DYES

Course Presentation

For

B.Sc. Chemistry (H) SEM VI

- **Dyes definition**: Dyes are colored organic compounds that are use to color various substances like fabrics, paper, food, hair and drugs etc.
- With regard to their solubility, organic colorants fall into two classes, *viz*. dyes and pigments. The key distinction is that dyes are soluble in water and/or an organic solvent, while pigments are insoluble in both types of liquid media. Dyes are used to color substrates to which they have affinity. Pigments can be used to color any polymeric substrate but by a mechanism quite different from that of dyes, in that surface only coloration is involved unless the pigment is mixed with the polymer before fiber or molded article formation.
- To be used dye must possess these four properties.

(i) Color

(ii) Solubility in water and/or an organic solvent.

(iii) Ability to be absorbed and retained by fiber (substantivity) or to be chemically combined with it (reactivity).

(iv) Ability to withstand washing, dry cleaning and exposure to light.

➢ Classification of Dyes

1. On the basis of source:

(a) **Natural dyes**: Natural dyes are dyes or colorants derived from plants, invertebrates, or minerals. The majority of natural dyes are vegetable dyes from plant sources—roots, berries, bark, leaves, and wood—and other biological sources such as fungi and lichens.

There are two types of natural dyes. **Additive dyes (non-substantive)** such as madder must use a mordant (a chemical that fixes a dye) to bond with fibers. These are the most common type and have been used for at least 2,000 years. **Substantive dyes** require no pretreatment to the fabric (e.g., indigo, orchil and turmeric) and there are three types: **direct dye** (for cotton, e.g., turmeric, safflower); **acid dye** (for silk and wool, e.g., saffron, lac) or **basic dye** (for silk and wool, e.g., berberine). **Mordants** are chemical compounds that combine with the fiber and the dye forming a chemical bridge between the two. Common mordants are weak organic acids, such as acetic or tannic acid, and metal salts including aluminum ammonium or potassium sulfate, ferrous sulfate, and copper sulfate. Usually, the textile to be dyed is simmered in a mordant solution before dyeing (pre-mordanting). Other options include adding the mordant to the dye bath or treating with another mordant after dyeing to shift the color.

- Natural mordant dyes are either monogenetic or polygenetic; monogenetic dyes produce only one colour irrespective of mordant, whereas polygenetic dyes produce different colours according to the mordant employed (e.g., logwood, alizarin, fustic and cochineal).

- **Disadvantages of Natural Dyes**

  Before the advent of synthetic dyes, natural dyes were widely used, often together with mordants such as alum, to dye natural fibres including wool, linen, cotton and silk, but their use declined after the discovery of synthetic dyes. However, interest in natural dyes has been revived owing to increasing demands on manufacturers to produce more environmentally friendly alternatives to petrochemical-derived dyes. One main issue associated with the use of natural dyes in the coloring of textiles is their poor to moderate light-fastness, and despite their long tradition, not all natural dyes are especially environmentally friendly. Some natural dyes have no or little affinity for the textile materials and they require heavy-metal salts as mordants for fixation and color-fastness. Natural dyes may be sustainable but they need water and land to produce and there is insufficient dye yield per acre of plant material to sustain industrial-scale production.

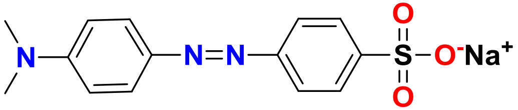
- **Synthetic Dyes:** Synthetic dyes are manufactured from organic molecules. Before synthetic dyes were discovered in 1856, dyestuffs were manufactured from natural products but batches of natural dye were never exactly alike in hue and intensity, whereas synthetic dyestuffs can be manufactured consistently. The use of computers and computer color matching (CCM) produces color that is identical from batch to batch.

- **Discovery of first synthetic dye**

William Henry Perkin, an eighteen-year-old English chemist, was searching for a cure for malaria, a synthetic quinine, and accidentally discovered the first synthetic dye. He found that the oxidation of aniline could color silk. From a coal tar derivative he made a reddish purple dye. The brilliant purple was called mauve. The dye was not stable to sunlight or water and faded easily to the color presently named mauve, a pale purple. This discovery resulted in additional research with coal tar derivatives and other organic compounds and an entire new industry of synthetic dyes was born. In the twenty-first century, synthetic dyes are less expensive, have better colorfastness, and completely dominate the industry as compared with natural dyes. Thousands of distinctly different synthetic dyes are manufactured in the world.

2. **On the basis of chromophore**: Dyes may be classified according to chromophore present in their strcutures.

(a) Azo dyes: Azo dyes are characterised by presence in the molecule of one or more azo groups —N = N—, which form bridges between organic residues, of which at least one is usually an aromatic nucleus. Many methods are available for preparing azo compounds, but manufacture of azo dyes is always based on the coupling of diazonium compounds with phenols, naphthols, arylamines, pyrazolones or other suitable components to give hydroxyazo or aminoazo compounds or their tautomeric equivalents. In the resulting dyes the azo group is the chromophore and the hydroxyl or amino group is an auxochrome. The importance of azo dyes is shown by the fact that they account for over 60% of the total number of dye structures known to be manufactured. A full range of shades is available, but on hydrophilic fibres the blues and greens lack fastness to light unless they are metallised; the metallised derivatives have dull shades. The chemistry of these dyes ranges from simple monoazo compounds to complex polyazo structures with a molecular weight of 1800 or more, and their properties vary accordingly.

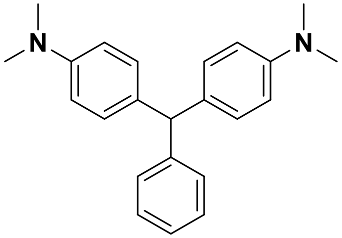


Methyl Orange Dye

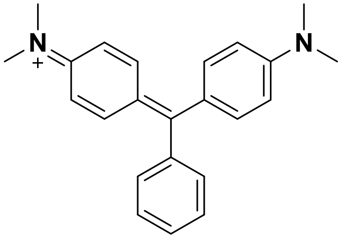
(b) Triphenylmethane Dyes: Synthetic organic dyes having molecular structures based upon that of the hydrocarbon triphenylmethane. They have poor resistance to light and to chemical bleaches and are used chiefly in copying papers, in hectograph and printing inks, and in textile applications for which lightfastness is not an important requirement.

The triphenylmethane derivatives are among the oldest man-made dyes, a practical process for the manufacture of fuchsine having been developed in 1859. Several other members of the class were discovered before their chemical constitutions were fully understood. Crystal violet, the most important of the group, was introduced in 1883.

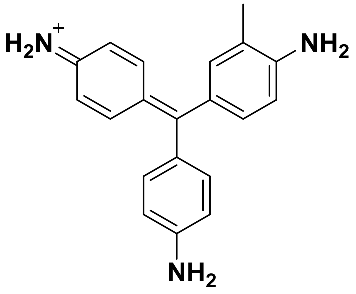
The range of colours is not complete but includes reds, violets, blues, and greens. They are applied by various techniques, but most belong to the basic class, which are adsorbed from solution by silk or wool, but have little affinity for cotton unless it has been treated with a mordant such as tannin.



Leucomalachite Green



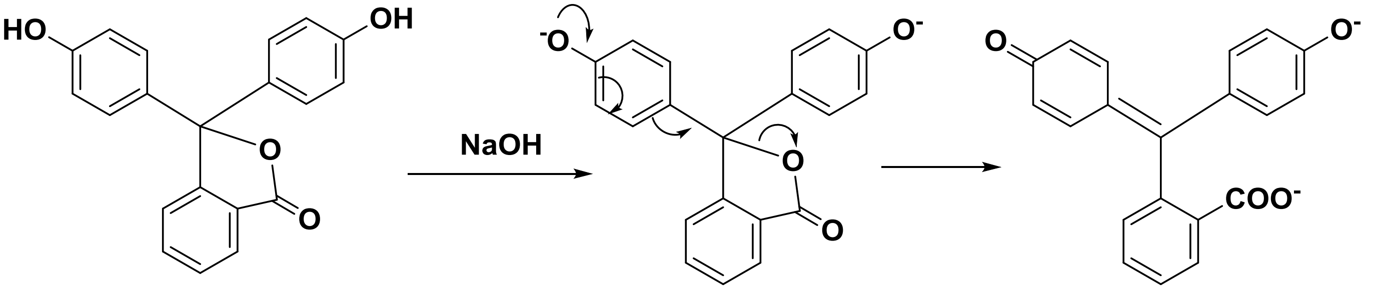
Malachite Green Dye



Rosaniline Dye (Fuchsine Dye)

(c) Phthalein dyes are a class of dyes mainly used as pH indicators, due to their ability to change colors depending on pH. They are formed by the reaction of phthalic anhydride with various phenols. They are a subclass of triarylmethane dyes.

- Common phthalein dyes include:
- *o*-Cresolphthalein
- Dixylenolphthalein
- Guaiacolphthalein
- α-Naphtholphthalein
- Phenolphthalein
- Tetrabromophenolphthalein
- Thymolphthalein
- Xylenolphthalein



Colorless (in acidic medium)

Pink (in basic medium)

Phenolphthalein Dye

c. On the basis of method of application:

Reactive Dyes, Acid Dyes, Premetallized Dyes, Direct Dyes, Azoic (Napthol) Dyes, Disperse Dyes, Vat Dyes, Sulfur Dyes, Basic Dyes.

(i) Reactive dyes are the most recent of dyes. These are the most popular in the world among fibre and fabric artists, used at first only by surface designers, but recently by weavers as well. There are now reactive dyes for a wide range of fibres, e.g. cotton (PROCION), silk and wool (PROCILAN). The dye actually reacts with the fibre molecules to form colour and is, as a result, extremely fast to both light and washing. There are hot and cold water reactive dyes, in fact there is a dye for almost every need. They can be most successfully used for silk painting, with a much better colour fastness than the traditional basic dyes, and are already used by batik artists. we can identify a reactive dye by the alkali used to set off the fixation process, which requires time to take place (silk and wool reactives uses acetic acid). Assistants used are salt, soda ash and resist salt, and sometimes bicarbonate of soda and urea. Reactive dyes are equally suited to screen printing polychromatic printing, fabric painting yarn and piece dyeing.

