hold the metal in stable combination or chelate groups.

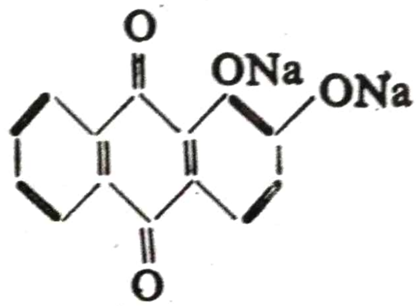
Mordants such as aluminium, chromium and iron salts are used depending upon the fibre and the class of the dye, *e.g.*

(*i*) **Chromium salts.** For dyeing wool and for printing cotton with mordant azo dyes.

(*ii*) **Aluminium salts.** For dyeing and printing cotton with alizarin.

(*iii*) **Iron salts.** For printing cotton with *o*-nitrosophenols.

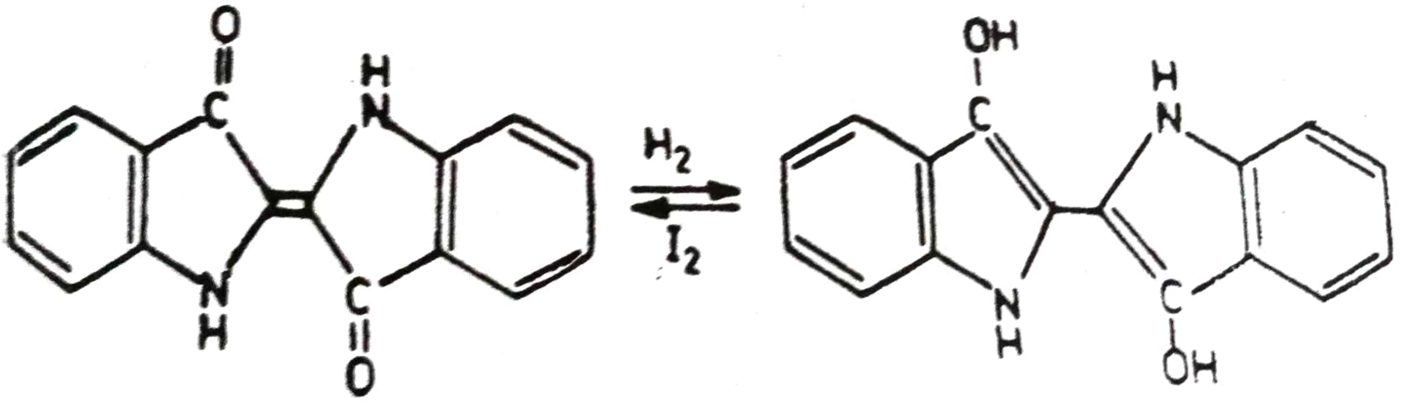
The only important dye used for dyeing cotton is alizarin. It does not have any affinity for the unmordanted fibres. However, when it is mordanted with aluminium hydroxide, it is precipitated in cotton fibre in the form of an *aluminium "lake"*.



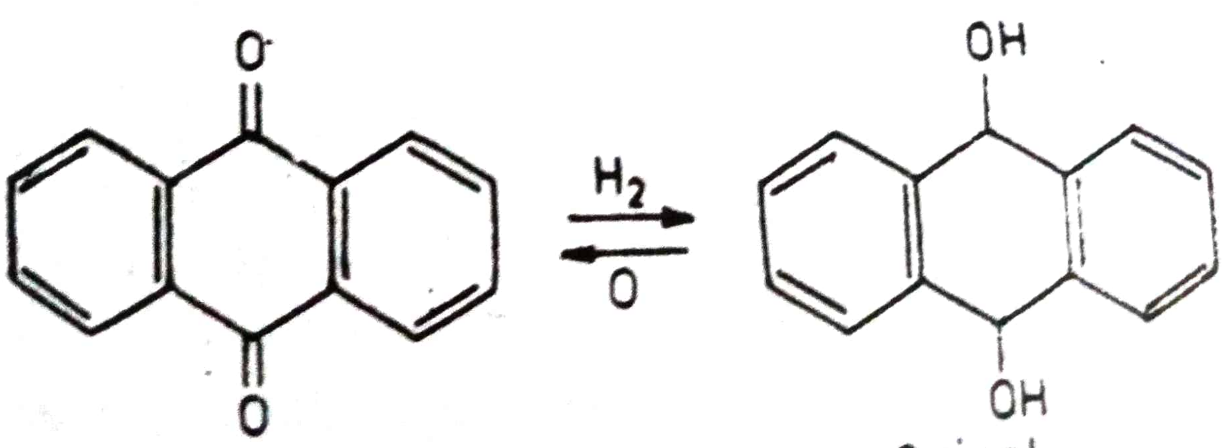
alizarin

Mordant dyes have declined in importance mainly because their use is no longer necessary. Equal or superior results can be obtained with other classes of dyes at less expense in time and fibre.

(*h*) **Vat dyes.** Like sulphur dyes, these dyes are insoluble. However, their reduced forms are soluble. Therefore, these dyes are applied in their reduced forms which are obtained by treating the compound with some reducing agent such as alkaline sodium hyposulphite in a large wooden vat, giving rise to the name vat dye. The cloth to be dyed is immersed in the vat, having a reduced vat dye. After the reduced dye has been adsorbed on the fibre, the original insoluble dye is reformed by oxidation with air or chemicals. The dyeings produced in this way are very fast to washing and, in most cases, the dyes are designed to be fast to light and bleaching as well. Examples of vat dyes are indigo and anthraquinone vat dyes.



Indigo blue (insoluble) Indigo white (soluble)



Anthraquinone Quinol

(*j*) **Disperse dyes.** The C.I. (Colour Index) definition was that these are a class of water-insoluble dyes originally introduced for dyeing cellulose acetate and usually applied from fine aqueous dispersion. Recent work has shown that such dyes do, however, dissolve to a very slight extent in water and the degree of solubility influences the dyeing and levelling processes.

Disperse dye molecules are generally small and have some hydroxyl or amino groups to give finite water solubility at dyeing temperatures.

Disperse dyes are usually ground in a mill to fine particles sizes (1-4 μ) in an aqueous solution containing a dispersing agent. The latter normally stabilises the dye suspension and acts as a restraining and retarding agent.

Disperse dyes may be applied by a dry heat process (Thermosol) to polyester fibres. In this case the dye achieves molecular form by sublimation (vaporisation) from the solid dye to the fibre process. Extremely small particle size is also important for this process.

The principal uses of disperse dyes are the dyeing of cellulose acetate, nylon polyester and polyacrylonitrile fibres. The mechanism in each case is believed to be one of solution in the fibre, no specific electrically charged dye sites being needed for dyeing to take place. Most polyester fibres must be dyed under pressure or with the use of organic swelling agents. The washing fastness of disperse dyes on these fibres is excellent. Disperse dyes are also used for dyeing woollen sheepskins (i.e., the skins to which the wool is still attached) and for the surface dyeing of plastics.

(*k*) **Reactive dyes**. These are a relatively new class of dyes that form covalent bonds with fibres possessing hydroxyl or amino groups. An important type of reactive dye has chlorine atoms which react with hydroxyl groups in cellulose when applied in the presence of alkali. It has been proved that an ether linkage is established between the dye and the fibre. An example of this type is the orange azo dyes.

Another important type of reactive dye involves an activated vinyl group which can react with a cellulose hydroxyl group in the presence of a base according to the following scheme :

$$\textit{Dye}—SO_2\,CH_2\,CH_2\,OSO_3\,Na \xrightarrow{OH^-}$$

$$\textit{Dye}—SO_2\,CH{=}CH_2 + HO—\textit{Cellulose}$$

$$\downarrow$$

$$\textit{Dye}—SO_2\,CH_2\,CH_2O—\text{Cellulose}$$

Reactive dyes offer excellent fastness to washing since the dye becomes a part of the fibre. The other properties depend on the structure of the coloured part of the molecule and the means by which it gets attached to the reactive part.

It is clear from the number of published patents relating to reactive dyes that this field is regarded as being of the highest importance by the dye-maker and dye-user.

15

Anthraquinone Dyes

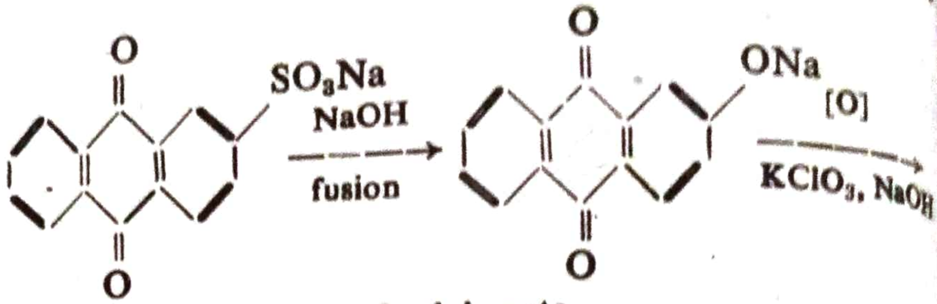
Introduction

Anthraquinone, the basic system of these dyes, has a faintly yellow colour, the edge of its long wave extends into the visible spectrum (λ_{max} 327 nm). It is not itself a dye. The introduction of relatively simple electron donors gives anthraquinone compounds which, according to the strength of the electron donors ($OH < NH_2 < NR_2 < NHAr$), absorb in any desired region of the visible spectrum. The position of the substitutents in anthraquinone not only influences the absorption maximum but also some of the other properties. For example, anthraquinone derivatives that have hydroxyl or amino groups in the β-position generally exhibit better resistance to sublimation, better solubility and better affinity for textile substrates than α-substituted compounds.

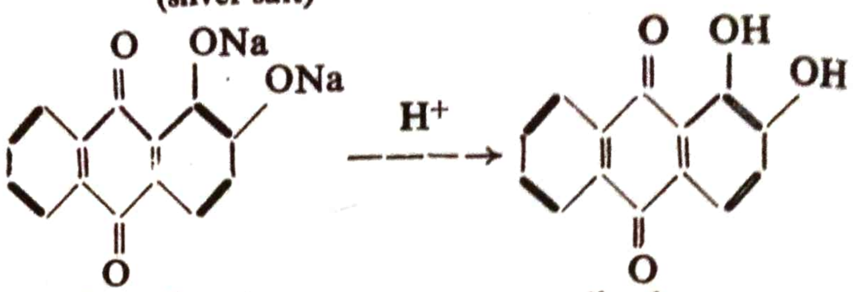
Dyes based on anthraquinone and related polycyclic aromatic quinones are of great importance. Many of the most light-fast acid, mordant, disperse, and vat dyes are of this kind. The chromophore is the quinoid group, $>C=O$.

(a) **Anthraquinone mordant dyes.** These contain groups such as hydroxyl or carboxyl group, which can combine with metal ions so as to form insoluble compounds called *lakes*. The colour of the lake depends upon the mordant, *i.e.*, the metal used. Some of the important anthraquinone mordant dyes are as follows :

(*i*) **Alizarin.** It is 1, 2-dihydroxyanthraquinone. It is also known as mordant red 11. Previously it was obtained from the roots of the madder plant but now-a-days it is obtained by heating, under pressure, *silver salt* (sodium anthraquinone-2-sulphonate, so called because of its silvery crystals), caustic soda, potassium chlorate and water in a steel autoclave at about 180°C. The resulting melt is blown into water and acidified to decompose the sodium alizarate, the precipitated alizarin is filtered, washed and used as a 20 per cent paste.



sodium anthraquinone-2-sulphonate
(silver salt)



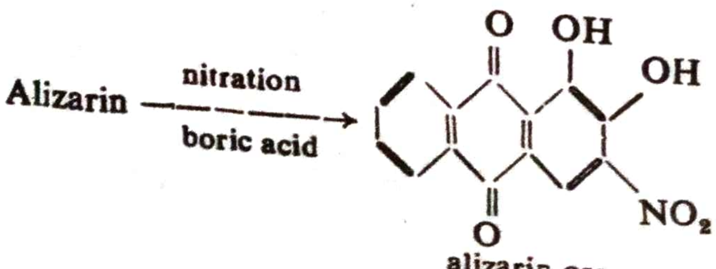
sodium alizarate alizarin

Alizarin is a red crystalline solid insoluble in water but soluble in alcohol and alkali. It is a mordant dye and combines with mordants, *i.e.*, metallic hydroxides, to form coloured insoluble compounds called *lakes*. The colour of the lake depends upon the mordant, *i.e.*, cation used. The colours of the lakes along with the respective mordants are given as follows :

Mordant used	Colour of the lake
Ca^{2+}, Ba^{2+}, Pb^{2+}	Bluish-red
Sr^{2+}	Red violet
Mg^{2+}, Sn^{4+}	Violet
Al^{3+}	Red
Cr^{3+}	Brownish-red
Fe^{+2}	Violet
Fe^{3+}	Brown black
Sn^{+2}	Red

When alizarin is applied to wool with an aluminium mordant, it gives the well known turkey red. Alizarin, when converted to its calcium salt, forms a bluish-red powder useful as a pigment.

