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Chemistry of Dyes and Fiber

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المحتوى :-

Dyes

Story of dye

Dyeing of textiles has been practiced for thousands of years . All dyes were natural substances obtained from plant, animal or mineral sources.

William Henry Perkin, while searching for a ، In 1856 cure for malaria, discovered the first synthetic dye, Mauve.

The mauve dye was a brilliant fuchsia color, but faded easily. Since that time, a great number of synthetic dyes have been manufactured.

Almost all garments purchased today are dyes with synthetic dyes

Definition of dyes

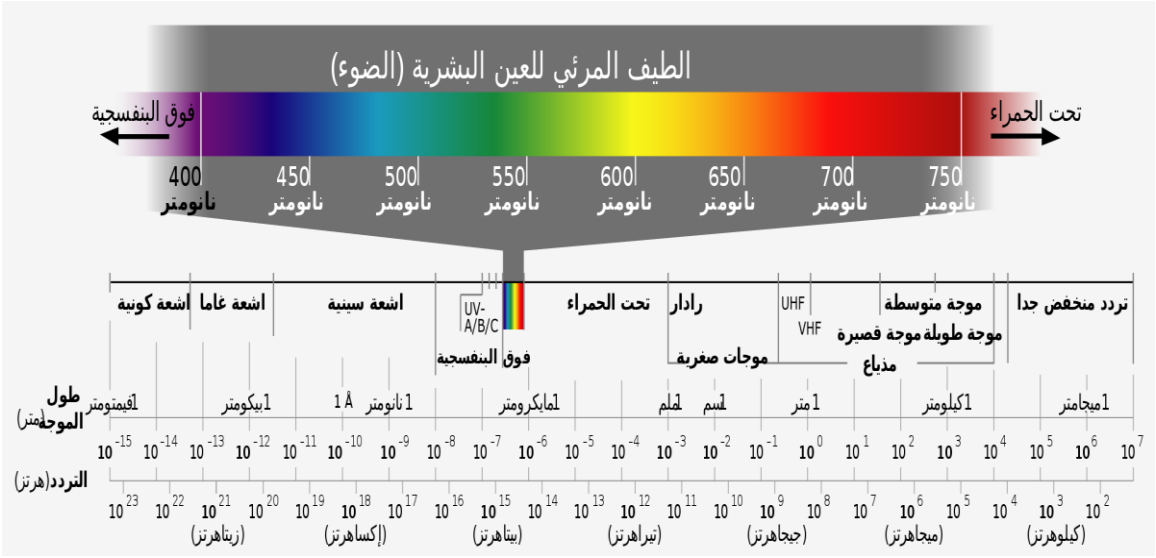
A dye is a colored substance that has an ability to dye another material

Interpretation of color ?

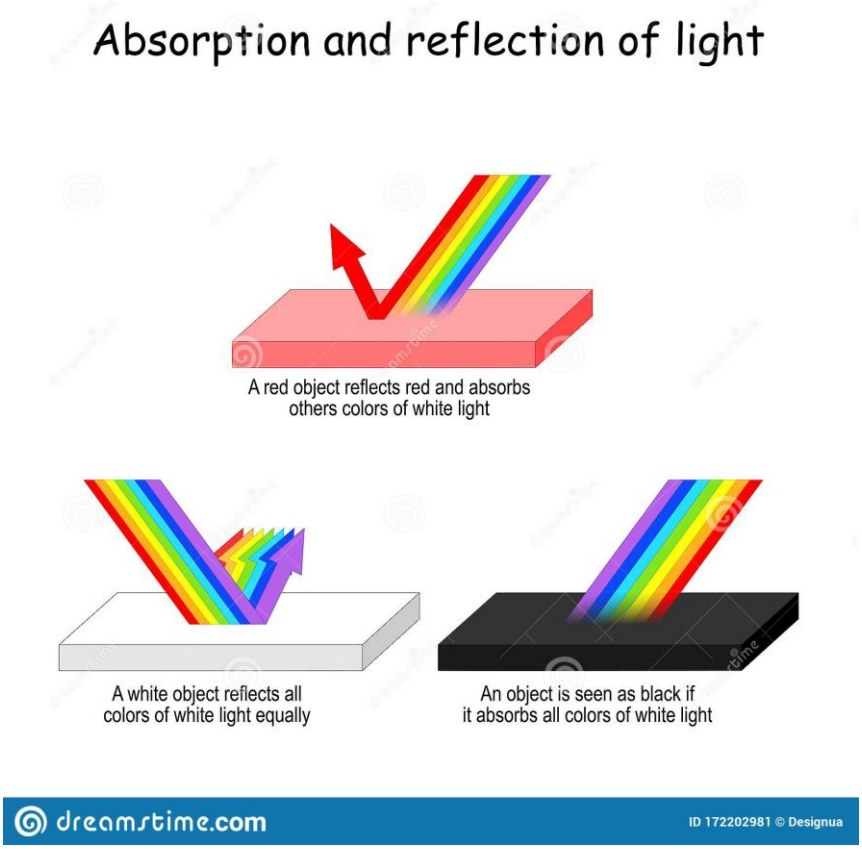
- **The color of the material depends on the material's ability to absorb part of the visible spectrum**