(ii) Acid Dyes are acidified basic dyes, intended for use on protein fibres but can be used on nylon and acrylics. They have a fair light fastness but poor wash fastness

(iii) Premetallized Dyes are an acid dyes with the addition of one or two molecules of chromium. The dyesgive mutetonings, not unlike those of natural dyes. They are the synthetic dyes mostly used by weavers who dye their own yarns.

(iv) Direct Dyes are **substantive dyes** colour cellulose fibres directly in a hot dyebath without a mordant, to give bright colours. They are not very fast to light or to washing. Direct dyes are generally any dyes which use salt as their only fixative, e.g. Dylon dyes (not to be confused with reactive dyes, which use salt plus other chemicals).

(v) Azoic Dyes are another sort of direct dye, but ones that are extremely fast to washing, bleach and light. They are intended for cellulose fibres and can be used successfully on protein fibres, although the colours are different. These dyes are widely used all over Asia and Australia for batik and direct application. They can be used to give interesting texture colour effects on fabric, thread or paper. Their use for straight silk painting is minimal because of the difficulty in achieving evenness of painted colour.

(vi) Disperse Dyes originally developed for acetate fibres, these are now the major dyes for synthetics. They are not soluble in water, but in the actual fibres themselves. They require a carrier to swell the fibres so that the finely ground particles can penetrate. They are dyed hot, like direct dyes, but do not use salt. Disperse dyes are widely used for heat transfer printing (Polysol). Dye is printed or painted onto paper and heat pressed onto fabric. Prints have excellent light and wash fastness and strong bright colours. Their major disadvantage is that only synthetic fabrics can be used.

(vii) Vat dyes are water insoluble dyes Vat dyes are insoluble in water and have to be dissolved in water by using sodium hydroxide and sodium hydrogen sulphite usually at 50 degrees for 15-20 minutes. Vat dyes are most important dyes for dyeing and printing on cotton and cellulosic fibres They have excellent all round fastness, which includes- washing, light, perspiration, chlorine and rubbing fastnesses. Vat dyes are especially fast to light and washing. Brilliant colors can be obtained in most shades. Originated in medieval Europe, vat dyes were so named because of the vats used in the reduction of indigo plants through fermentation.

(viii) Basic Dyes are very bright, but not very fast to light, washing, perspiration. Fastness is improved if they are given an after-treatment or steaming, e.g. French Silk dyes are basic dyes and should be steamed to fix.

Chemistry of Dyeing

- The process of applying color to fiber stock, yarn or fabric is called dyeing. There may or may not be thorough penetration of the colorant into the fibers or yarns.
- The dyeing of a textile fibre is carried out in a solution, generally aqueous, known as the dye liquor or dye bath.
- For true dyeing to have taken place, coloration of fabric and absorption are important determinants.
- **Coloration**: The coloration must be relatively permanent: that is not readily removed by rinsing in water or by normal washing procedures. Moreover, the dyeing must not fade rapidly on exposure to light.
- **Absorption**: The process of attachment of the dye molecule to the fiber is one of absorption: that is the dye molecules concentrate on the fibre surface. There are four kinds of forces by which dye molecules are bound to the fiber:

1) Ionic forces 2) Hydrogen bonding 3) Vander Wals' forces and 4) Covalent chemical linkages.

- **Exhaustion**: In any dyeing process, whatever the chemical class of dye being used, heat must be supplied to the dye bath; energy is used in transferring dye molecules from the solution to the fiber as well as in swelling the fiber to render it more receptive. The technical term for this process is exhaustion.

Levelness: An Important Quality, evenness of dyeing, known as levelness is an important quality in the dyeing of all forms of natural and synthetic fibers. It may be attained by the control of dyeing conditions.

Conditions to attain Levelness

By agitation to ensure proper contact between dye liquor and substance being dyed and by use of restraining agents to control rate of dyeing or strike. Solvent Dyeing Serious consideration has recently been given to the methods of dyeing in which water as the medium is replaced by solvents such as the chlorinated hydrocarbons used in dry cleaning. The technological advantages in solvent dyeing are:

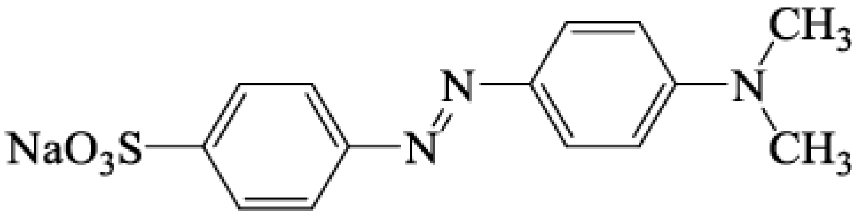
1. Rapid wetting of textiles
2. Less swelling
3. Increased speed of dyeing per given amount of material
4. Savings in energy, as less heat is required to heat or evaporate per-chloro-ethylene. Thus it eliminates the effluent (pollution) problems associated with the conventional methods of dyeing and finishing.

Methyl Orange

Diazo Coupling

A Synthesis of Methyl Orange

In this experiment the azo dye **methyl orange** is prepared by a electrophilic substitution with arenediazonium salts (diazo coupling).



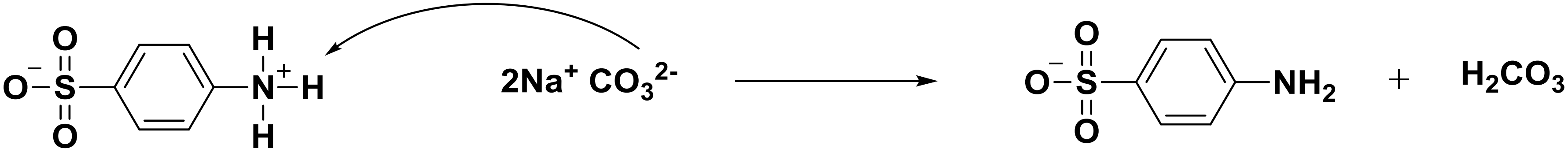
***p*-Dimethylamino-Azobenzenesulfonic Acid (Methyl Orange)**

Methyl orange is a pH indicator and due to its clear color change it is very often used in titrations. Methyl orange changes color at the pH of a mid-strength acid and is usually used in titrations for acids. Unlike a so called universal indicator, methyl orange does not have a full spectrum of color change, but has a sharper end point.

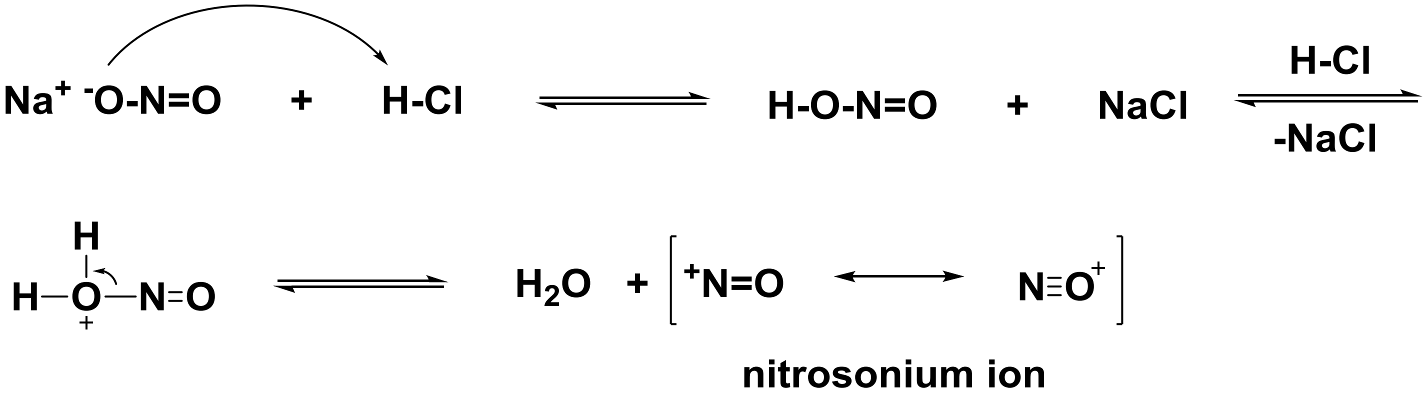
Methyl orange is prepared from sulfanilic acid and *N,N*-dimethylaniline. The first product obtained from the coupling is the bright red acid form of methyl orange, called **helianthin**. In base, helanthin is converted to the orange sodium salt, called methyl orange.

Preparation:

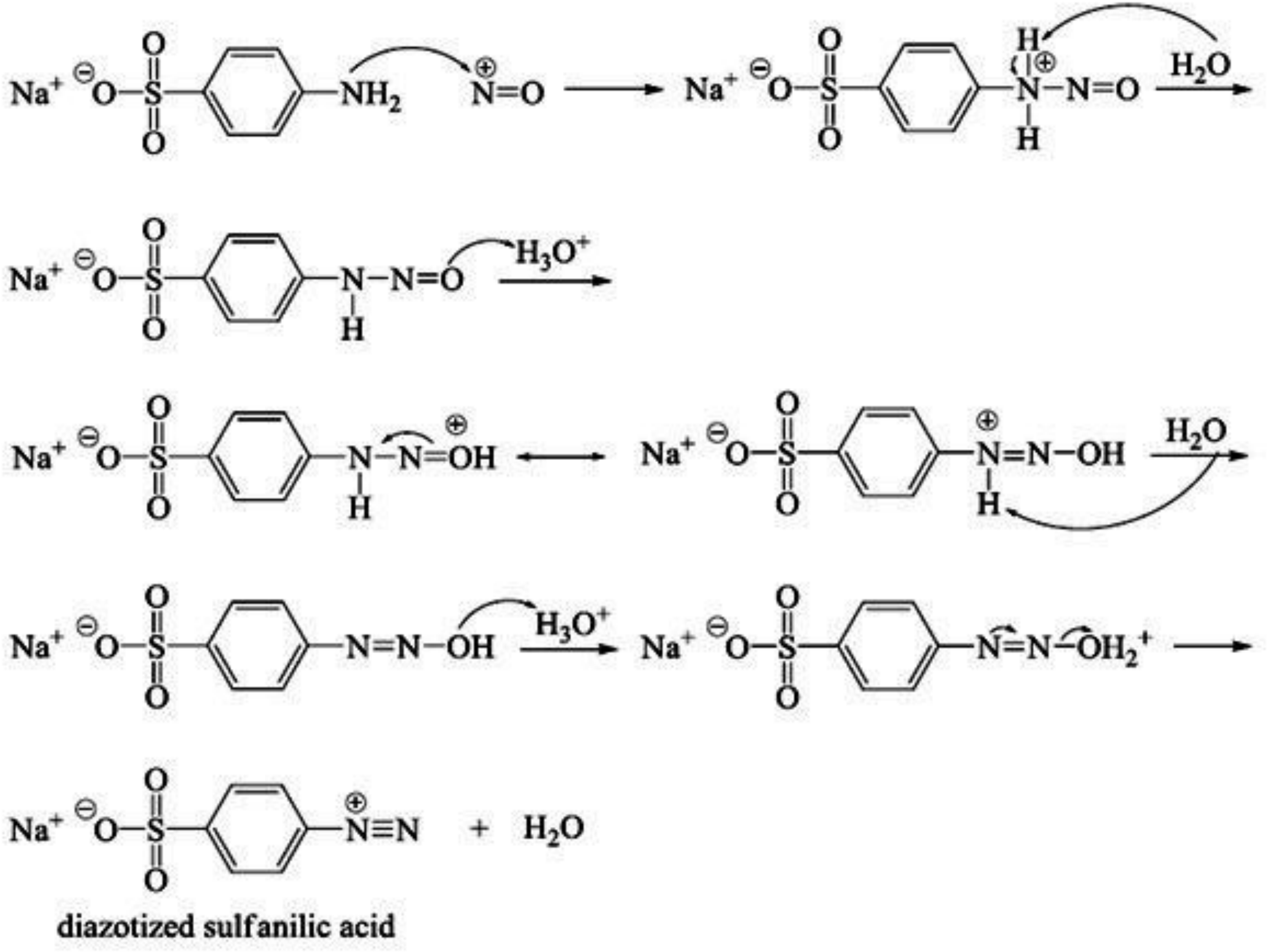
Step-1. The first step is to dissolve sulfanilic acid in basic solution.



Step-2. Formation of Nitrosonium Ion

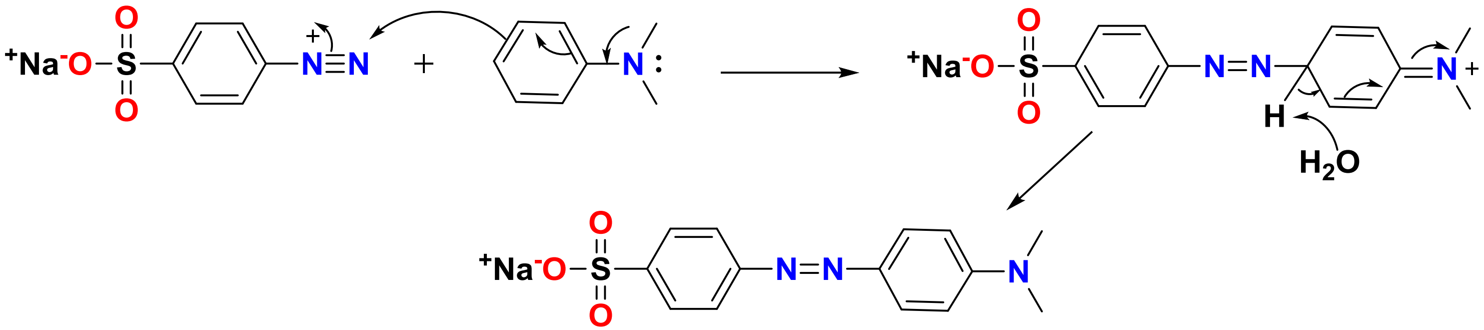


Step-3. Formation of Diazotized Sulphanilic Acid



diazotized sulfanilic acid

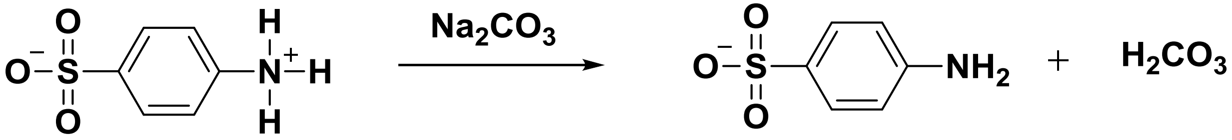
Step-4. Addition to N,N-Dimethylaniline



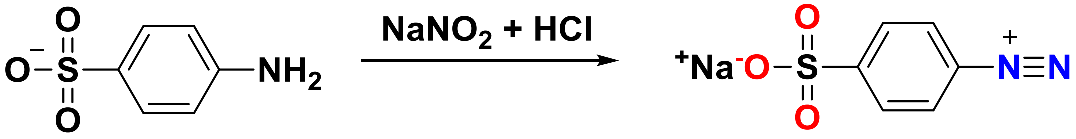
Methyl Orange Dye

Overall preparation of methyl orange

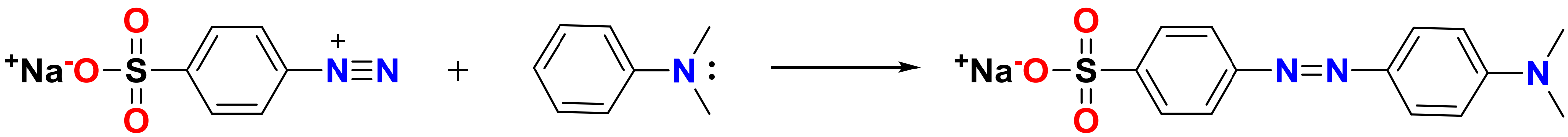
Step-1



Step-2



Step-3



Methyl Orange Dye

Malachite Green Dye

- It is a type of triphenylmethane dyes.
- bright green in color.
- can be applied directly to wool & silk.
- by addition of mordant,can be applied to cotton.

USES:

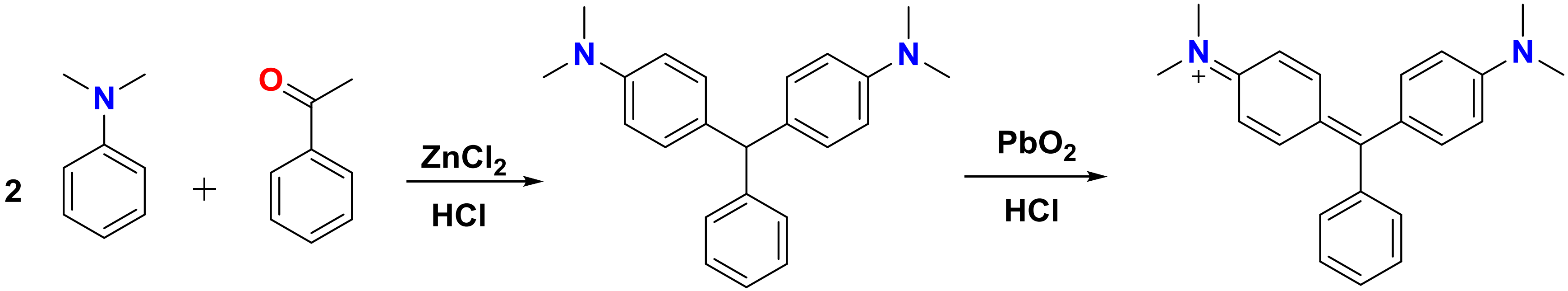
- As spot test reagent for detection of sulphurus acid and cerium.
- As an antiseptic for bacterial infections.

Special Points

- Triphenylmethane is usually colorless: known as leuco base.
- Upon oxidation, leuco base forms carbinol base.
- Reaction with acid, carbinol base forms colored dyes.

leuco base (colorless)→ carbinol base(colorless) → dye(colored)