(*ii*) **Alizarin Orange.** It is obtained by nitrating alizarin in the presence of boric acid.



alizarin orange

Diphenylmethane Dyes

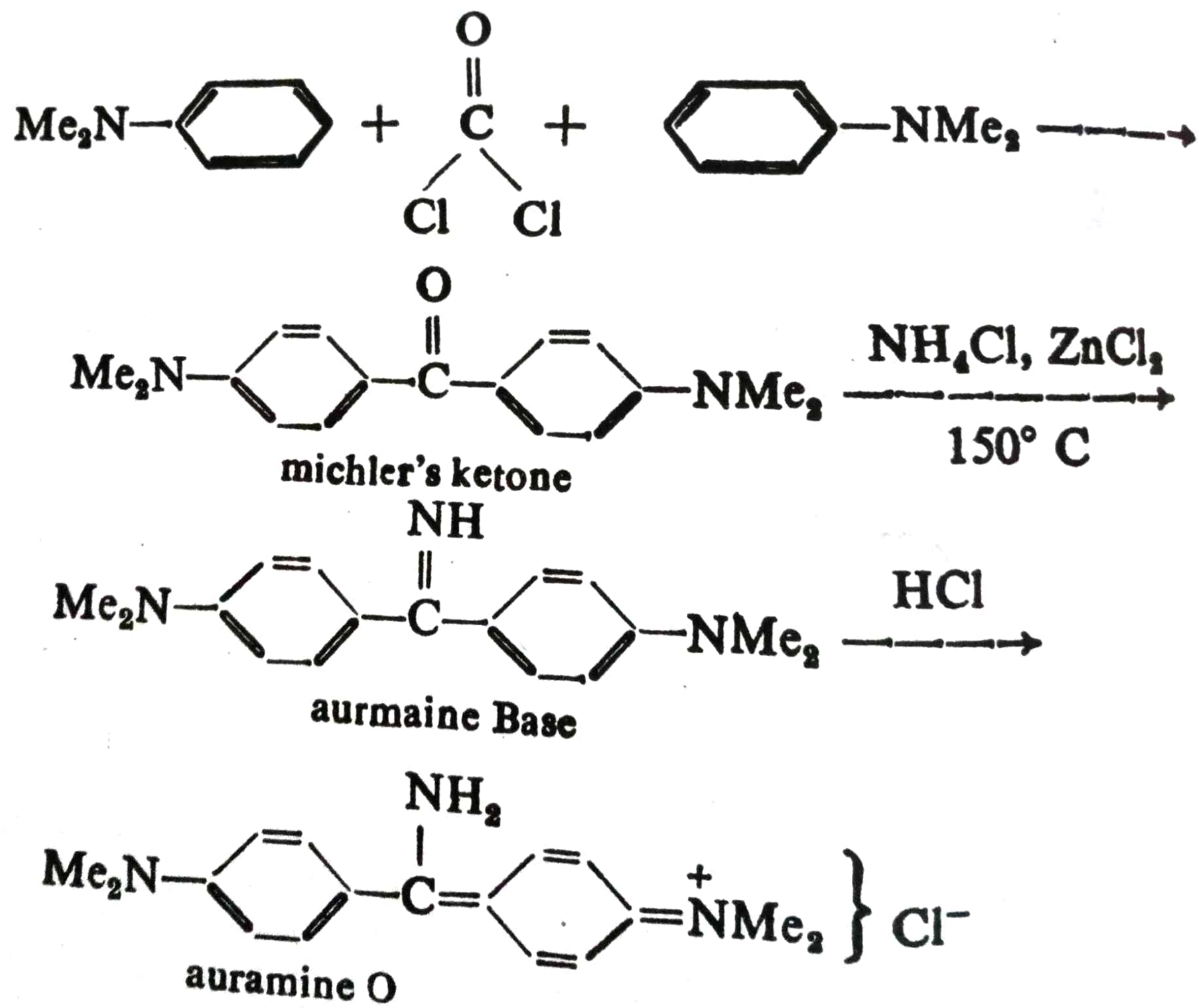
9·1. Introduction

The diphenyl methane dyes are characterised by the presence of a diphenylmethane nucleus. Only few dyes belonging to this class are commercially important.

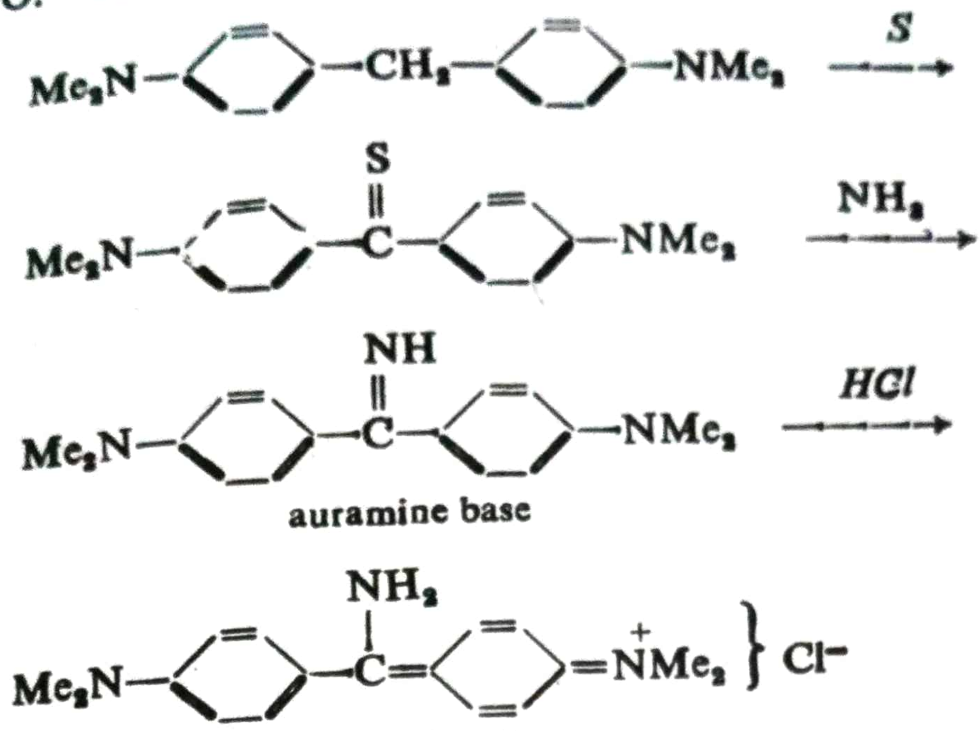
9·2. Some Examples of Diphenylmethane Dyes

Some examples of these dyes are described as follows :

1. **Auramine O.** Kern and Karo prepared this dye by heating michler's ketone with ammonium chloride and zinc chloride at 150—160° C. The auramine base so obtained on treatment with HCl is converted into auramine O. The michler's ketone required for this synthesis is prepared by condensing N-dimethylaniline with phosgene.



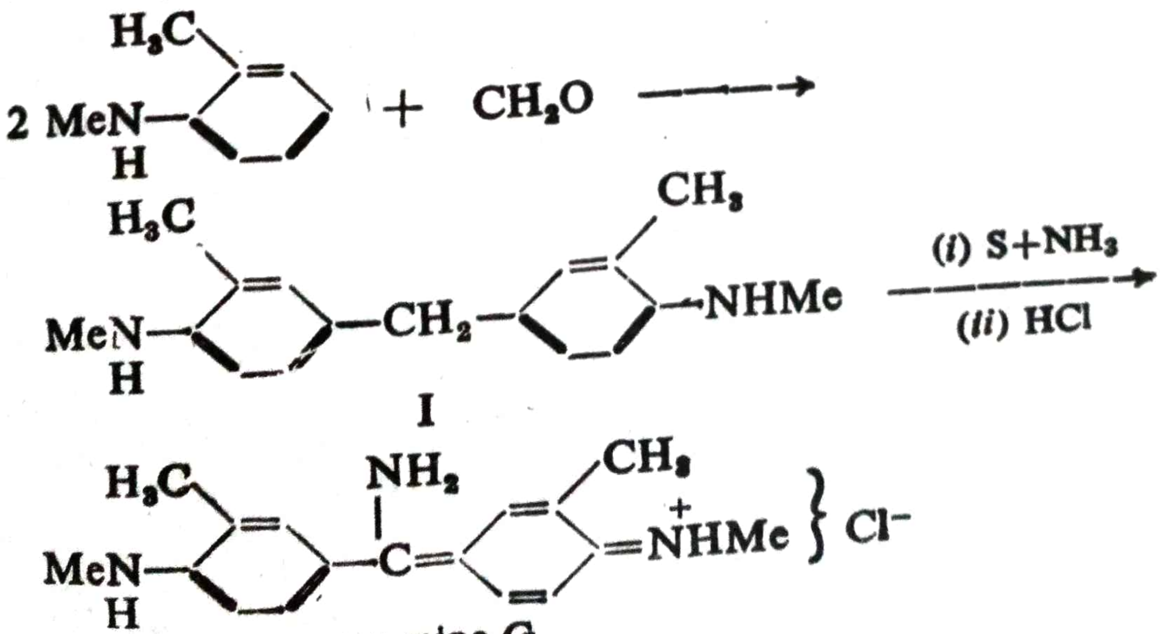
Now-a-days, it is prepared by heating 4,4′-bis (dimethylamino-phenyl) methane with sulphur, ammonium chloride and large excess of sodium chloride in an atmosphere of ammonia at 175° C. The auramine base so produced is treated with hydrochloric acid to get auramine O. The sodium chloride is purely as a diluent.



auramine O

It is marketed in the form of hydrochloride. It is a cheap, brilliant yellow and extensively used dye for dyeing of paper, silk, leather and Jute. The yellow colour produced by it is not fast to light and is destroyed by boiling with water, and on treatment with hot acids and alkalis. However, it is still employed due to its cheaper cost than the other dyes of comparable colour.

2. **Auramine G**. The condensation of N-monomethyl-*o*-toluidine with formaldehyde yields the product I which on heating with sulphur in a current of ammonia, followed by treatment with hydrochloric acid yields Auroamine G.



auramine G

It is greenish yellow dye.

10

Triphenylmethane Dyes

10·1. Introduction

This group of dyes is one of the oldest known synthetic dyestuff groups. They are of brilliant colour due to resonance and cover a range of shades from red to blue, including violet and green. However, the colour fades rapidly in light and due to this reason they find less uses in textiles but are used for colouring papers, type writer ribbons and other articles where fastness to light is not of much significance.