(400-750 nm) and can reach to 800 nm (angstrom= 0.1 nm)

The spectra are mainly classified into main three region as shown



- **When light fall on substance, part is absorbed and other reflected, and we see the reflected part**
- **Black substance absorb all light**
- **White substance reflect all the incident light**



The absorption of radiation by molecules

- **According to quantum theory $\Delta E = h\upsilon = hc/\lambda$**
- **For any substance to be colored its molecules must contains mobile electrons (present in chrmophores) which can raised from ground state to excited state at values of ΔE**

***At higher ΔE, so higher υ and hence shorter λ (blue shift)**

***At lower ΔE, so lower υ and hence longer λ (red shift)**

Approximately wavelength	Color of absorbed light	Color of reflected light
400-435	violet	Green-yellow
435-480	Blue	Yellow
500-560	green	Red
595-605	orange	Green blue
605-750	Red	Blue green

<u>General characters of the dye molecule</u>:

Substance to be used as a dye it must have the following characters

1-It must have a suitable color.

2-It must be fixed to the fabric by itself or by anther agent

3-Dye must have fastness properties to light, washing acids, alkalis, and perspiration, rubbing.

So this lead to know the different between dyes

and pigment

Key Difference Between Pigments & Dyes

Category of difference	Dyes	Pigments
Solubility	Soluble	Insoluble
Lightfastness	Vulnerable to fading	Resistant against fading
Bonding	Functional groups bond between dye and substrate	Functional groups do not bond; typically requires a binder
Structure during application	Structure alters	Retains particulate form
Combustion properties	Often combustible	Relatively less combustible
Chemical properties	Typically organic	Typically (but not always) inorganic
Longevity	Shorter	Longer

Relation between color and chemical constitution:

The organic compound to be colored it must have

a) Chromophores.

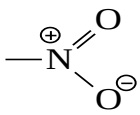
b) Auxochromes.

c) Quinoid structure.

A) Chromophores:

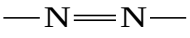
- Chromophores are these groups with multiple bonds

examples of chromophores



nitro

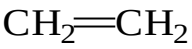
nitroso



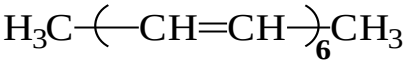
azo

***The compound contain the chromophores is called chromogen.**

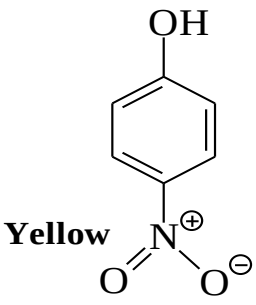
***Single conjugated is not sufficient to produce color but a number of conjugated must be attached with chromophores to produce color and as number of conjugated increase the degree of color increase.**

e.g. 

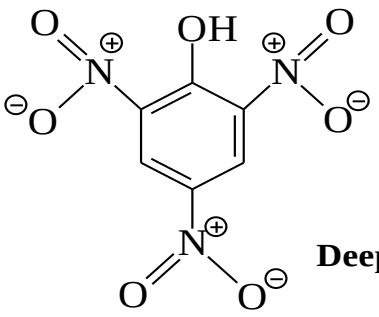
Colourless



Yellow



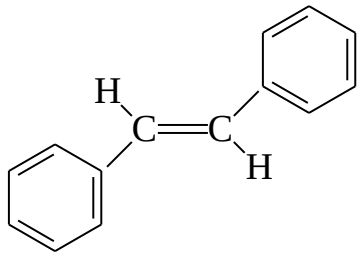
Yellow



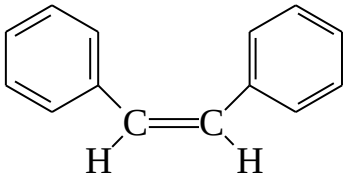
Deep Yellow

The position of groups in space can affect on color

e.g. stillbene



Trans
(Coloured)