Preparation



Leucomalachite Green

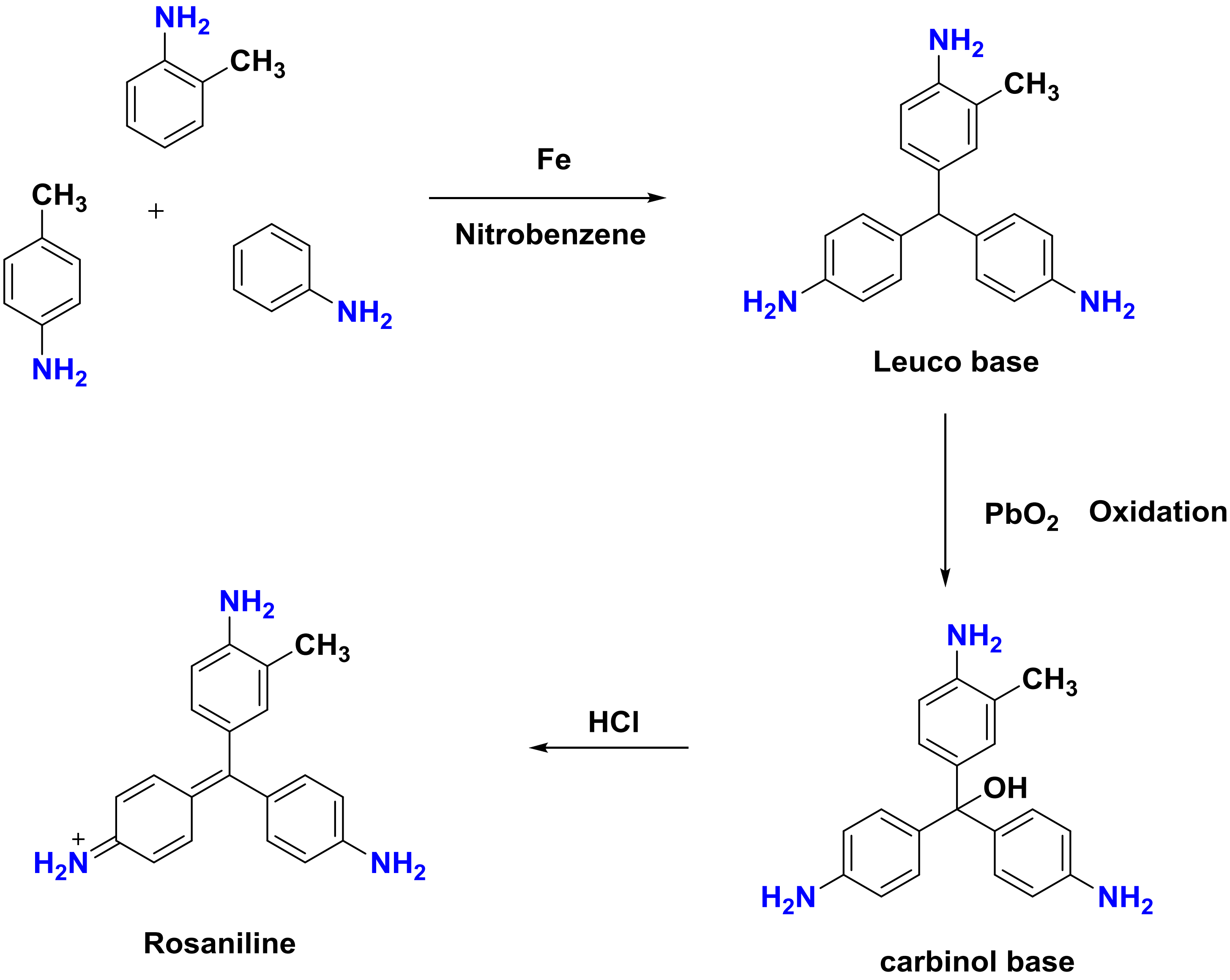
Malachite Green Dye

- During reaction, 2 moles of Dimethylaniline reacts with 1 mole of benzaldehyde yields leucobase form of malachite green. Upon oxidation of this leucobase, carbinol base is formed, whose acidification yields quninoid form of malachite green dye which is colored in nature. Whereas leucobase and carbinol bases are colorless.
- Color of quninoid form is due to conjugation present in it.

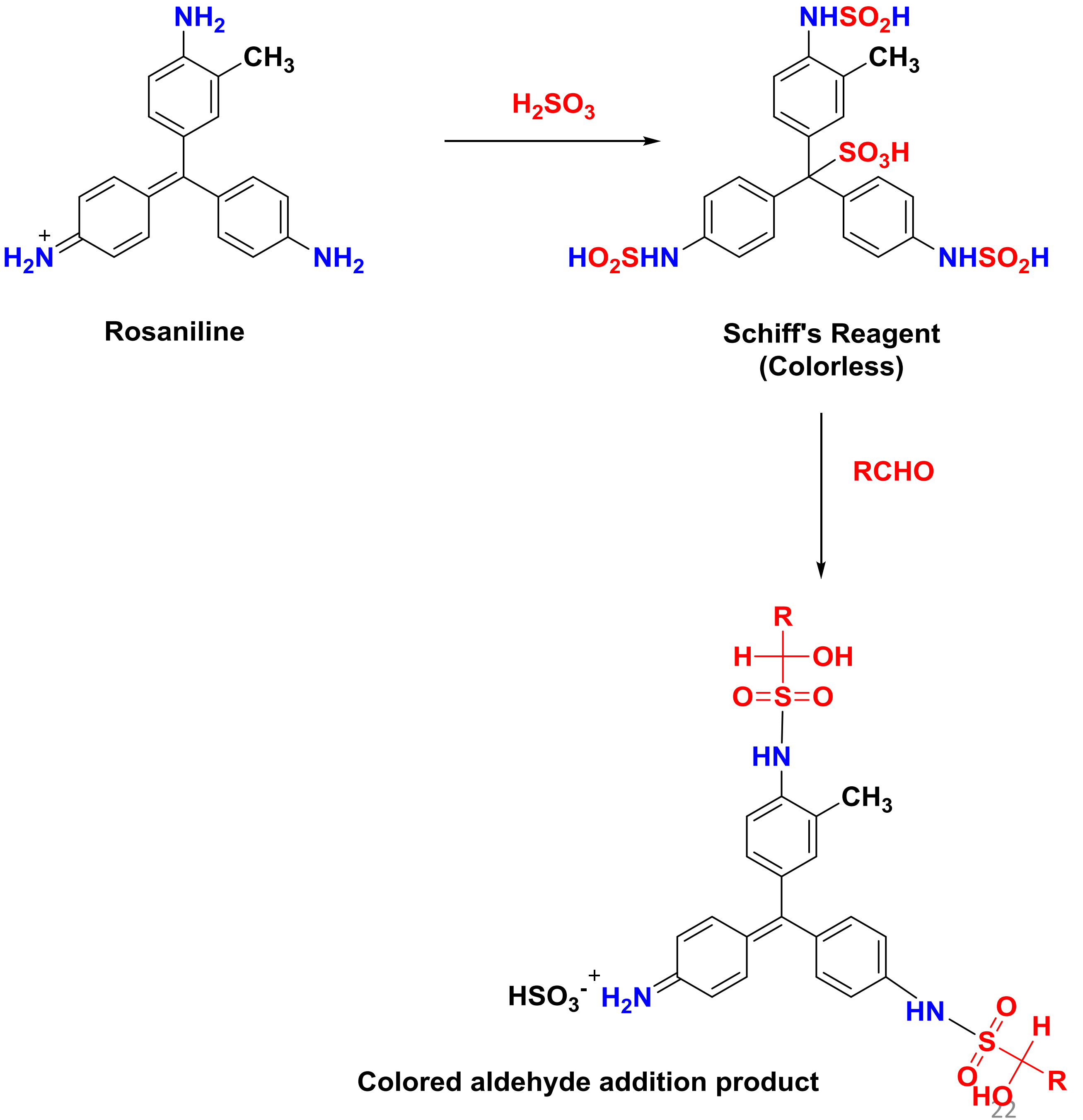
Rosaniline Dye

- A **rosaniline hydrochloride t**hat is the one of the major constituents of Basic fuchsin, together with pararosanilin, magenta II and new fuchsin.
- **Fuchsine** (sometimes spelled **fuchsin**) or **rosaniline hydrochloride** is a magenta dye with chemical formula $C_{20}H_{19}N_3 \cdot HCl$. There are other similar chemical formulations of products sold as fuchsine, and several dozen other synonyms of this molecule.
- It becomes magenta when dissolved in water; as a solid, it forms dark green crystals. As well as dying textiles, fuchsine is used to stain bacteria and sometimes as a disinfectant. It is well established that production of fuchsine results in development of bladder cancers by production workers. Production of magenta is listed as a circumstance known to result in cancer.
- When sulphur dioxide is passed through it we get a colorless solution called **Schiff's Reagent**. Schiff regent is used for testing of presence of aldehydes.
- Rosaniline has green mettalic lustre in solid form and red color in aqueous media.
- It dyes wool, silk and cotton.

Synthesis of Rosaniline



SCHIFF'S TEST



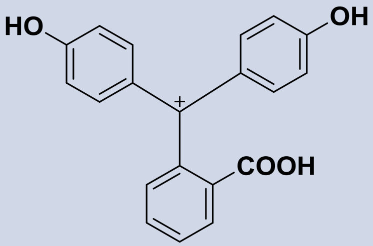
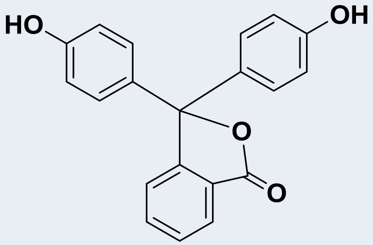
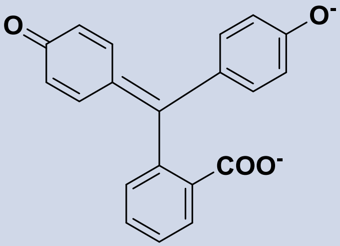
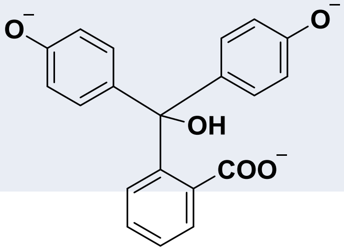
Rosaniline

Schiff's Reagent (Colorless)

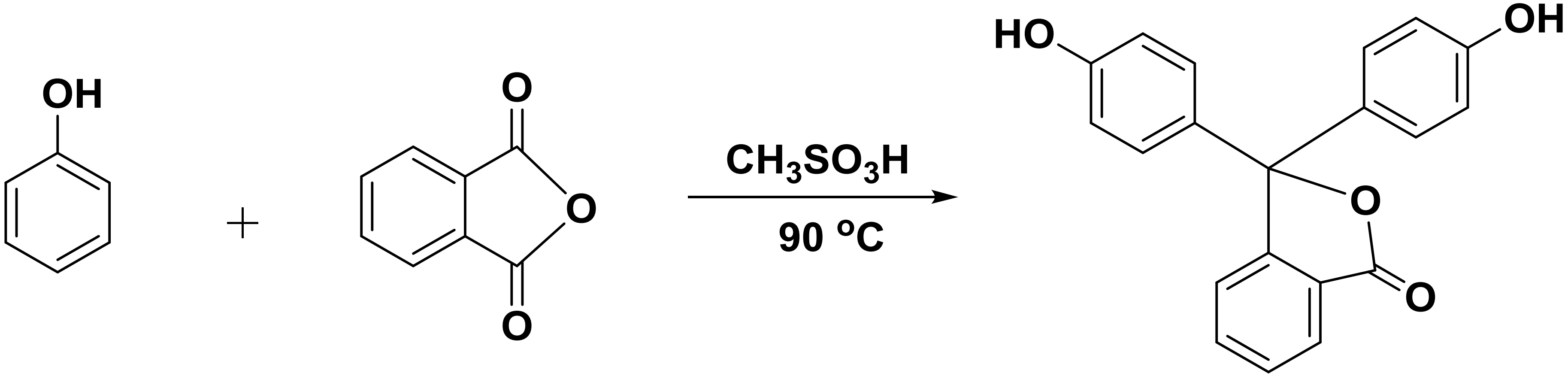
Colored aldehyde addition product

Phenolphthalein Dye

- Phenolphthalein is an organic compound used as a laboratory reagent and pH indicator.
- Phenolphthalein exerts laxative effects by stimulating the intestinal mucosa and constricting smooth muscles. However, phenolphthalein is no longer used as a laxative due to the suspected carcinogenicity of this compound.
- Phenolphthalein is often used as an indicator in acid–base titrations. For this application, it turns colorless in acidic solutions and pink in basic solutions. It belongs to class of dyes known as phthalein dyes.
- Phenolphthalein is slightly soluble in water and usually is dissolved in alcohols for use in experiments.
- Phenolphthalein adopts four different states in aqueous solution: Under very strongly acidic conditions, it exists in protonated form (HIn^+), providing an orange coloration. Between strongly acidic and slightly basic conditions, the lactone form (HIn) is colorless. The doubly deprotonated (In^{2-}) phenolate form (the anion form of phenol) gives the familiar pink color. In strongly basic solutions, phenolphthalein is converted to its $In(OH)^{3-}$ form, and its pink color undergoes a rather slow fading reaction and becomes completely colorless above 13.0 pH.