These dyes have the quinonoid group as their chromophores. These dyes are obtained by the introduction of NH_2, NR_2 or OH groups into the para positions of the benzene ring of triphenyl methane. The compounds so obtained are colourless and are called *leuco-compounds.* These on oxidation are converted into the corresponding tertiary alcohols called *colour bases* which on treatment with acid are changed from the colourless benzenoid forms to the quinonoid dyes due to salt formation. The coloured salts on treatment with alkali are converted into the leuco-base.

$$\underset{\text{(colourless)}}{\text{leuco-base}} \underset{\text{reduction}}{\overset{\text{oxidation}}{\rightleftharpoons}} \underset{\text{(colourless)}}{\text{colour base}} \underset{\text{akali}}{\overset{\text{acid}}{\rightleftharpoons}} \underset{\text{(coloured)}}{\text{dye}}$$

Some structures of this class of dyes involve an aryl group than phenyl and, therefore, in general this class can be called *triarylmethane dyes.*

10·2. Classification

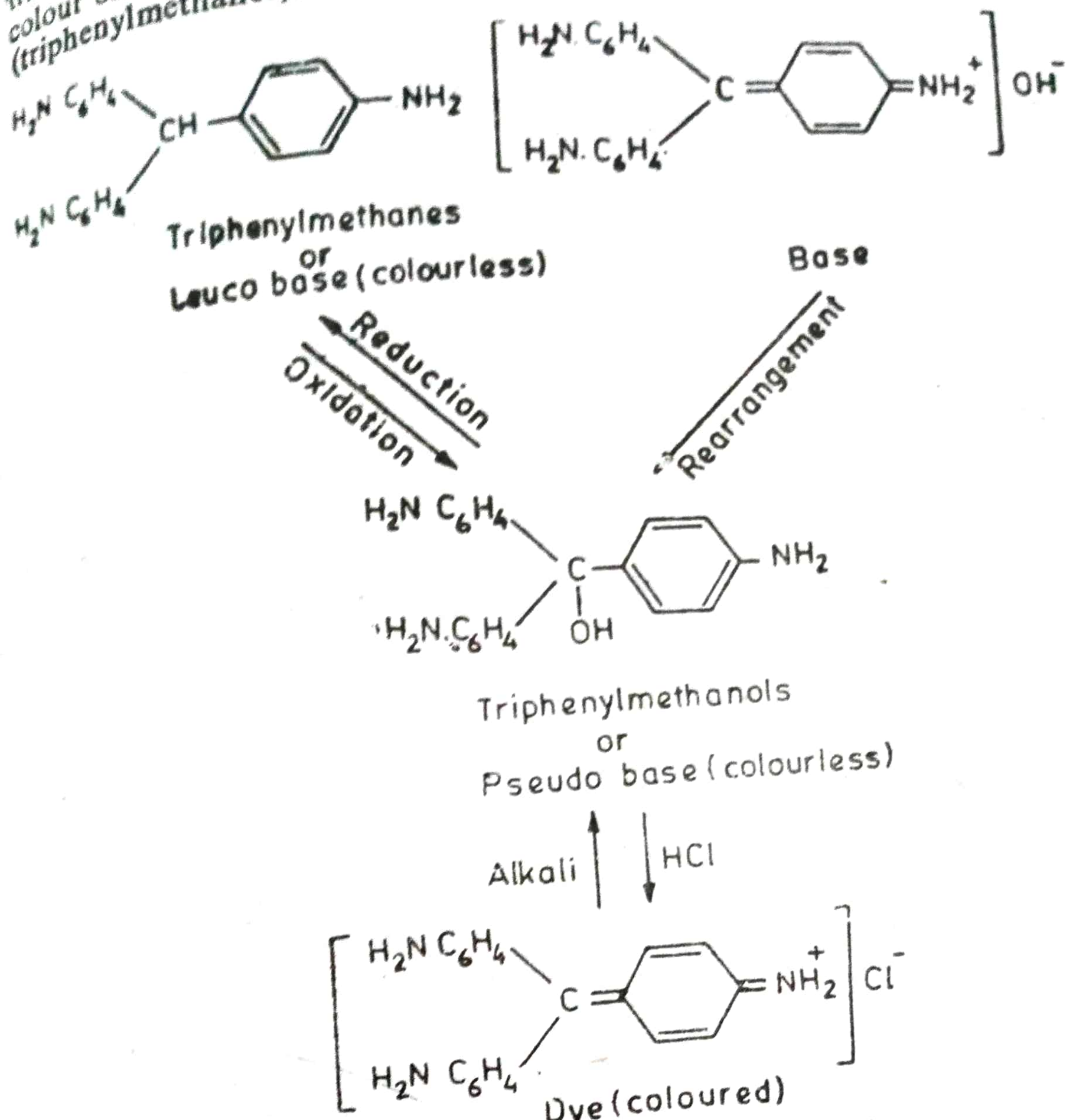
The triphenylmethane dyes have been further classified into the following types :

1. Aminotriphenylmethane dyes.
2. Hydroxytriphenylmethane dyes.

Let us discuss these one by one.

1. **Aminotriphenyl methane dyes.** These are the salts which are obtained by the actior of mineral acids on certain di-or

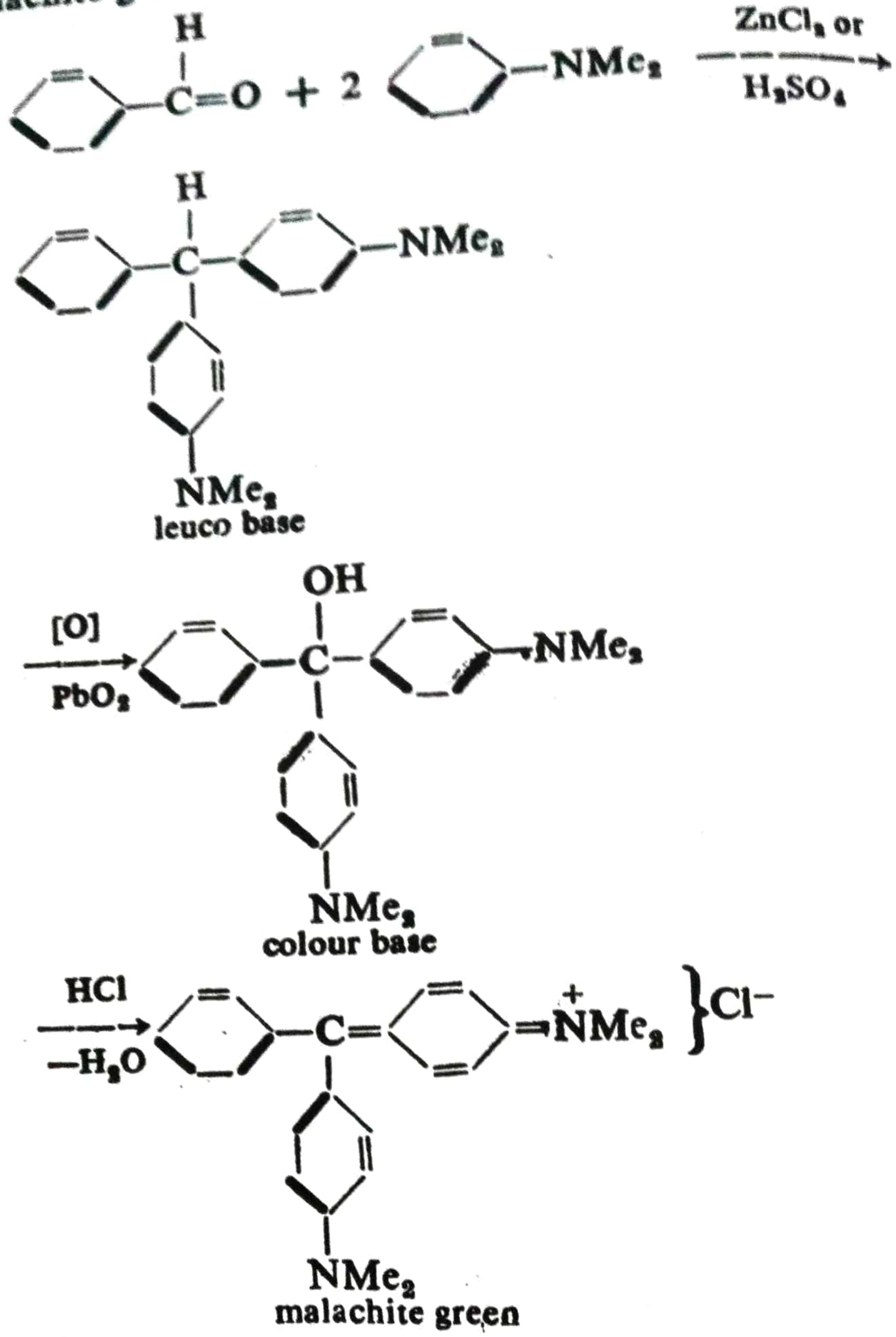
tri-amino. substituted triphenylmethanols (colour bases). The colour bases are in turn prepared by the oxidation of the leuco base (triphenylmethanes).



The intense colour of this group of dyes has been attributed to the resonance of unsymmetrical triphenylcarbonium ions. This resonance will be only possible if two or more of the benzene rings of the triphenyl carbonium ions have amino or substituted amino groups (generally in the *p*-position). The resonance energy stabilises the positive ion of the dye, thereby, favouring the formation of salt from the colour base.

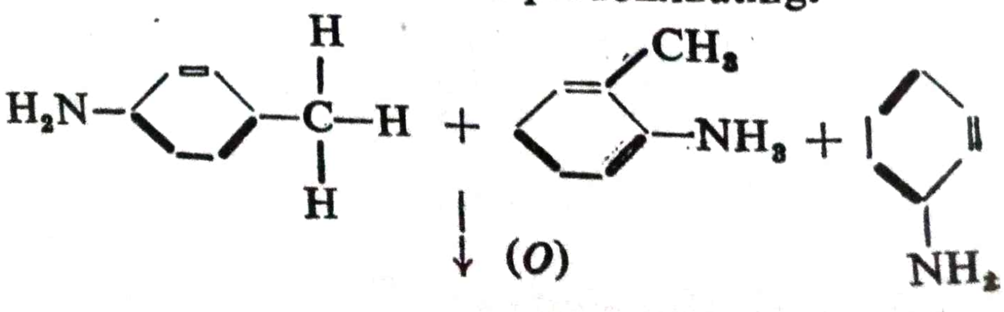
We will now discuss the various important triphenylmethane dyes.

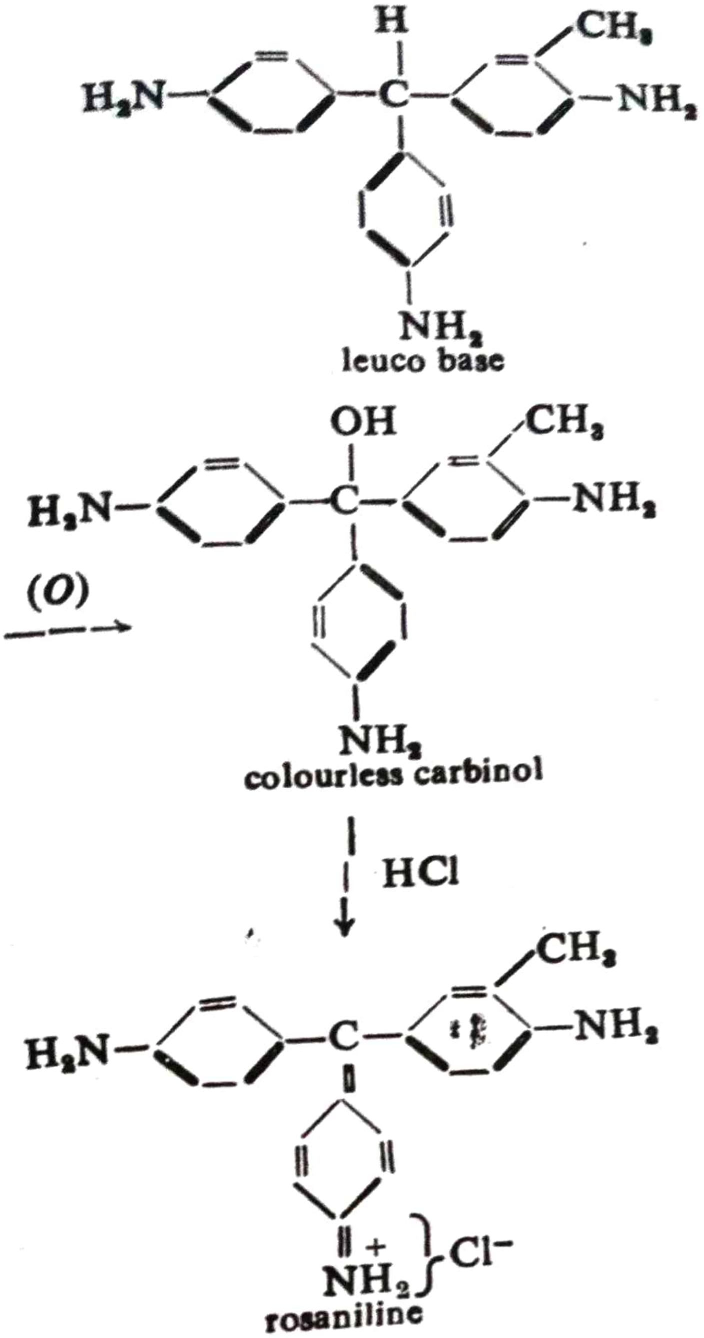
(*a*) **Malachite green.** On a large scale it is prepared by condensation of 2 moles of dimethylaniline with one mole of benzaldehyde at 100° C in the presence of zinc chloride or conc. sulphuric acid. The leuco-base produced is oxidised with lead dioxide in a solution of acetic acid having hydrochloric acid. The resulting colour base on acidification with excess of hydrochloric acid gives malachite green.