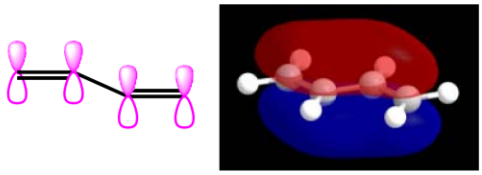
Cis
(Colourless)

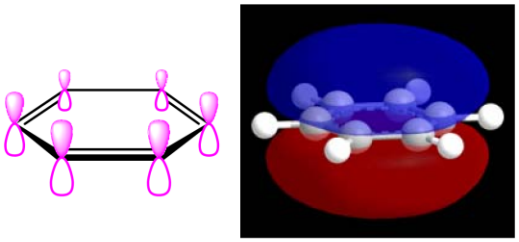
- In case of trans (colored) the molecule is planner so conjugation involves two benzene rings and one double bond.

-In case of cis (colorless) the molecule not planner due to sterice hindrance of two benzene rings so conjugation is extended only on one benzene ring and double bond.

1. Molecular Orbital Theory and Absorption

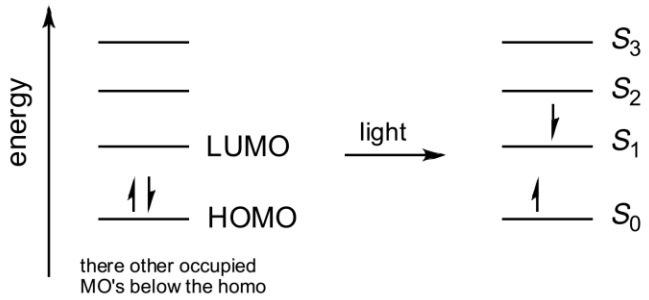
- The *p* orbitals of conjugated π bonds and aromatic compounds interact together to form a large orbital known as a *molecular orbital* (MO).



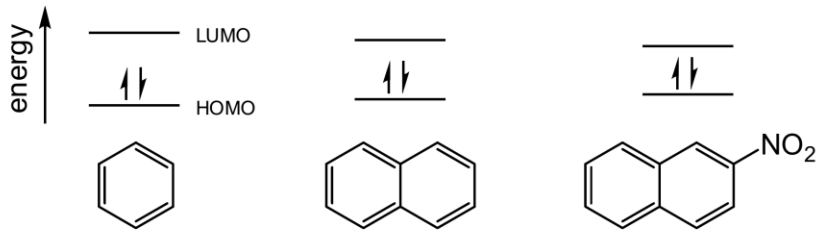


- π bonds are higher in energy than σ bonds. The MO derived from the π bonds is the one highest in energy that contains electrons, and it is termed the *highest occupied molecular orbital*, or HOMO. (MO theory is actually much more complicated!)
- MO's that are even higher in energy exist, but they are empty. The empty MO that is lowest in energy is the *lowest unoccupied molecular orbital*, or LUMO.

- Light absorption causes the excitation of an electron from the HOMO to the LUMO.
- The e^- have opposite spins and are said to be in a *singlet state*. The HOMO and LUMO are S_0 (ground state) and S_1 (lowest excited state), respectively.



- The HOMO/LUMO gap narrows when there is extended conjugation and when polar groups are also present. A smaller gap corresponds to a lower difference in energy, which results in the absorption of longer-wavelength light. (Particle-in-a-box theory).



B) Auxochromes:

-Auxochromes e.g. NH_2 the presence of these groups only in substance does not cause the appearance of color, but these groups work only beside chromophores.

-Auxochromes divied into two group

Acid group	**OH**	**SO3H**	**COOH**
Basic group	**NH2**	**NHR**	**NR2**

-Auxochromes are known as bathochromic groups, which makes shift from violet to red *(red shift)*.

-Groups which decrease the depth of color are known as hypochomic groups e.g $NHCOCH_3$ such groups shift the color from red to violet *(blue shift)*.