Phenolphthalein Structure	PH Range	Color
	< 0 Strongly Acidic	Orange
	0-8.2 Acidic or near neutral	Colorless
	8.2-10.0 basic	Pink
	> 10.0 Strongly basic	Colorless

Synthesis of Phenolphthalein

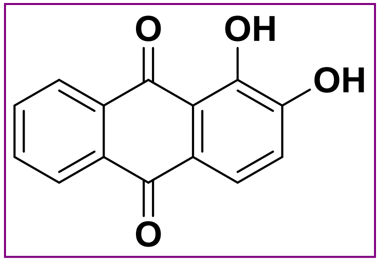


2 mole Phenol

Phthalic Anhydride

Phenolphthalein

Phenolphthalein is synthesized by electrophilic aromatic substitution of phthalic anhydride and 2 equivalents of phenol in the presence of concentrated methanesulfonic acid at 90 °C to yield the product, phenolphthalein.



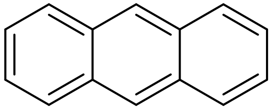
ALIZARIN DYE

The compound **alizarin** comes from the root of the madder plant. It is used as a dye to color fabrics. Alizarin dates back to the tenth century where it was used in Asia Minor. Ancient Egyptians, Romans, and Greeks also used the madder root for it's bright red color. It was used by the British Army to make their "red coats" red during the American Revolution. Alizarin can also be used as a pH indicator. Although it had been extracted from the root of the madder plant for many centuries, chemists Graebe and Liebermann figured out how to make alizarin in a laboratory in 1868. This eliminated the need for the cultivation of the madder root plant, and actually wiped out an entire industry dedicated to growing the plants.

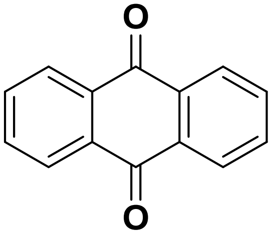
Alizarin is an orangish red powder. It has a melting point of 287 °C and a sublimation point (when a substance turns directly from solid to gas) of 430 °C. It will partially dissolve in water. Alizarin will catch fire in the presence of a flame. Alizarin can be irritating if it is inhaled, gets into eyes, or touches skin.

Structure Elucidation of Alizarin

- Alizarin chemical formula is $C_{14}H_8O_4$.
- From the reactions of the alizarin (conversion to anthracene and anthraquinone)it is clear that it is a derivative of the anthraquinone.



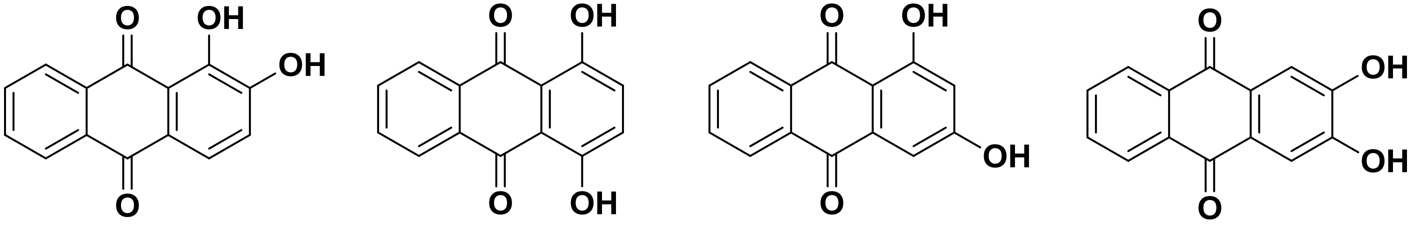
Anthracene



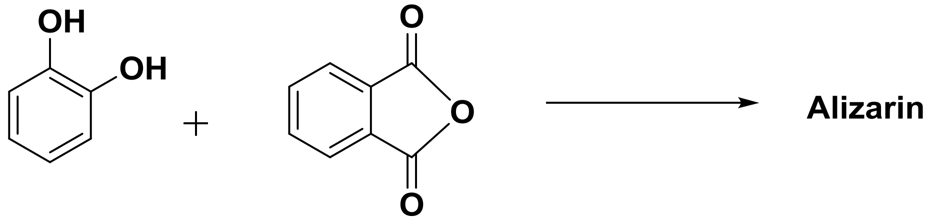
Anthraquinone

- The formation of disodium salt and a diacetyl derivative suggest the presence of the 2 hydroxyl groups in alizarin.
- When it undergoes vigorous oxidation, it gives phthalic acid with no hydroxyl group. This shows that both the hydroxyl groups are present in the same ring.

Four possible structures:



- Alizarin is obtained when catechol is condensed with the phthalic anhydride in the presence of the anhydrous Aluminium chloride or conc sulphuric acid at 140-150 ^{o}C.

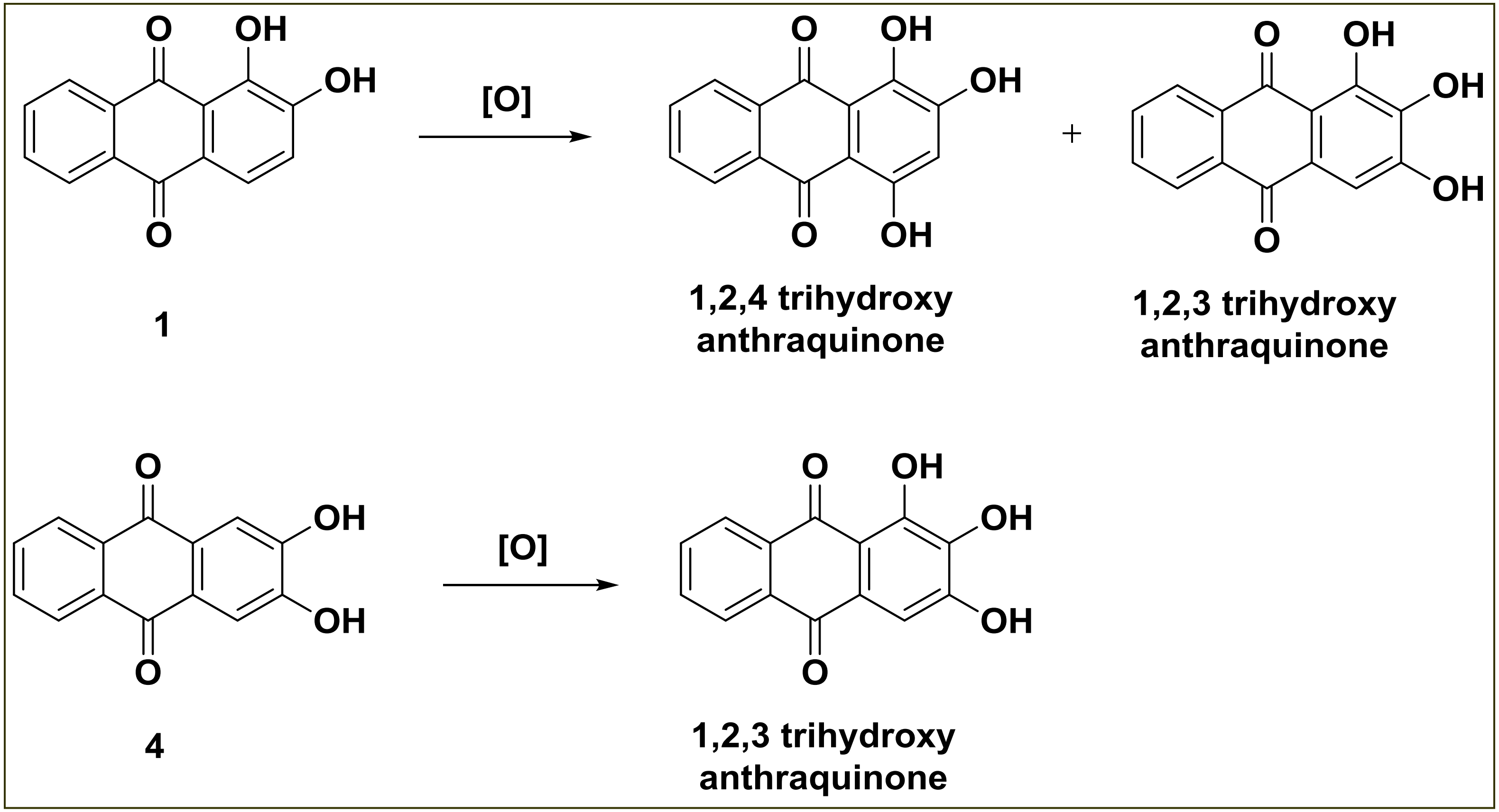


Catechol Phthalic Anhydride

- So this shows that the alizarin should have the 2 hydroxyl groups at the adjacent positions.
- Out of these structures, 2nd & 3rd structures are ruled out. Alizarin is either structure 1 or 4.
- Mild oxidation of alizarin gives **purpurin**, a trihydroxyanthraquinone.
- Structure 1 gives two isomers of trihydroxy anthraquinone where as structure 4 gives one trihydroxy derivative.
- Further purpurin on vigorous oxidation gives phthalic acid. That means the 3 hydroxyl groups are present in the same ring.