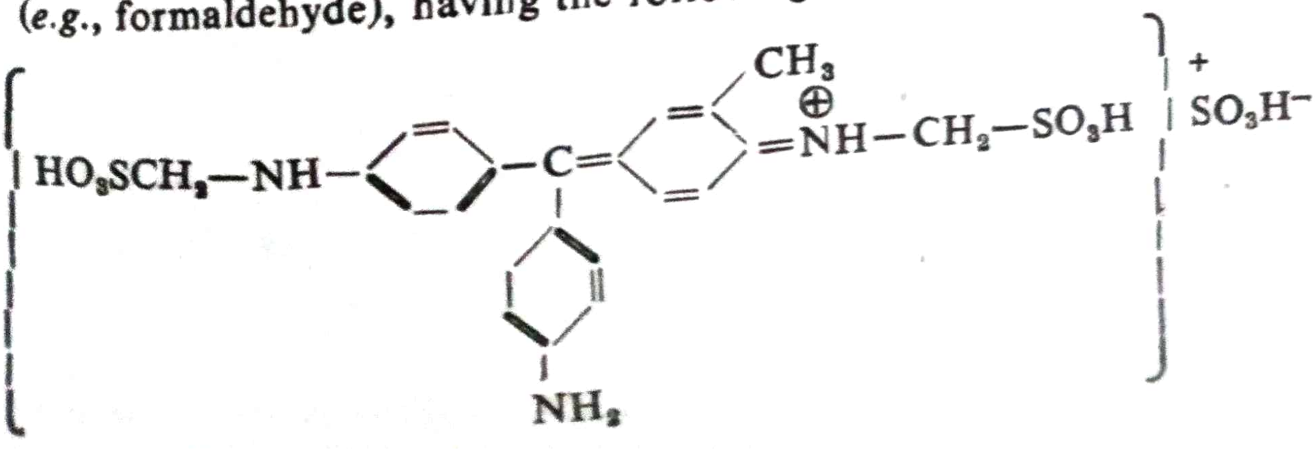
Malachite green dyes wool and silk directly, and cotton mordanted with tannin.

(*b*) **Rosaniline** (*Magneta or Fuchsine*). It is prepared by oxidising an equimolecular mixture of aniline, *o*- and *p*-toluidines, and their hydrochlorides, with nitrobenzene in the presence of iron filings. The product so obtained is a mixture of rosaniline and pararosaniline in which the former is predominating.



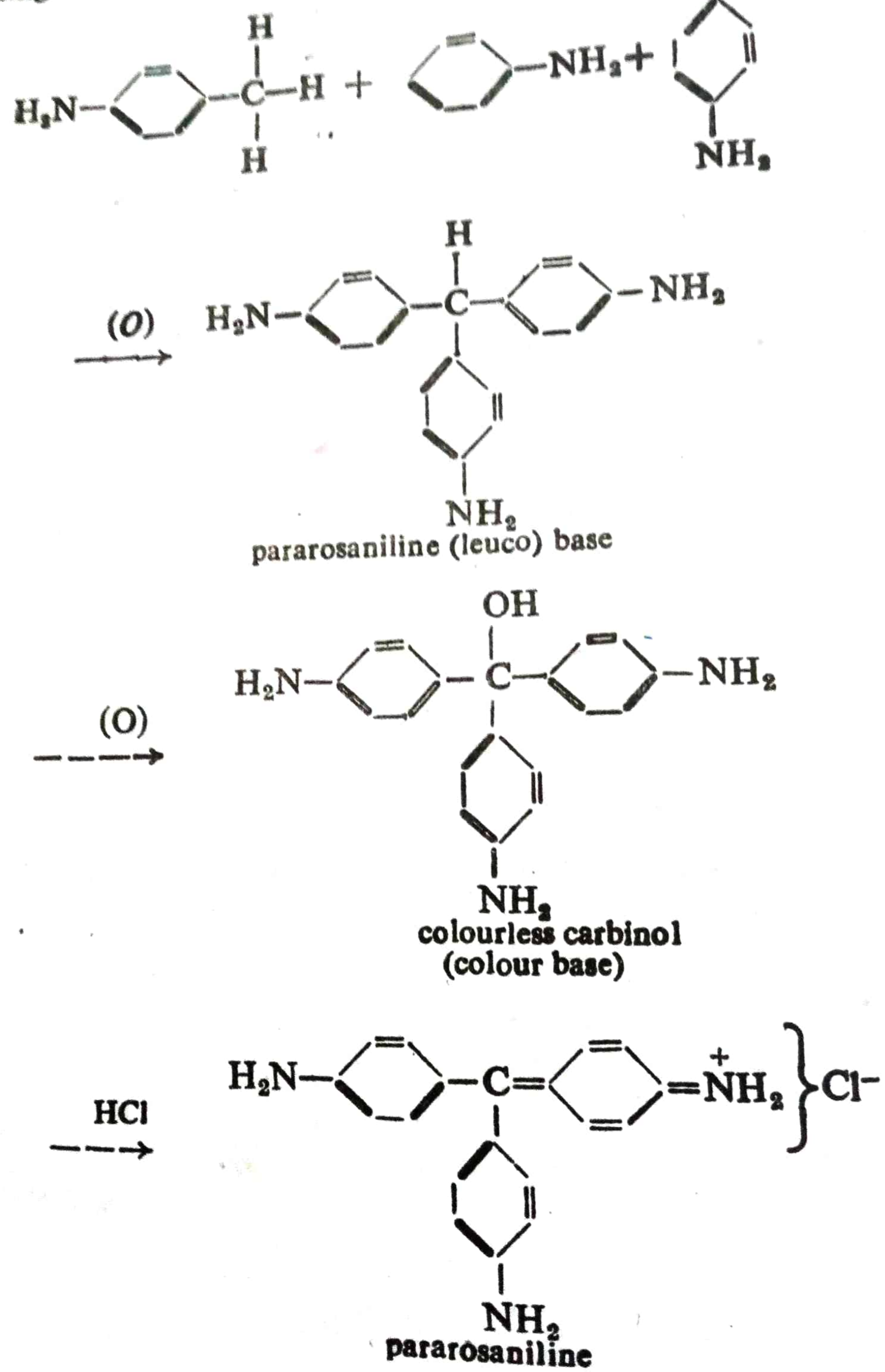


Rosaniline forms crystals which show a green metallic lustre. It dissolves in water, giving a deep red solution. This solution is decolourised by sulphur dioxide and is then called **schiff's reagent.** This reagent is used as a test for aldehydes. The restoration of the colour may be probably due to the formation of a dye with aldehyde (*e.g.*, formaldehyde), having the following structure.

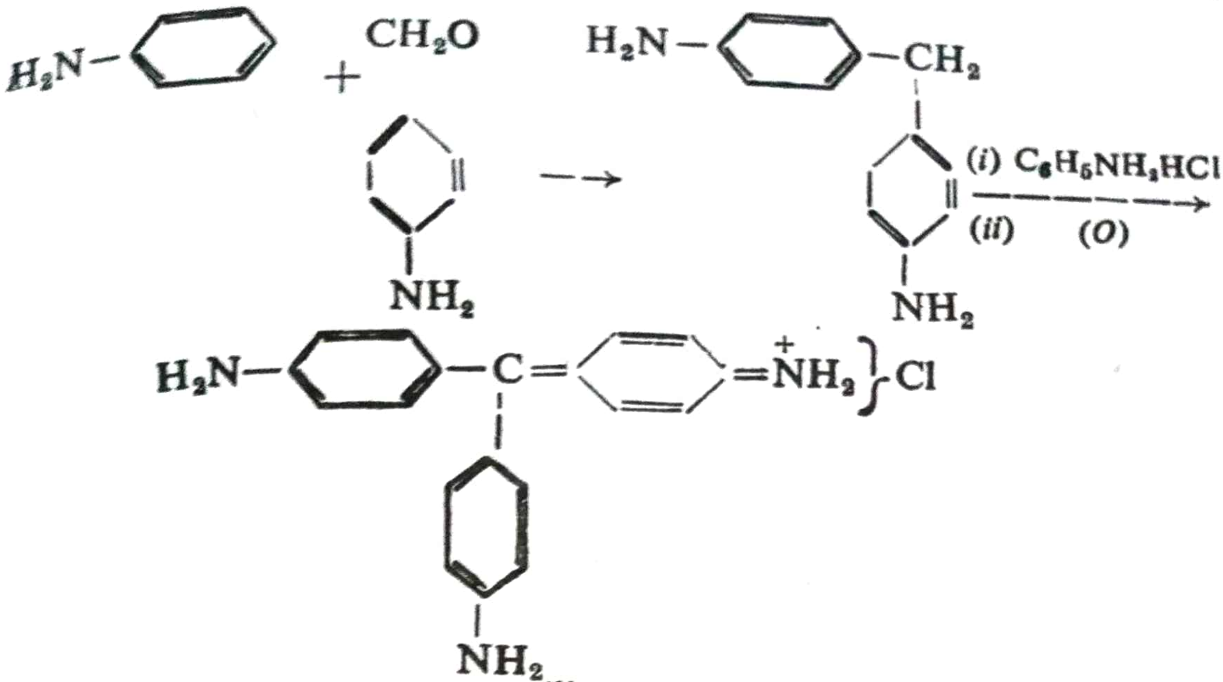


Rosaniline is used to dye wool and silk directly, producing a violet-red colour ; however, cotton must be mordanted with tannin.

(c) **Pararosaniline** (*para fuchsine*). On a large scale it is generally prepared by oxidising a mixture of two moles of aniline and one mole of *p*-toluidine with arsenic acid or nitrobenzene. The resulting colour base on treatment with acid yields the dye.



It is also possible to prepare pararosaniline by the following method :

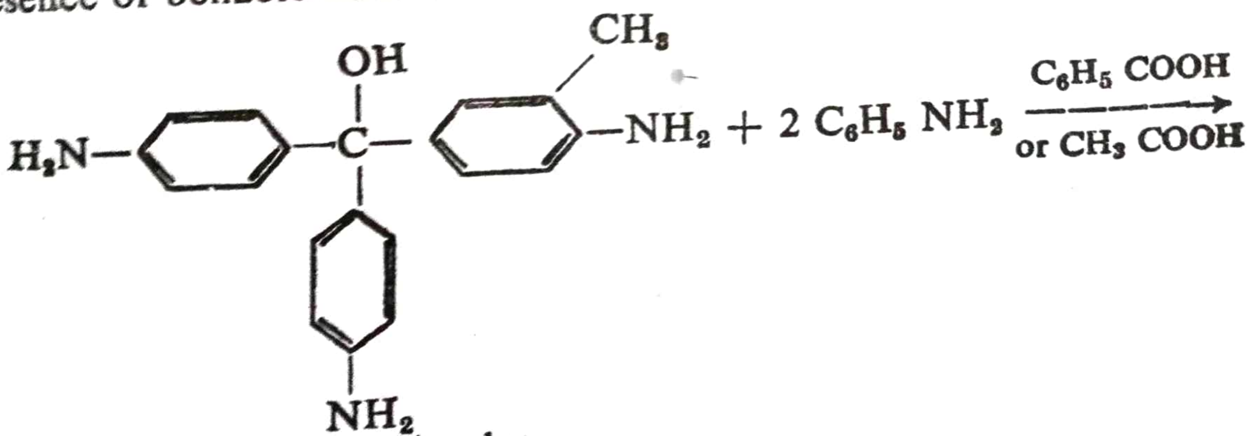


pararosaniline

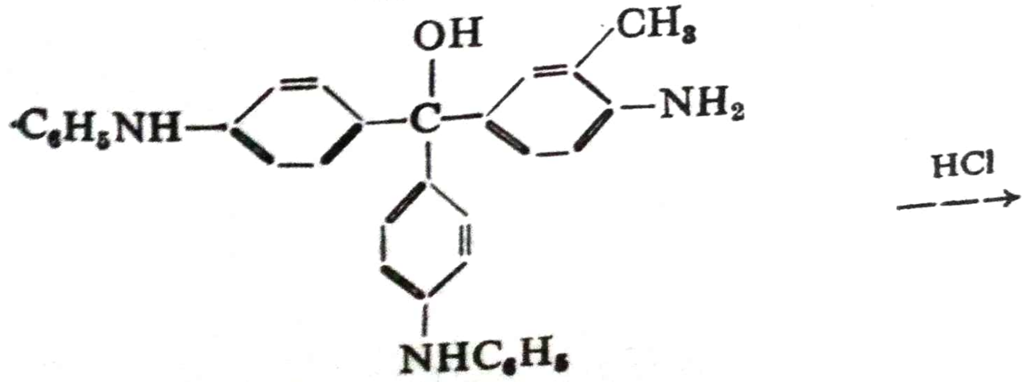
Pararosaniline has the same properties as that of rosaniline. Like rosaniline, it dyes wool and silk directly, producing a violet-red colour ; cotton must first be mordanted with tannin.