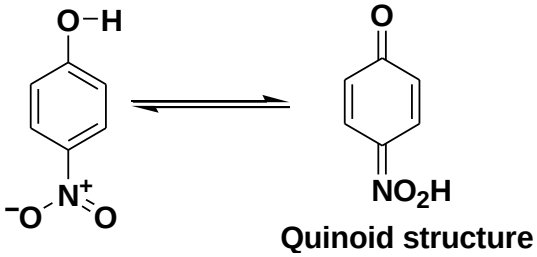
-Presence of auxochromes with chromogen make chromogen dye because it:

1- **Deepen the color.**

2- **Fix the dye with fabric by formation of salts.**

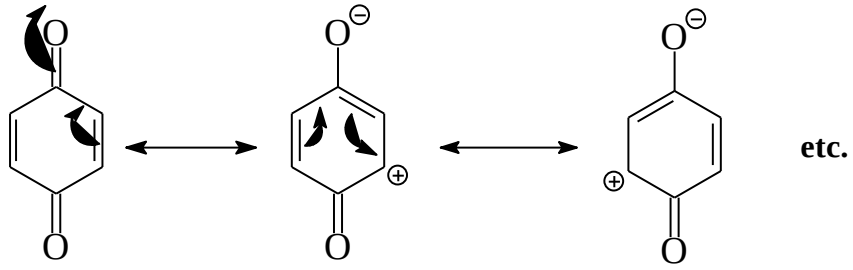
C) Quinonoid structure:

-Presence of quinoid structure is essential for the production of color in compound containing benzene ring.



Quinoid structure

-The color of quinoid structure can be explained via resonance.



Classification of dyes according to application:

Dye class	Description	Fiber application
1- Acidic (anionic)	Contain SO_3Na or-COONa	Wool, silk
2- Basic(cationic)	Contain NR_2, NHR, NH_2, as salt	Cotton, silk
3- Direct dye	Water soluble dye of azoic dye contain -COONa or SO_3Na	Vegetable fiber
4- Mordant	Has no affinity to fiber so must be pretreated with metal oxide	Vegetable and protein fiber
5- Azoic dye	Contain N=N, water insoluble pigments formed	Cotton

	within the fiber	
6- Vat dye	**applied in reduced (leuco) form (soluble) and oxidized on fiber (insoluble)**	**Cotton**
7- Reactive dye	**Forms covalent bond with fiber**	**Cotton, wool**
8- sulphur e.g thioindigo	**Contain S, applied in reduced form and oxidized on fiber**	**Cotton**

-<u>Chemical classification of dyes:</u>

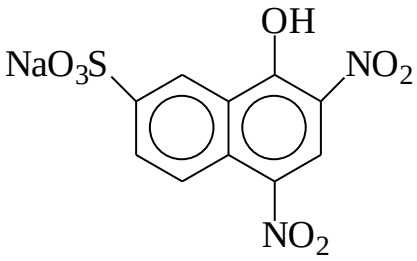
-It is classified according to the groups present or main nucleus

Examples: Nitro dyes - Nitroso dyes - Azo dyes - triphenyl methane dyes,

<u>1) Nitro dyes:</u>

Dyes contain -NO_2 as chromophore and OH as auxochrome e.g.

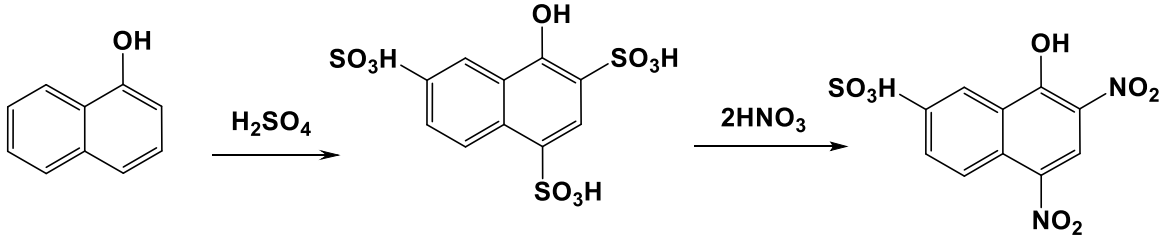
Used in dyeing wool and cotton.