- Further purpurin on vigorous oxidation gives phthalic acid. That means the 3 hydroxyl groups are present in the same ring.

- When phthalic anhydride is condensed with hydroquinone and the product is oxidized with the manganese dioxide, we get purpurin. This shows that it is 1,2,4-trihydroxyanthraquinone.



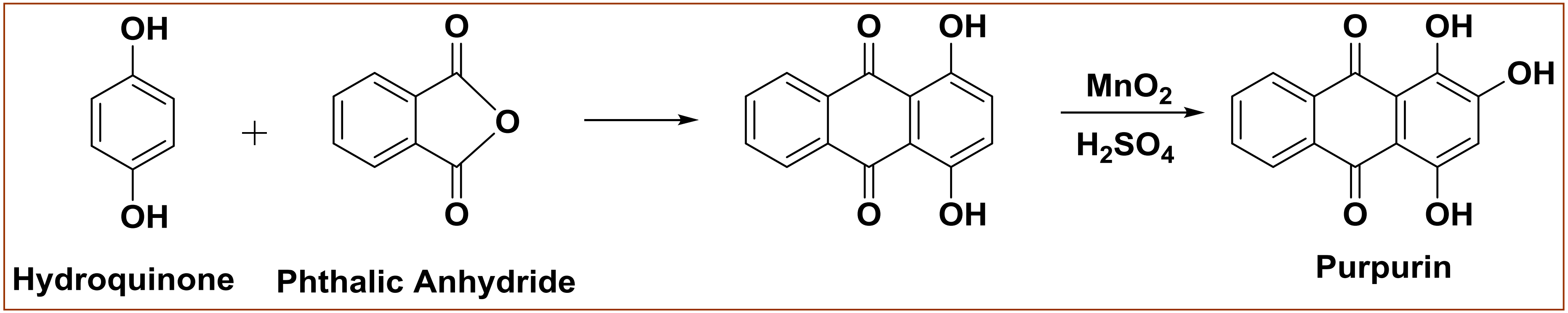
1

1,2,4 trihydroxy anthraquinone

1,2,3 trihydroxy anthraquinone

4

1,2,3 trihydroxy anthraquinone

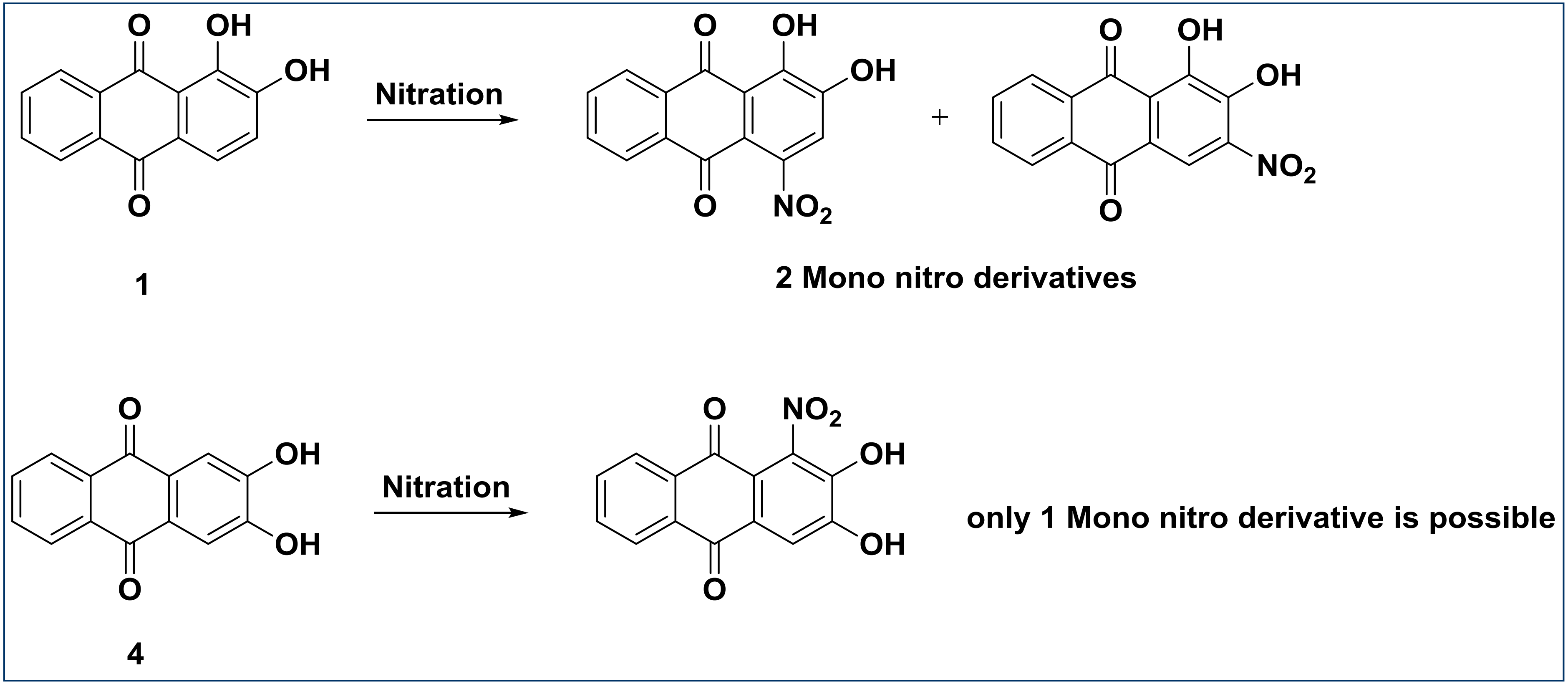


Hydroquinone

Phthalic Anhydride

Purpurin

- Alizarin on nitration gives 2 isomeric mono-nitro derivatives .
- The 2 nitro derivatives are only possible from the 1,2 dihydroxyanthraquinone .