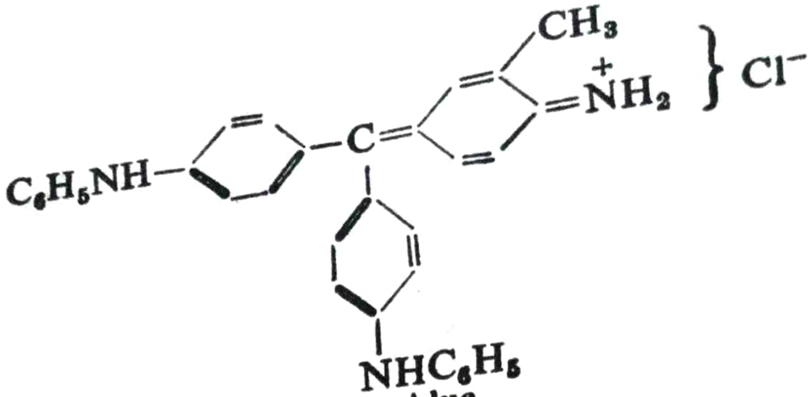
The N-phenylated sulphonic acid derivatives of pararosaniline are more important than the parent dyes. These are known as *ink blues* and are valuable acid dyes.

(*d*) **Aniline blue** (*diphenylrosaniline*). On a large, scale it may be obtained by heating rosaniline dye base with aniline in the presence of benzoic acid or acetic acid.



rosaniline dye base

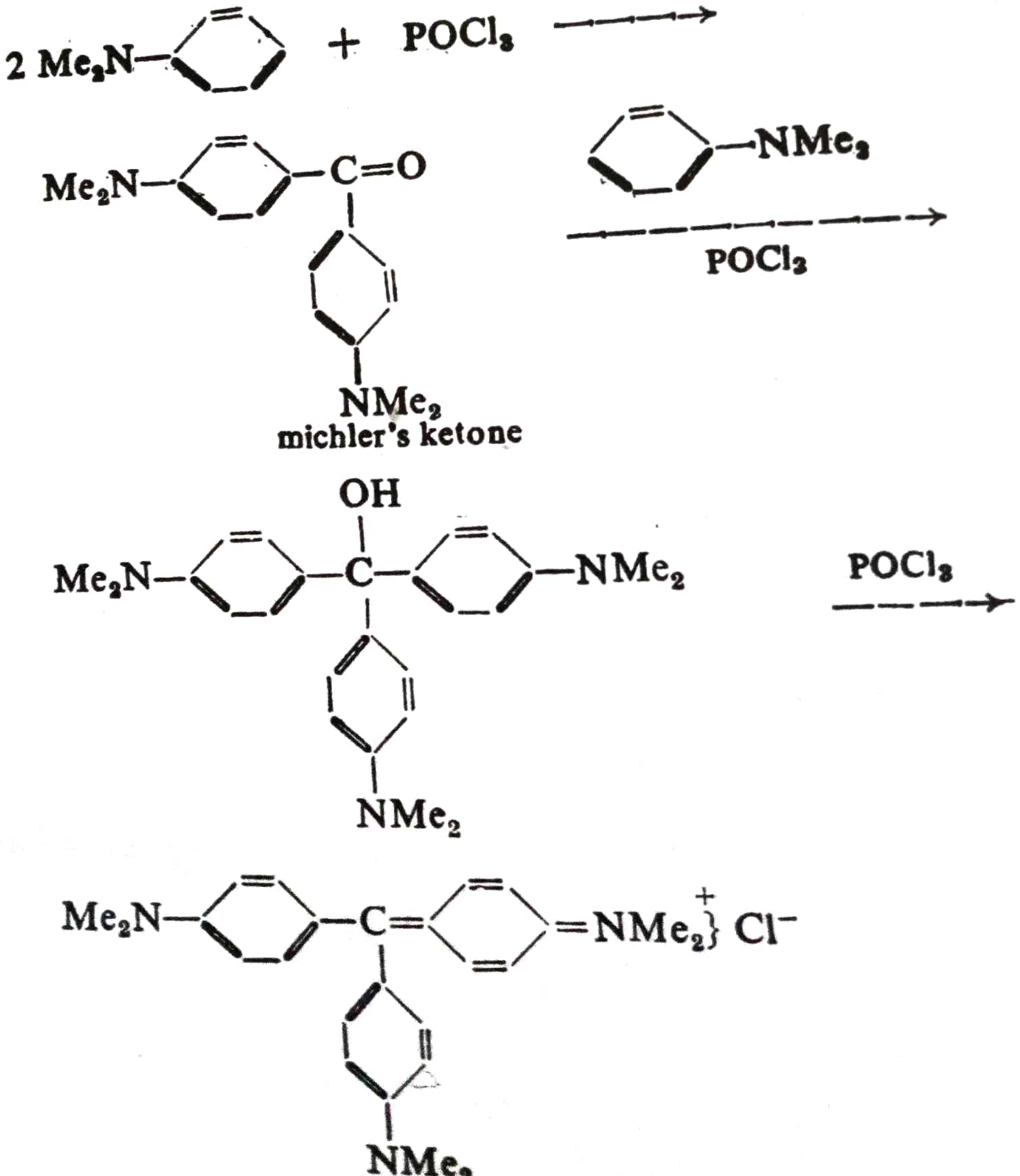




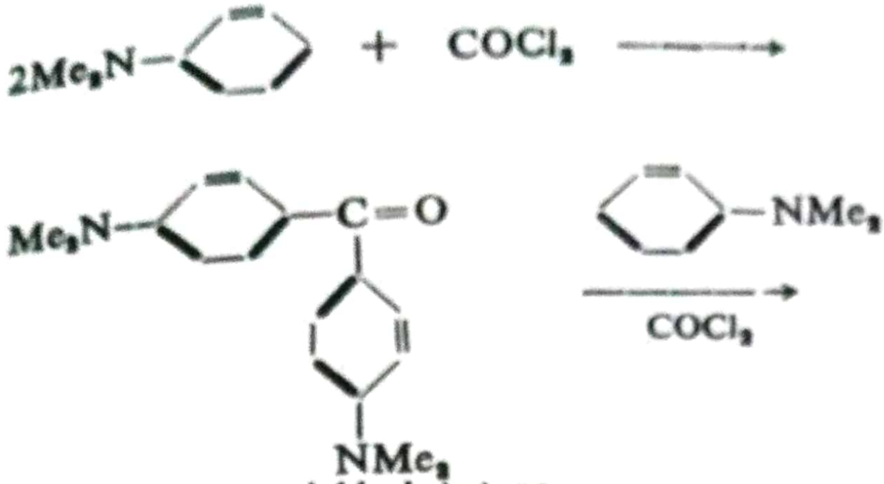
aniline blue

It is important to remember that the phenylation of the amino group is prevented by the *o*-methyl group.

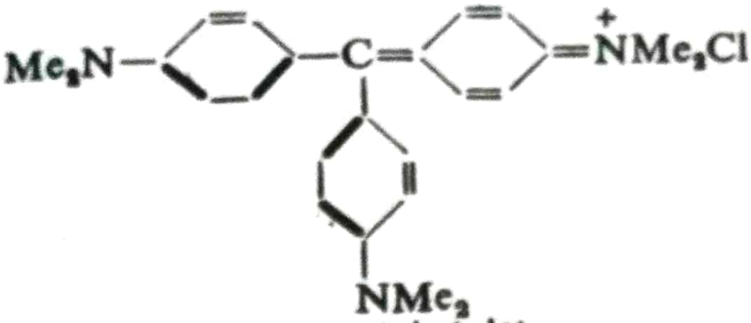
(*e*) **Crystal violet** (*hexamethyl parafuchsine or hexamethyl-pararosaniline hydrochloride*. It may be obtained by heating michler's ketone with dimethylaniline in the presence of phosphoryl chloride or carbonyl chloride. If the latter compound is used, then crystal violet may be prepared directly by heating carbonyl chloride and dimethylaniline.



crystal violet



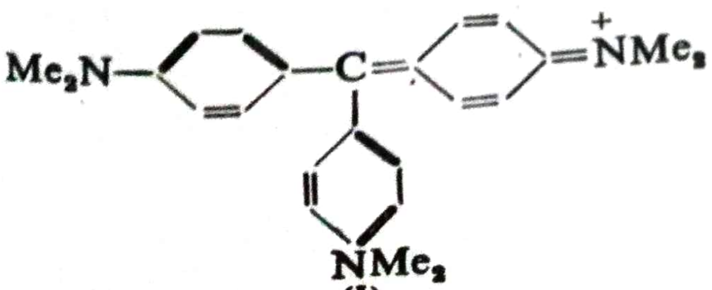
michler's ketone



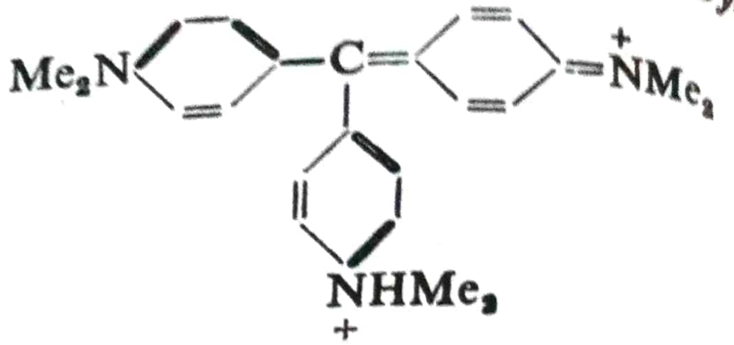
crystal violet

Its weak acid solution is violet, its strongly acid solution is green and its very strongly acid solution is yellow. The colour changes may be explained as follows :

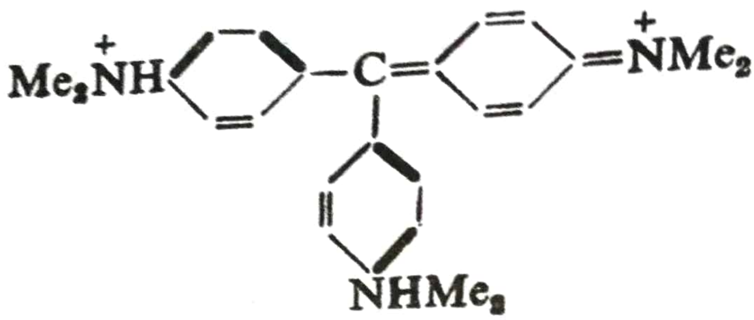
In weakly acid solution, the crystal violet has been found to exist as the singly charged ion (I). In this state, two-thirds of the charge will undergo oscillation in the horizontal direction. In strongly acid solution, it has been found to exist as the doubly charged ion (II). In this state, the whole unit of charge will undergo oscillation in the horizontal direction and, therefore, the colour deepens. It is important to remember that the vertical direction of oscillation gets inhibited due to the fixation of the lone pair by proton addition. In very strongly acid solution, it has been found to exist in form (III) having three charges. In this ion, relatively little resonance (with oscillation of charge) is possible and therefore the colour lightens.



(I)



(II)



(III)

Crystal violet is used to dye silk, wool and tannin-mordanted cotton to bluish violet colour but the colour is not fast to light. Crystal violet is used in making indelible ink and pencils, in stamping pad, etc. It is used as an indicator in the determination of hydrogen-ion concentration of solution.