Naphthol Yellow S

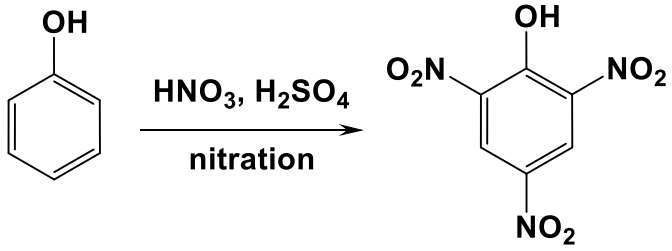
2,4-dinitro Naphthol-7-sulphonic acid sod. s

Preparation:



2-picric acid dye:-

This type of can be used for dyeing silk and wool with yellow color.

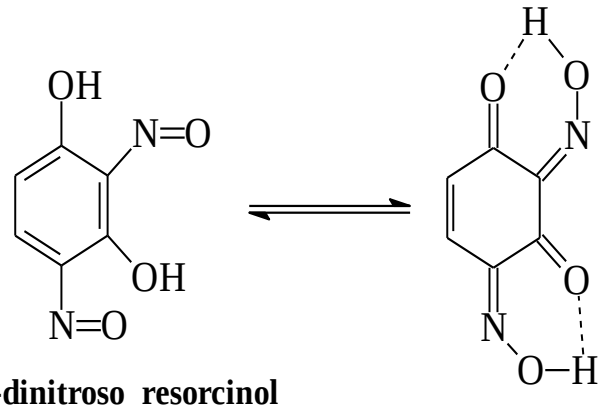


2) Nitroso dyes:

Dyes contain N=O as chromophore and OH as auxochrome e.g. R green O.

a-Resorcine green :-

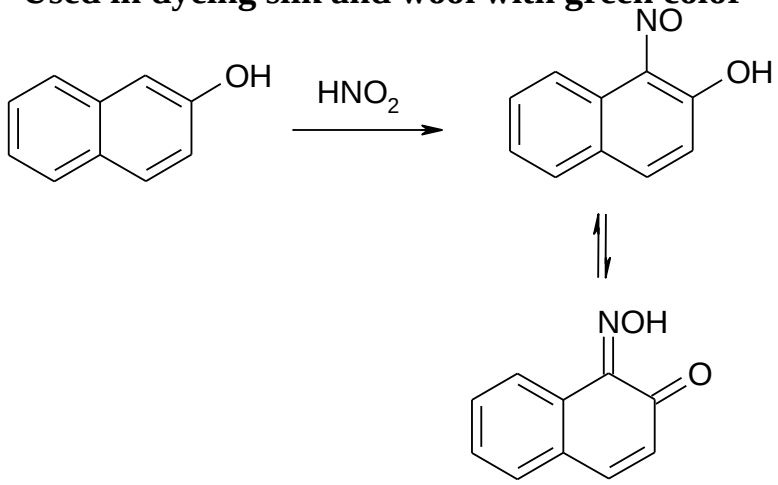
Used in dyeing silk and wool with green color.



2,4-dinitroso resorcinol

b-naphthol green

Used in dyeing silk and wool with green color



Devolped dyes

Azo dyes:

-Azo dyes which contain N=N as chromophre and NH_2 or OH as auxochromes and both chromophore (-N=N-) and auxochrome attach with one more aromatic system.

The dye is called monoazo if contain one N=N and is called diazo if it contain two N=N and so on.

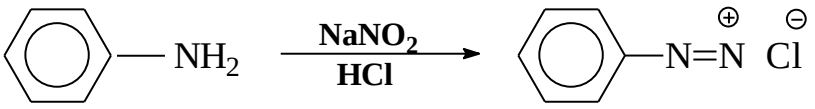
- Azo dye is prepared through two steps:

1- Diazotization.

2- Coupling.

1- Diazotization:

-Diazotization is conversion of aromatic amine to diazonium salt.



benzene diazonium chloric

Mechanism of diazotization:

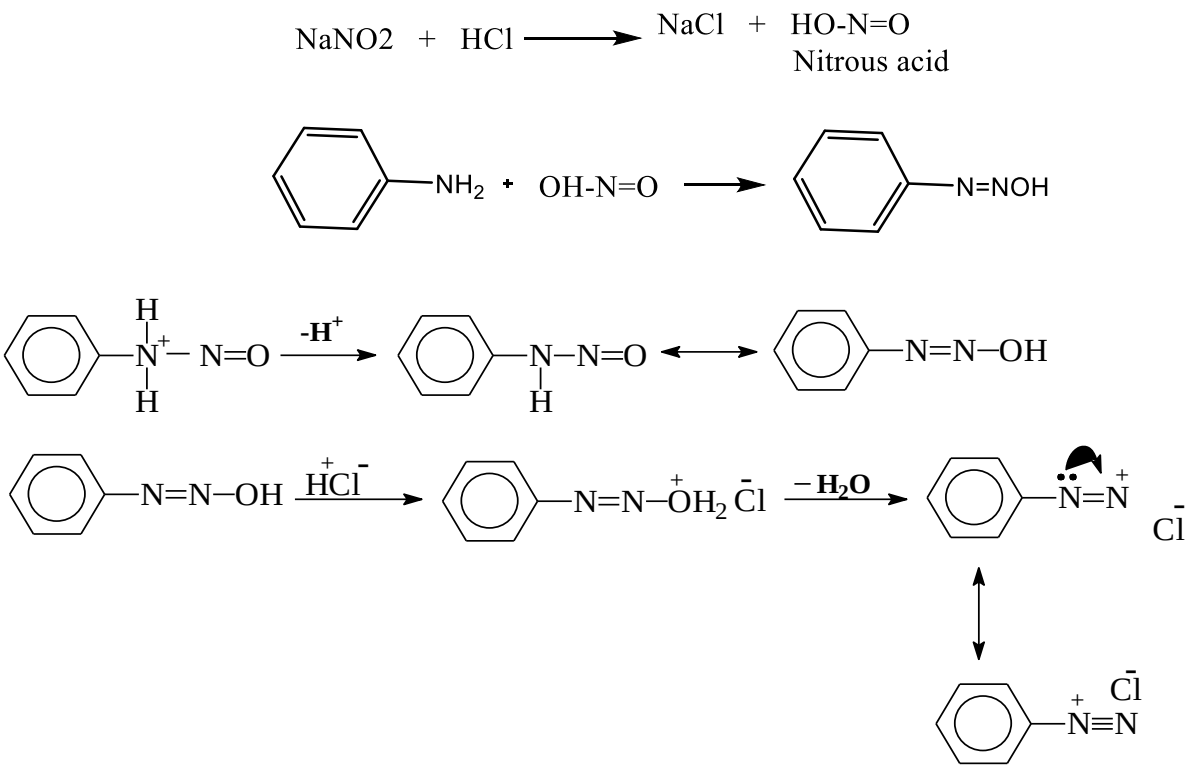
It occur by the following steps:

1-Nitrosation of amines and this occur by nitrosating agent e.g.

$$\overset{\oplus}{NO}\ ,\quad NOCl\ ,\quad H_2\overset{\oplus}{O}-N=O\ ,\quad N_2O_3$$

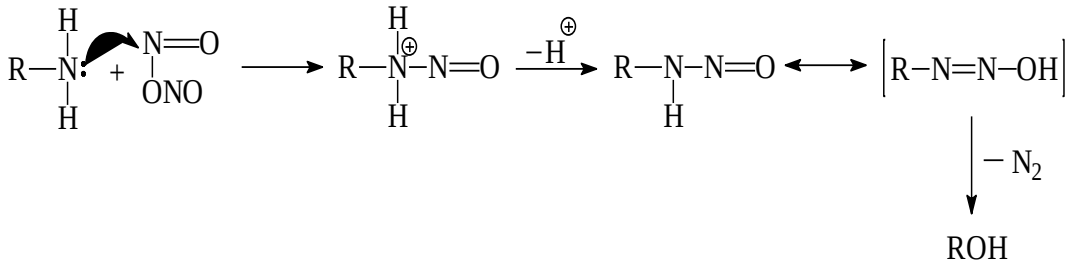
2-Conversion of N-nitroso to diazonism salt.

A) Mechanism of diazotization of 1ry (primary) aromatic amine:



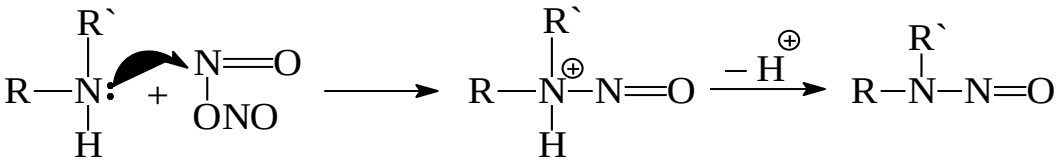
benzene diazonium chlorid

B) 1ry aliphatic amines:



i.e. No diazotization of aliphatic amines.