1

2 Mono nitro derivatives

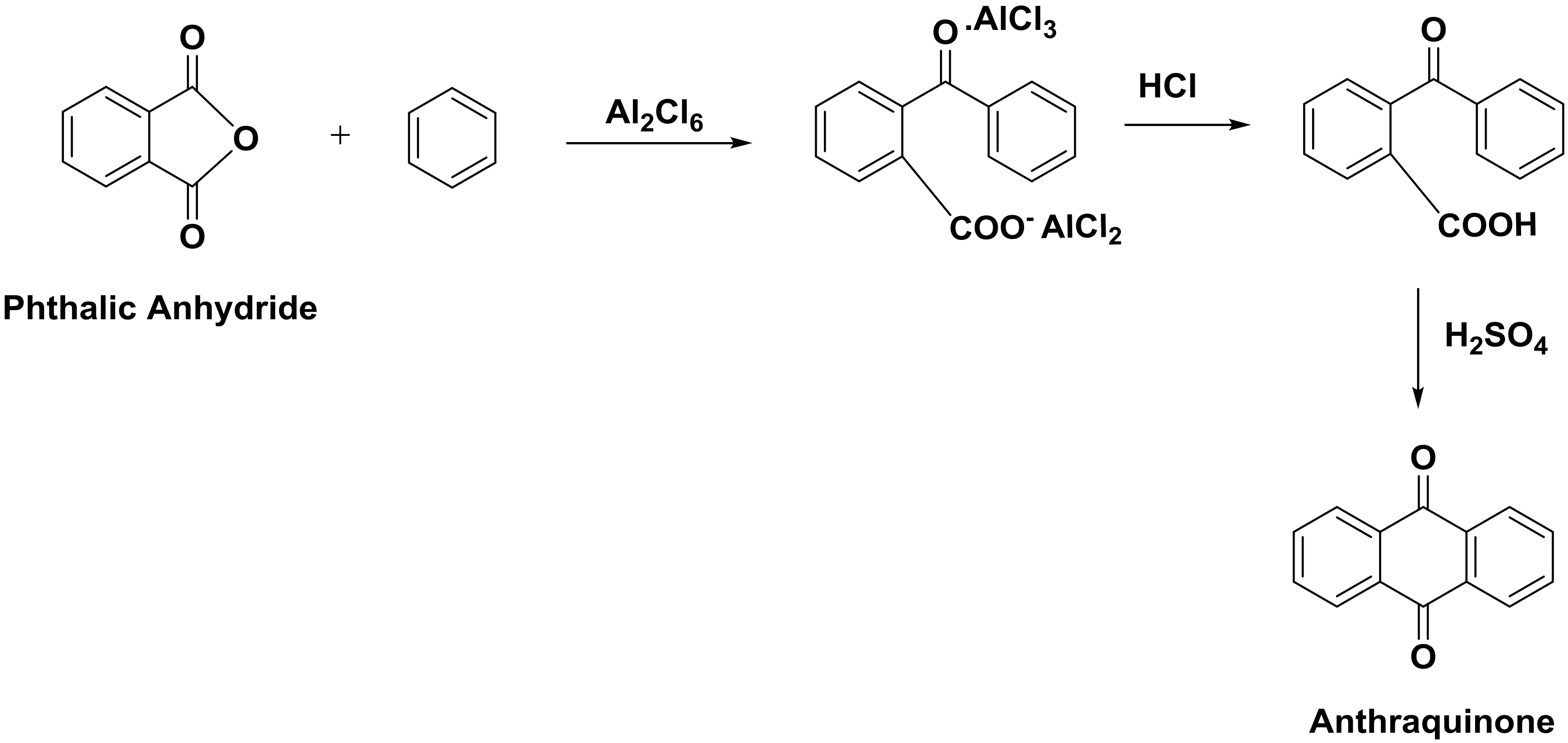
4

only 1 Mono nitro derivative is possible

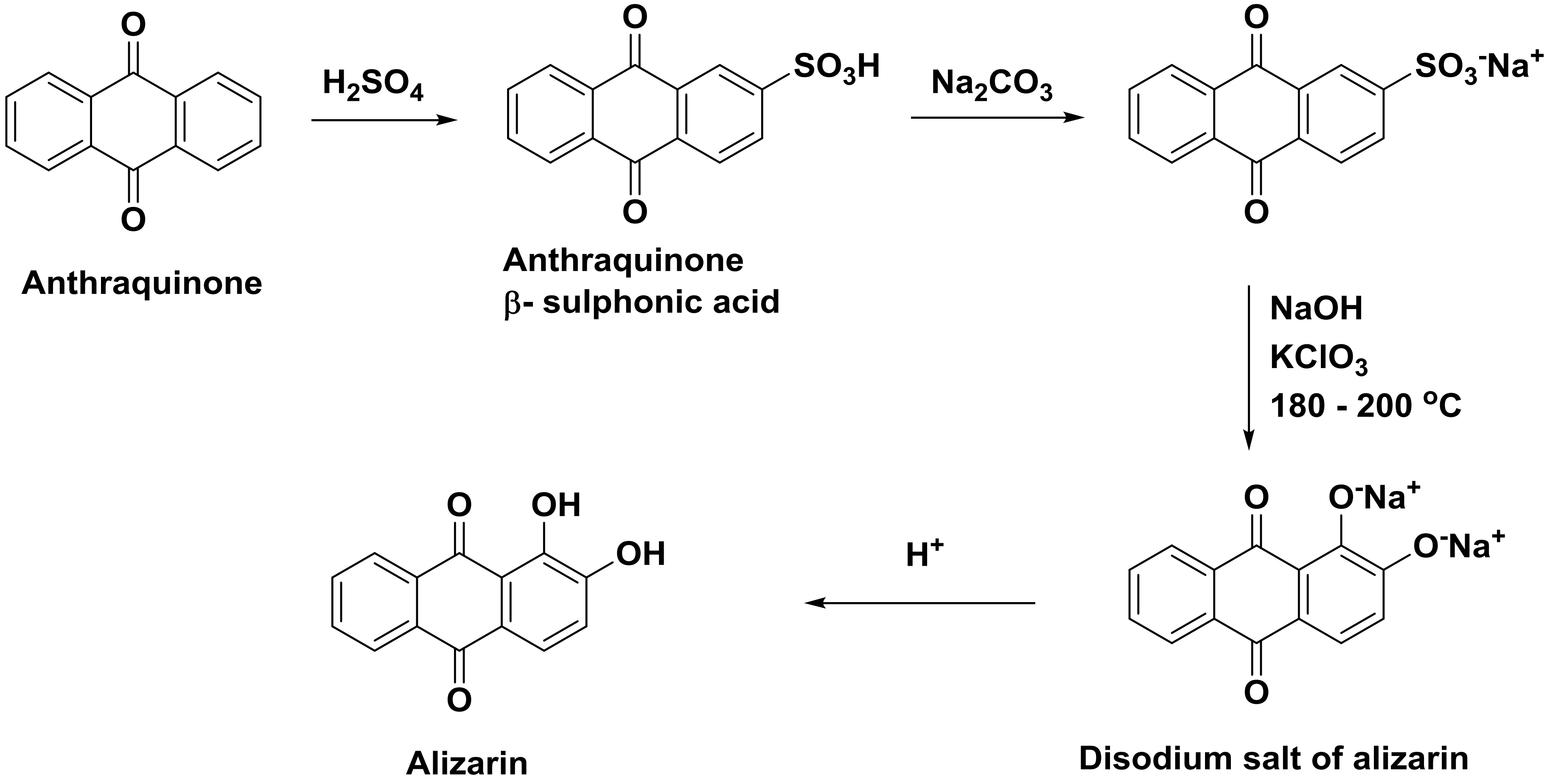
Hence, it follows that the alizarin has the structure 1,2-dihyroxyanthraquinone.

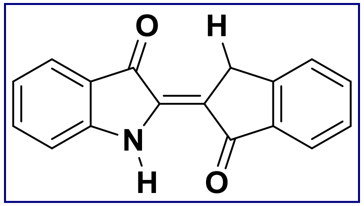
Synthesis of Alizarin

- The starting material for the alizarin is anthraquinone. Anthraquinone can be obtained from Phthalic anhydride.



Anthraquinone to Alizarin



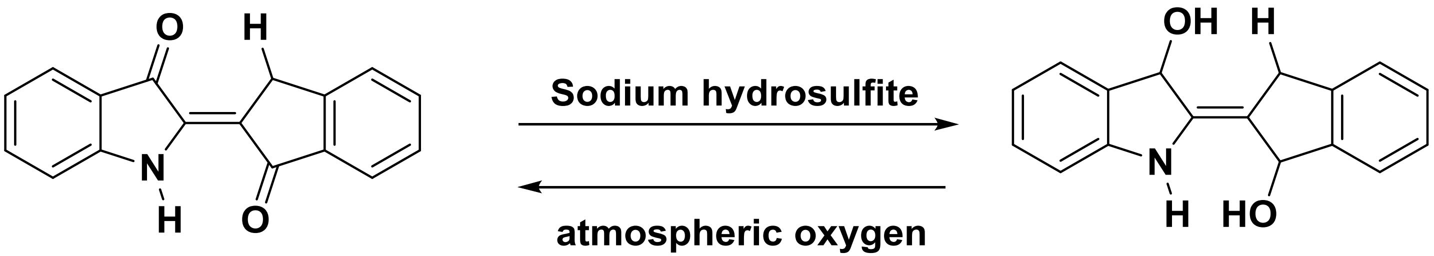


INDIGOTIN DYE

- Indigo is an ancient compound, and has been known and used as a distinctive blue dye since prehistoric times. The earliest users were from India, and the country gained its English name from the ancient Greek word for *indigo*. Historically, indigo played an important role in the economies of many countries because natural blue dyes are rare. Today it will be most familiar to you as the dye used to color blue jeans.

- The chemical in indigo which is responsible for the blue colour is indigotin, which is a dark blue powder at room temperature and is insoluble in water and ethanol. It is most soluble in chloroform, nitrobenzene and sulphuric acid.

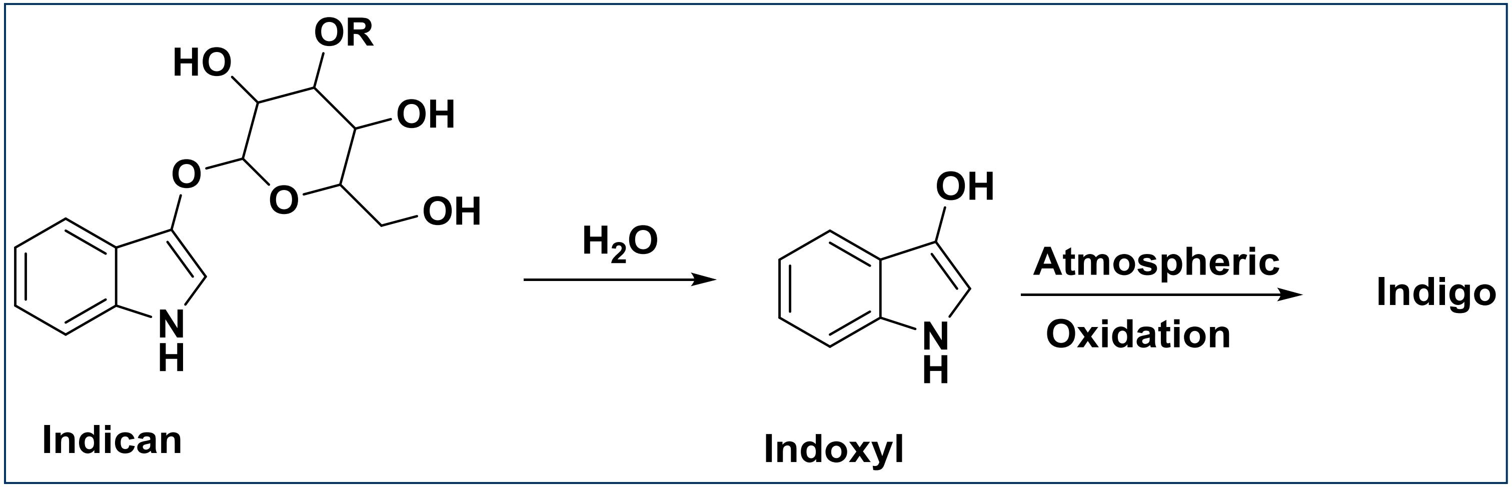
- **Indigotin White**: Indigo in its synthesised or purified form is insoluble in water and other polar solvents. To overcome this problem, the dye is reduced to soluble leucoindigo (known as '**white indigo**'), and applied to clothes in this form. When exposed to atmospheric oxygen it re-oxidises to the insoluble form and regains its colour. Originally this reduction was done with urine, although synthetic urea replaced it in the 19th century and later sodium hydrosulfite was employed as a much more effective reducing agent. Once the problem of applying the dye to the clothing had been overcome the insolubility of the dye is of course beneficial - it will not wash out of the fabric in water.



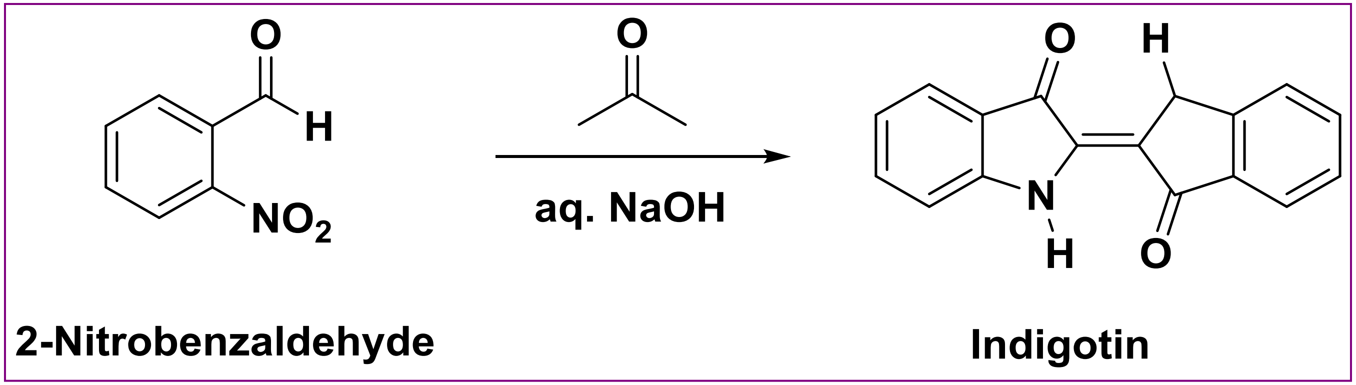
Indigotin
(Insoluble in water)

Leucoindigotin
or
Indigotin White
(Soluble in water)

- **Extraction**: Indigo has been known since ancient times and originally came from a plant extract. Plants of the *Indigofera* genus contain a glycoside called *indican* in their leaves and stems, which is extracted, and acid-hydrolyzed into indoxyl. Mild oxidation in atmospheric oxygen will then produce indigo.