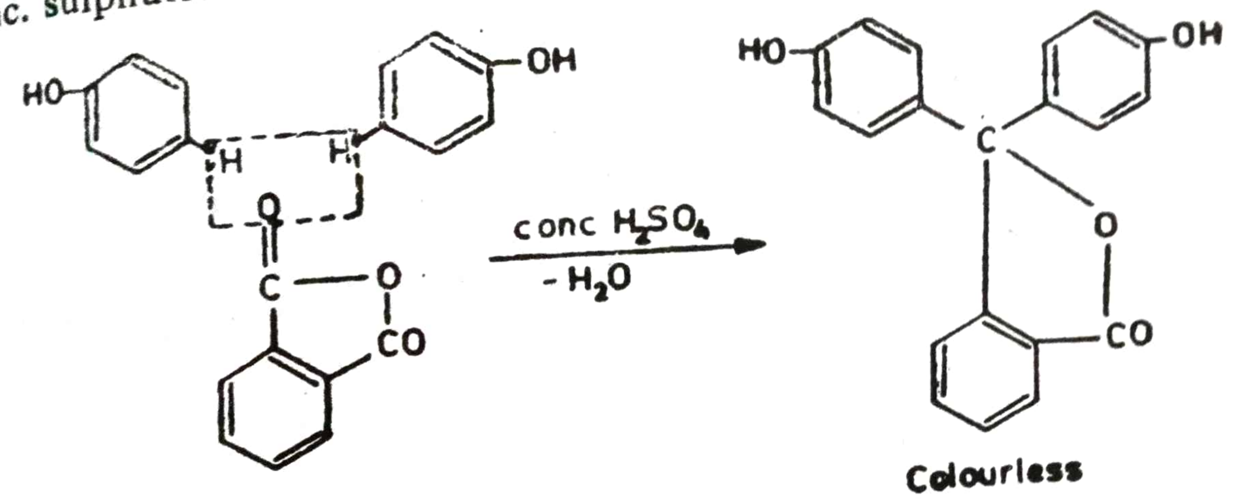
11

Phthaleins

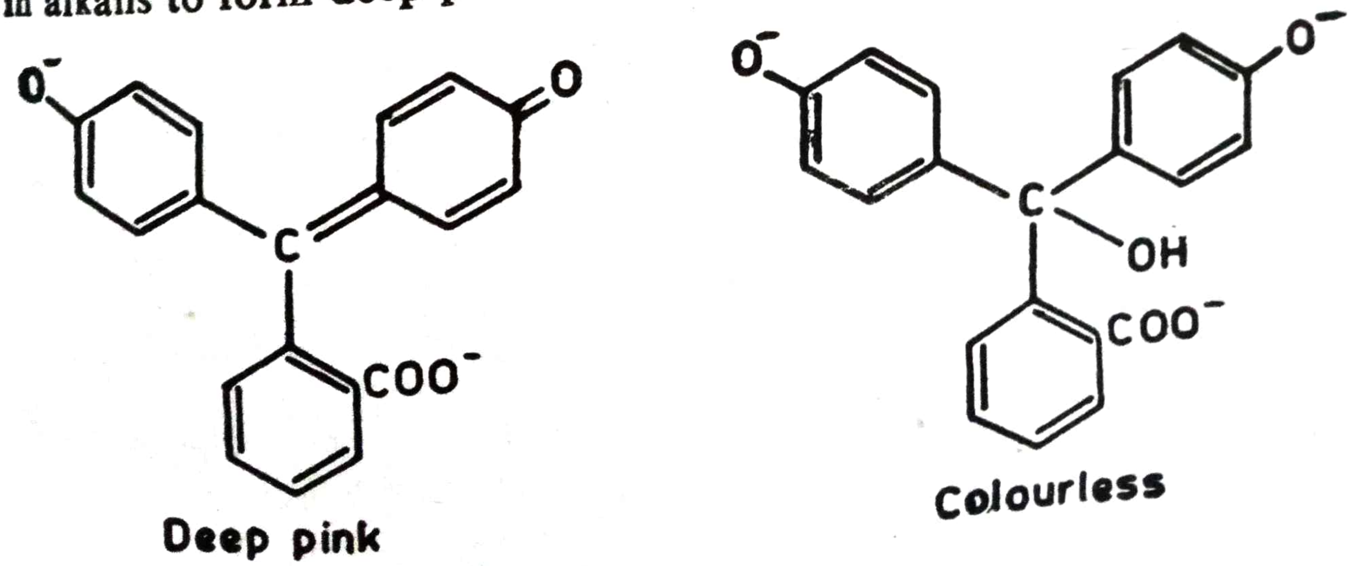
11.1. Introduction

These are dihydroxytriphenyl methane derivatives with a carboxyl or sulphonic acid group ortho to the central carbon atom in the third phenyl ring. These are used as indicators because they are sensitive to the action of alkali solutions. Phenolphthalein is the most important member of this group.

(*a*) **Phenolphthalein.** It is prepared by heating phthalic anhydride (1 molecule) with phenol (2 molecules) in the presence of conc. sulphuric acid as a condensing agent.



It is a white crystalline solid insoluble in water but soluble in alkalis to form deep pink solution.



If the excess of strong alkali is added to the pink solution, it becomes colourless again due to the loss of quinonoid structure and resonance.

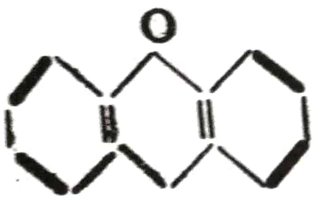
Its 1% solution in alcohol is used as an indicator in acid-alkali titrations. It is also used as a laxative in medicine.

12

Xanthene Dyes

12.1. Introduction to Xanthene Dyes

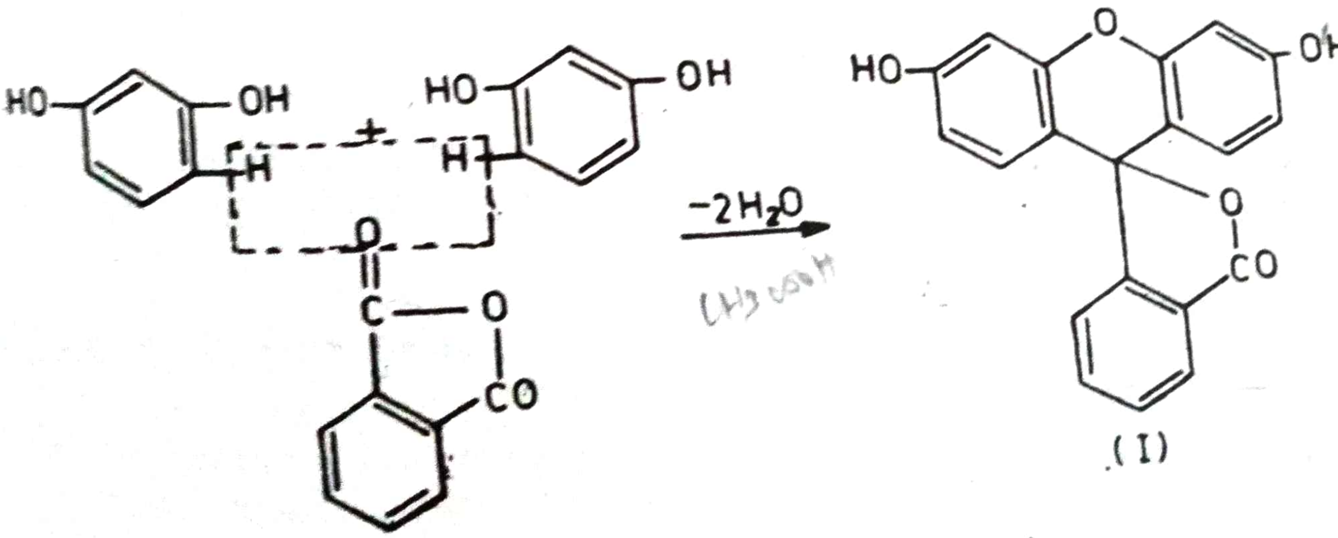
These are derivatives of xanthene. This group gives rise to brilliant fluorescent dyes having red to yellow colour. Xanthene dyes obtained from xanthene by the introduction of auxochromes such as amino or hydroxyl group into positions 3 and 6, *i.e.*, the *para*-positions with respect to the carbon atom linking the two benzene nuclei :



xanthene or xanthen

Some important members of this group of dyes are described as follows :

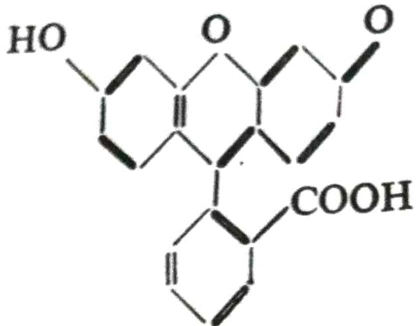
(*a*) **Fluorescein.** It is a xanthene derivative and is obtained by heating phthalic anhydride (1 molecule) with resorcinol (2 molecules) at 200° C or 110-120° C with anhydrous oxalic acid.



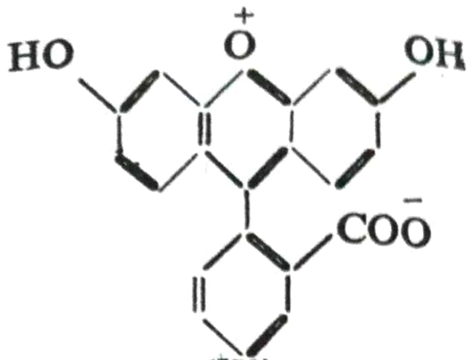
(I)

Fluorescein is red powder. It is insoluble in water.

As fluorescein is coloured, the structure (I), which is the non-quinonoid uncharged structure, is unsatisfactory. However, two quinonoid structures have been postulated in which the structure (II) is having the *p*-quinonoid structure while the structure (III) is having *o*-quinonoid structure (this contains tercovalent oxygen).



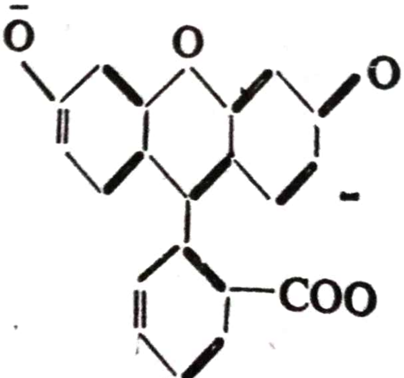
(II)



(III)

When Davies *et al.* (1954) recorded the infrared spectra of phenol, phenolphthalein, fluorescein and some of their alkali derivatives, they concluded that the structure (I) is preferred over other structures (II) and (III). The structure (II) is eliminated due to the absence of the characterised absorption of the carboxyl group. Similarly, the structure (III) is eliminated because the frequencies of the carboxylate ion in (III) are absent.

When fluorescein is dissolved in alkalis, it gives a reddish-brown solution which on dilution gives a strong yellowish-green fluorescence. The structure of fluorescein anion is (IV).



(IV)

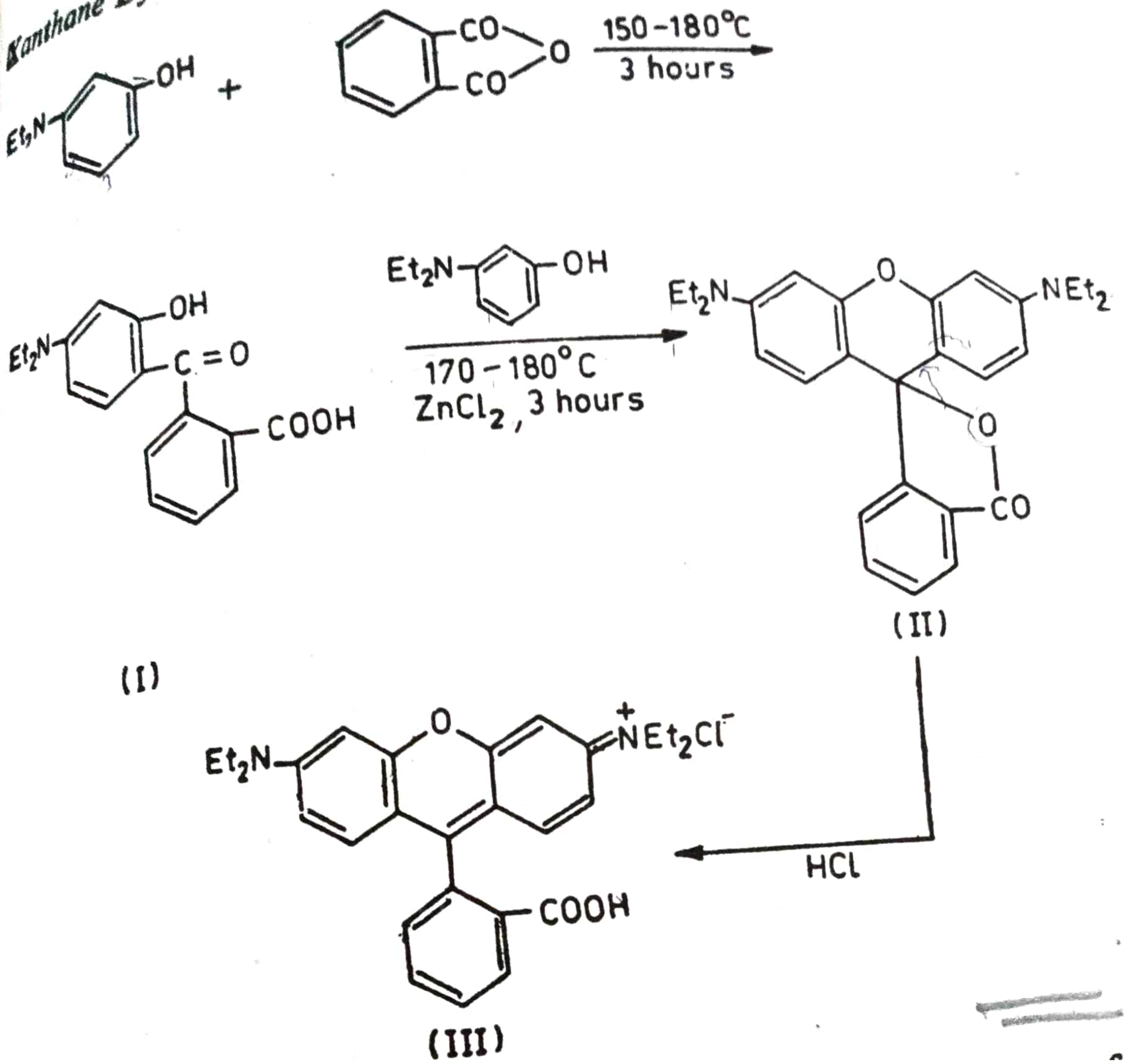
The sodium salt of fluorescein is known as *uranine*. Uranine is used to dye wool and silk yellow from an acid bath ; the colours are fugitive.

Fluorescein is used in tracing underground currents in sea and rivers as well as a marker during accidents.

(*b*) **Eosin.** It is tetrabr...

(*e*) **Rhodamines.** These are basic dyes belonging to xanthene class. Rhodamines range in shades from yellowish red to blue. Two most commonly used basic rhodamines are rhodamine B and rhodamine 6 G.

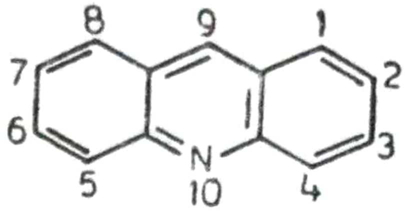
Rhodomine B is obtained by condensing *m*-diethylaminophenol (1 molecule) with phthalic anhydride (1 molecule) at 150—180°C for 3 hours to yield the reaction product (I). Then the reaction product (I) is condensed with another molecule of *m*-diethylaminophenol in the presence of zinc chloride at 170—180°C for 3 hours to yield the dye base (II) which is converted into the dye (III) by treatment with dil. hydrochloric acid.


Et2N
OH
+
CO
O
CO
150–180°C
3 hours
Et2N
OH
C=O
COOH
Et2N
OH
170–180°C
ZnCl2, 3 hours
Et2N
O
NEt2
O
CO
(II)
(I)
Et2N
O
NEt2Cl
COOH
HCl
(III)

Arcridine Dyes

Introduction

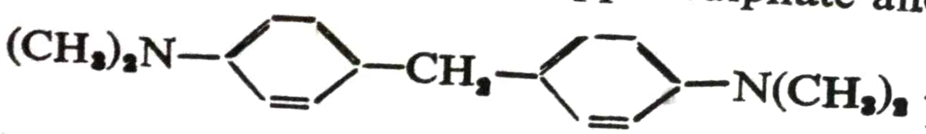
Acridine dyes have basically acridine skeleton. Most of these dyes have amino or substituted amino groups in 3 and 6 positions or only in 6 position.



acridine nucleus

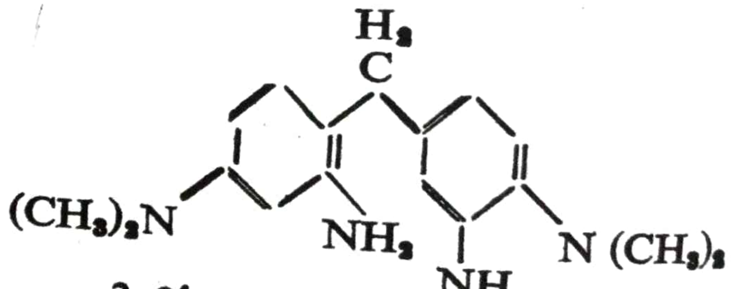
Like xanthene dyes, the acridine dyes can be divided into two subgroups corresponding to diphenylmethane and triphenylmethane derivatives. In the latter case the third phenyl ring is present in 9 position.

Among the acridine dyes, acridine orange NO is important. It is prepared from 4, 4′-bis (dimethylaminophenyl) methane (A) by nitration and subsequent reduction with zinc and hydrochloric acid to yield 2, 2′-(diamino)-4, 4′-bis (dimethylaminophenyl) methane (B) which then gets cyclised. The cyclisation of (B) is done either by heating the reduction mixture to boil and isolating the dye as zinc chloride dauble salt or by heating (B) with aqueous sulphuric acid at 140°C under pressure and salting out the dye by the treatment of common salt in the presence of copper sulphate and air at 80°C.



Nitration → Reduction

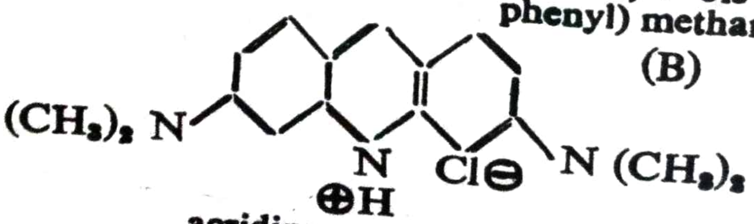
(A)



2, 2′-diamino-4, 4′-bis (dimethylamino phenyl) methane.

(B)

Cyclisation →



acridine orange NO

Acridine orange NO is used to dye silk orange with a green fluorescent. However, it has poor fastness properties. Acridine orange NO is used for leather dyeing and in ink manufacture.

18

Reactive Dyes

Introduction

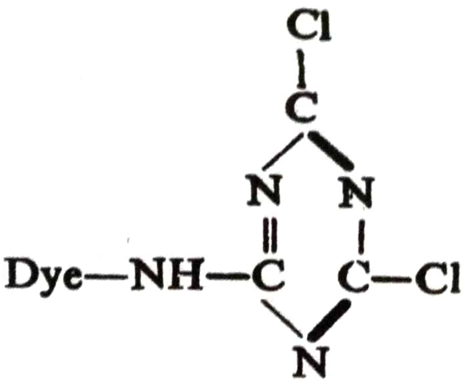
Rys and Zollinger defined a reactive dye as follows :

"It is a coloured compound which has a suitable group capable of forming a covalent bond between a carbon atom of the dye ion or molecule and an oxygen, nitrogen or sulphur atom of a hydroxy, an amido or a mercapto group respectively of the substrate".

This definition excludes mordant dyes and 1 : 1 chromium azo dye complexes which, in dyeing protein fibres, may form covalent bonds between metal ion and nucleophilic groups of the fibre.

The first reactive dye was introduced by I.C.I in 1956.

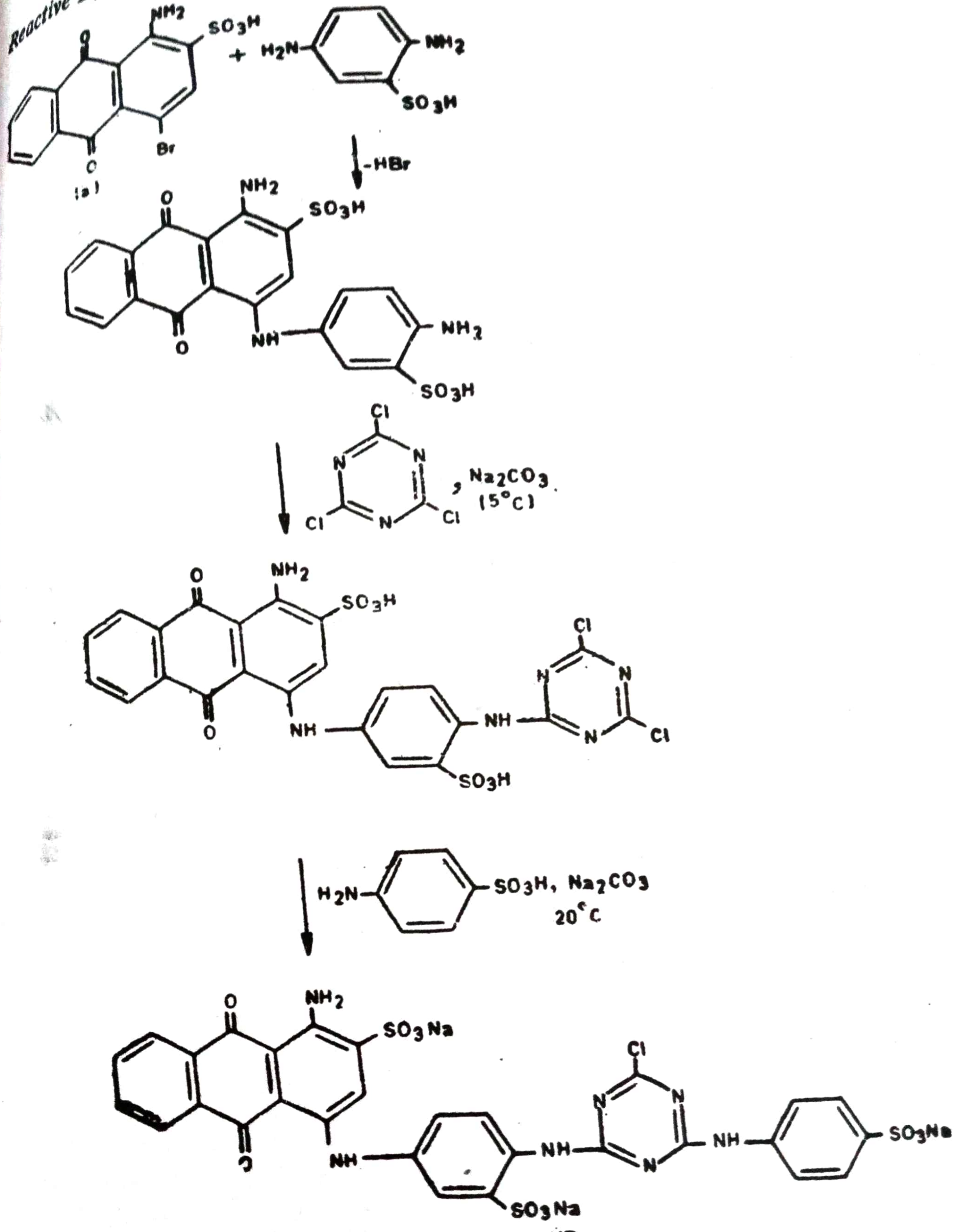
The reactive dyes contain dichlorotriazinyl group. These dyes were made by condensing a dye containing amino group with cyanuric chloride.



cyanuric chloride is cheap and readily available. The reactivity of the chlorine atom in cyanuric chloride is due to the electron withdrawing properties of the nitrogen atoms.

The dyeing with reactive dyes is carried out at 70°-100°C under higher alkaline conditions. These dyes were sold as procion H brand and cibacron reactive dyes.

2. Procion blue HB. It is obtained by condensing 1-amino-4-bromo-3-anthraquinone sulphonic acid (*a*) with 2-sulpho-*p*-phenylene diamine (*b*). The resulting product is next condensed with cyanuric chloride in presence of sodium carbonate at low temperature. It is now condensed with sulphanilic acid and ultimately converted into its sodium or potassium salt.