Synthesis: Dissolve 1 g. of o-nitrobenzaldehyde in 3 ml of pure acetone, add about an equal volume of water, which leaves a clear solution, and then, drop by drop, sodium hydroxide solution. Heat is developed and the solution becomes dark brown. After a short time the dye separates in crystalline flakes. Collect the precipitate at the pump after five minutes and wash, first with alcohol then with ether. Indigo so prepared is specially pure and has a beautiful violet lustre.



Structure Elucidation

1. **Empirical and molecular formula**: From the elemental analysis, the empirical formula of indigo is found to be C_8H_5ON. Vapor density determination reveals that its molecular formula is $C_{16}H_{10}O_2N_2$.
2. **Degradation of Indigo**:

(i) Vigorous oxidation of indigo with nitric acid forms two molecules of **Isatin**.

$$\underset{\text{Indigotin}}{C_{16}H_{10}O_2N_2} \xrightarrow{[O]} \underset{\text{Isatin}}{2 \text{ x } C_8H_5O_2N}$$

(ii) On distillation with zinc dust at high temperature, indigo gives a new product known as **Indole**.

Inference: From these two reactions, it follows that there exists a close structural similarity among indigo, isatin and indole. Further indigo and indoxyl are structurally related to each other because indoxyl on oxidation yiels indigo.

3. Structure of Isatin:

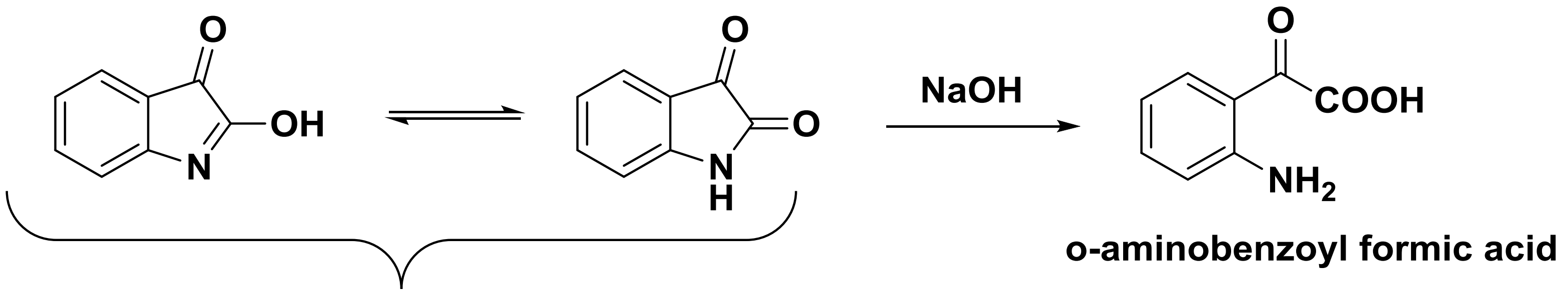
(i) Molecular formula: $C_8H_5O_2N$.

(ii) Action of PCl_5 : Reaction of Isatin with PCl_5 indicates the presence of hydroxyl group in isatin.

$$\underset{\text{Isatin}}{C_8H_5O_2N} \xrightarrow{PCl_5} \underset{\text{Isatin Chloride}}{C_8H_4ONCl}$$

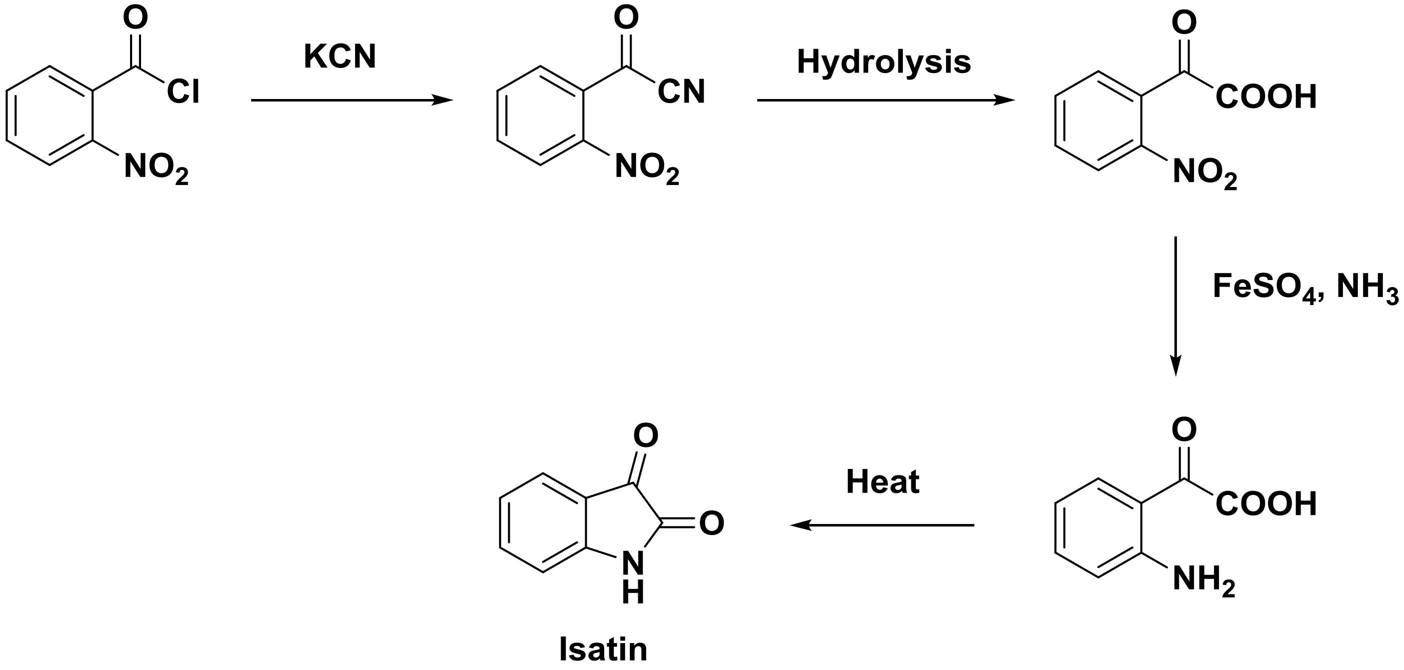
(ii) Action with hydroxylamine: Isatin forms oxime with hydroxylamine which indicates the presence of carbonyl group in isatin.

(iii) Action with Alkali: On boiling with an alkali like NaOH, it forms o-aminobenzoyl formic acid indicating that isatin has structure I. The reaction involved is represented as under:

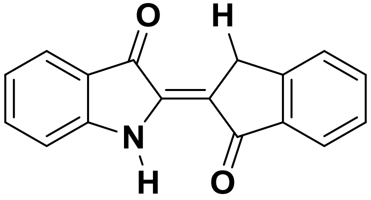


Isatin
(I)

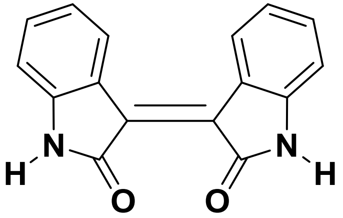
(iv) Synthesis of Isatin: The structure I for isatin has further been confirmed by its synthesis from o-nitrobenzoyl chloride.



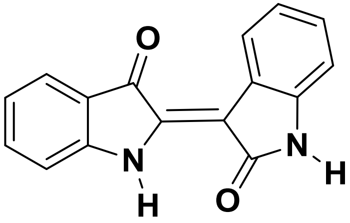
4. Structure of Indigo: On the basis of abose structure of Isatin, Indigo may possess either of the following structure (II, III and IV). All of them when oxidized yield two molecules of Isatin.



II

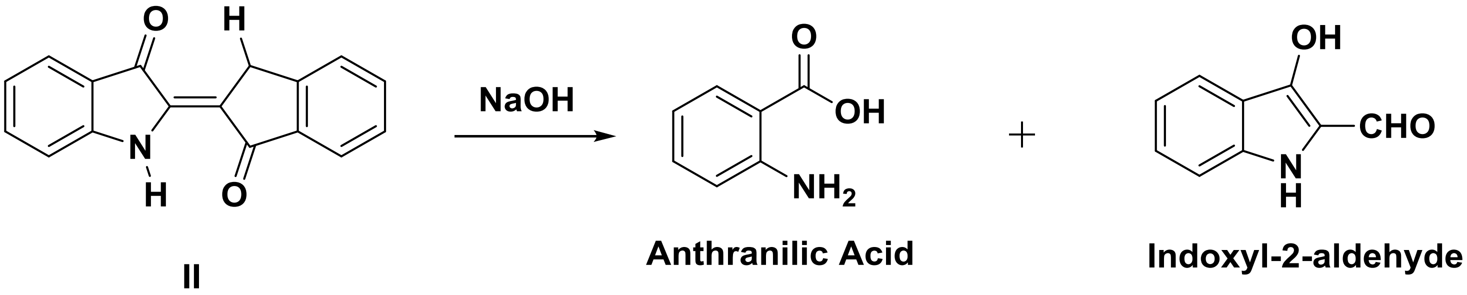


III



IV

Out of these structures, the structure II is found to be correct because indigo when hydrolyzed with dil. NaOH yields anthranilic acid and indoxyl-2-aldehyde.



5. **Synthesis**: The structure of indigo has been further confirmed by the various synthesis of indigo.