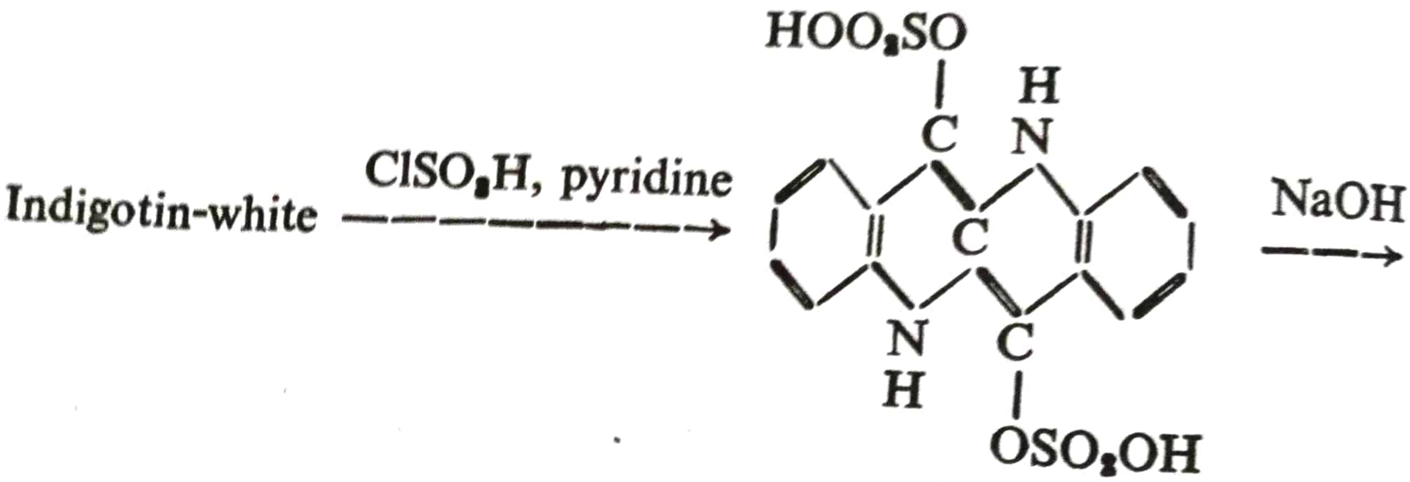


Procion Blue HB

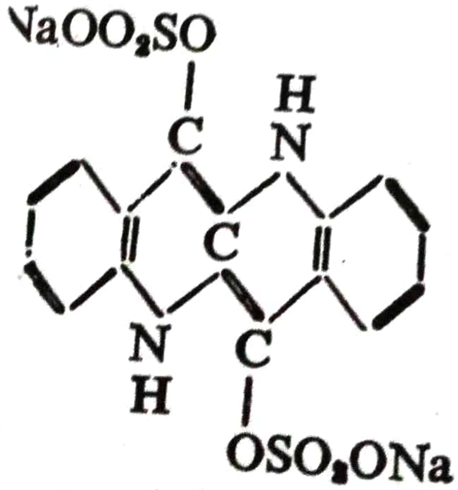
It is used as a reactive dye. It gives a royal-blue shade.

(*b*) **Indigosol O** (*C.I. solubilised blue 1,73002*) Indigotin-white is not stable. Therefore in ordinary dyeing, indigotin-white is first converted to its disulphonic ester (I) by treatment with chloro-sulphonic acid in the presence of pyridine. The alkaline solution of ester (I) is called the indigosol O (II).

When the indigosol O is applied to the fibre and is then subjected to oxidation with sodium nitrite in acid solution, the original blue dye is regenerated.



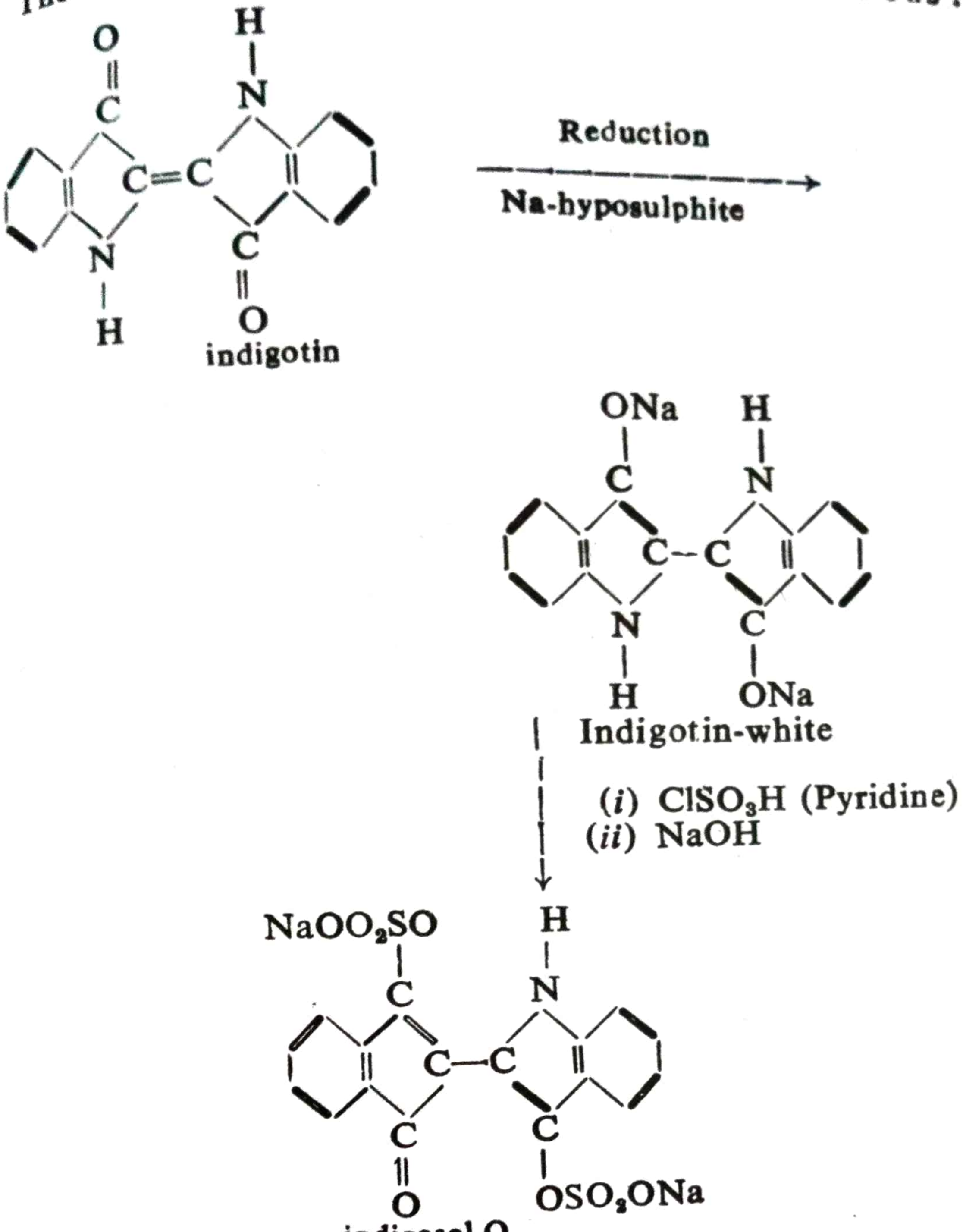
(I)



(II)

indigosol O

The above representation may be represented as follows :

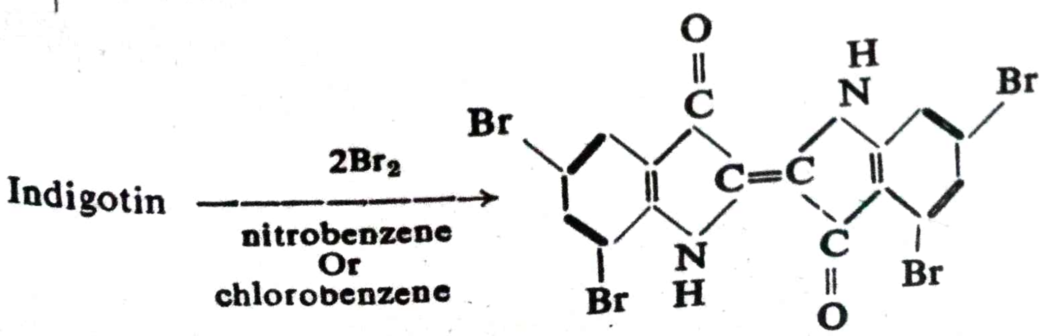


indigotin

Indigotin-white

indigosol O

(c) **Tetrabromoindigo ciba blue 2B** (*C.I. vat blue 5,73065*). It is obtained by bromination of indigotin in nitrobenzene or dichlorobenzene.



between the two prop...

Various Methods of Dyeing. These are as follows:

(a) **Direct dyeing.** The method of dyeing depends on the absorptive power of the fibre, the nature of the dye and the conditions of dyeing. However, it is necessary that the dye applied is fast to light, washing, bleaching and other treatments and possesses an intensity comparable to the standard sample.

As wool and silk are amphoteric proteins, they can be dyed directly either by acidic or basic dyes. However, mordant dyeing is used to get faster and brighter shades. The dye bath is prepared by dissolving the dye in cold water and to this small quantities of sodium sulphate and sulphuric acid or acetic acid are added. The material to be dyed is now introduced into the dyeing bath. Then, the temperature of the bath is gradually raised to about 60°C. At this juncture, exhausting agent like common salt or Glauber's salt is added and the temperature is raised to boiling. The material is rinsed cold and dried after dyeing is complete. The washing fastness is improved by after treatments of the dyed fibre in a separate bath. The various treatments are as follows:

(i) Development with diazonium salts.
(ii) Diazotisation and development,
(iii) Treatment with chromium fluoride or sulphate and sulphate.
(iv) Treatment with formaldehyde, and
(v) Treatment with copper salts.

Treatments (i) and (ii) are quite useful in modifying the shade of the dyed fibre.

The cotton, linen and rayons do not show affinity for many dyes which are used for dyeing wool and silk. However, they can be dyed with substantive dyes by direct dyeing method. The dye is dissolved in hot water. To this dye bath, 5—20% sodium sulphate and 0.5—2% sodium carbonate are added. Now the fibres are introduced in the dyeing bath which is first maintained at 50—60°C and then raised in half an hour to 85—95°C. The dyeing is completed in about 1 hour.

As the synthetic fibres are hydrophobic, they are resistant to the usually cotton dyes. However, they can be best dyed from an aqueous dispersion of a water-insoluble anthraquinone or azo dye in the presence of a dispersing agent such as soap. In this process of dyeing, the dye enters the fibres in the form of a solid solution.

(b) **Vat dyeing.** The ability of a colouring substance to function as a vat dye has been found to depend upon (i) the property of the insoluble dye to form a soluble alkali salt by reducing with alkaline reducing agent such as sodium hydrosulphite and (ii) the affinity of the leuco salt for textile fibres especially the cellulose fibres. If fibre is immersed in the alkaline solution of a reduced dye (called vat) and exposed to atmospheric oxygen or oxidising agent the insoluble dye is regenerated by oxidation which remains fixed to the fibre.

The dye bath for vat dyeing is prepared by adding the dye (in the form of paste with water) and a dispersing agent to water containing caustic soda and hydrosulphite. Vat dyeing is carried out partly by a continuous process in which the cotton cloth is impregnated with vat liquor. Then, it is steamed so that there occurs proper fixation of the leuco compound to the fibric. Further, it is allowed to pass through a bath which contains oxidising agent such as chromate and acetic acid or perchlorate. This generates the colour. Finally, it is soaped, rinsed and dried.

When sulphur dyes are applied by vatting, sodium sulphide is used as a reducing agent. Vatting method cannot be used to dye wool and silk because the alkali used damages the fibre.

The best example of vat dye is Indigo. Its two carbonyl groups are reduced to hydroxyls. The sodium salts of these hydroxyl groups are substantive to cotton. The two of the four carbonyl groups of Indanthrene Blue RNS are reduced to hydroxyl groups.

Vat dyes are quite expensive and must be applied with care. They offer excellent fastness when properly selected. They are the dyes most often used on cotton fabrics.

(c) **Mordant dyeing.** Whenever mordant dyes are applied, a pretreatment of the fibre with a mordant material designed to bind the dye is essential. The mordant becomes attached to the fibre and then combines with the dye to form an insoluble complex called a lake. An example of mordant is aluminium hydroxide which is precipitated in cotton fibre. This mordant binds such dyes as Alizarin by formation of an aluminium lake.

When the mordant dyes are applied to wool, there occurs the combination of a metal with the wool fibre and the lacking of the dye with combined metal gives the fibre very good fastness to washing. The metal used for wool is commonly chromium which can be applied before, during or after dyeing. The colour can be changed using various metals.

The dyeing bath for mordant dyeing is made by adding 2—5% acetic acid (40% solution) and 10% sodium sulphate solution to the dye solution. The temperature of the bath is initially maintained at 50-60%. When the fibre is introduced in the dyeing bath, the temperature of th bath is gradually raised to boil till level dyeing is obtained. The tempera ture is allowed to drop and sodium dichromate, equal to half the weigh of the dye is added. Finally the material is rinsed.

Mordant dyes have declined in importance mainly because equal o superior results can be obtained with other classes of dyes at less expens in time and labour.

(d) **Disperse dyeing.** This method is now used for dyeing polyeste fibres although it was originally developed for cellulose acetate and polyamide fibres.

In disperse dyeing, the dye is pasted to the fibre with water at abou 40°C. Now a suitable dispersing agent and carrier (trichlorobenzene, biphenyl or *o*-phenyl phenol) are added to the dye bath for maintaining a fine dispersion and the dyeing is carried out at 80°C. Alternatively, disperse dyes may be applied by a dry heat (Thermosol) process to polyester fibres. In this case the dye achieves molecular form by sublimation (vaporisation) from the solid dye to the fibre surface. Extremely small particle size is also important for this process.