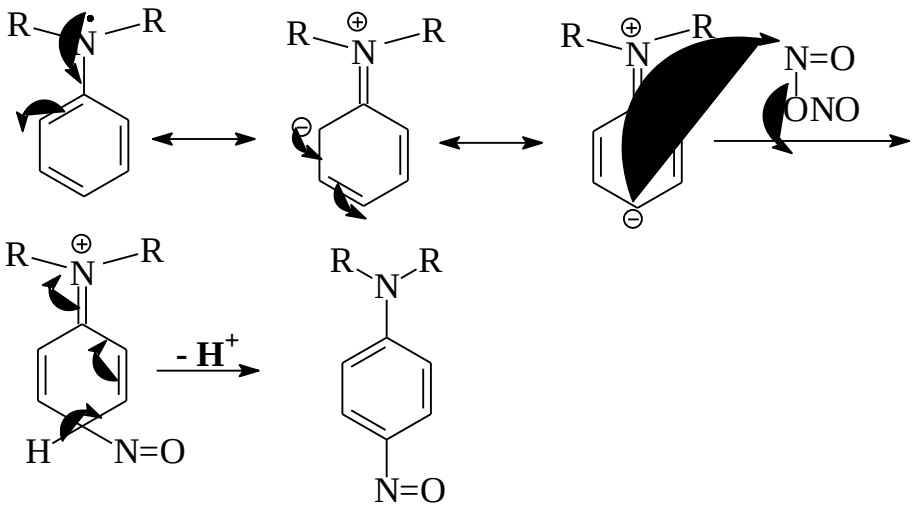
C) 2nd aromatic and aliphatic amines:



R may be aliphatic or Aromatic

N Nitroso compound

a) t- aromatic amines



P-Nitroso-N,N-dialkylaniline

_ For t-aliphatic amine, it does not react.

From the above only 1ry aromatic amines can be diazotized.

Effect of substituents on diazotization:

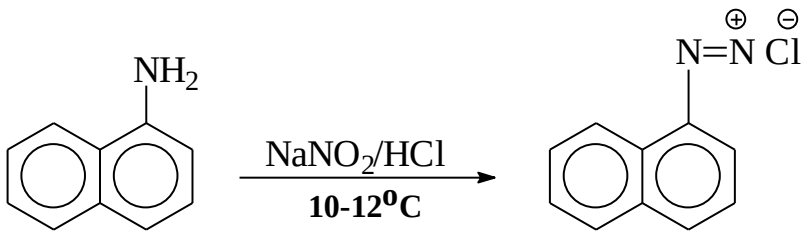
Diazotization of 1ry aromatic amines depends on nature and position of substituent groups.

1- for unsubstituted 1ry aromatic amine:

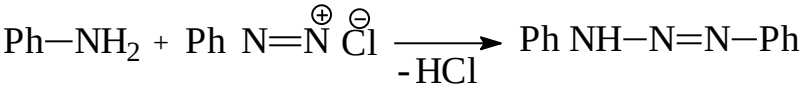
It need equal molar of $NaNO_3$ and 3 equivalent of HCl e.g.

$$\underset{\text{aniline}}{Ph{-}NH_2} \xrightarrow[\textbf{0-5}^{\textbf{o}}\textbf{C}]{NaNO_2/HCl} Ph{-}N{=}\overset{\oplus}{N}\ \overset{\ominus}{Cl}$$

For amino naphthalene



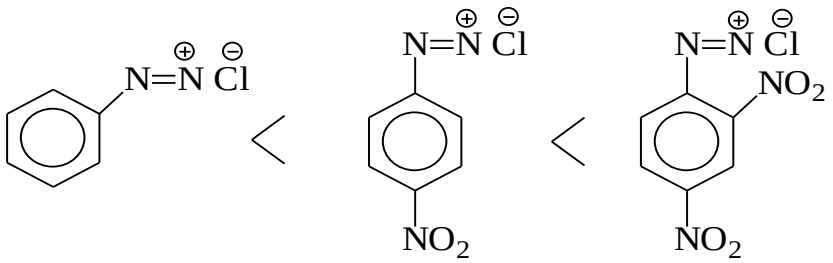
Secondary reaction can occur if some aniline is unreacted.



2- for nitro anilines:

- NO_2 group decreases the basicity of amines so it needs 7-equivalnt HCl.

- NO_2 group decrease the basicity because it act as electron withdrawing group but it increase the activity of diazonium salt so:



3- In case of acidic substituent:

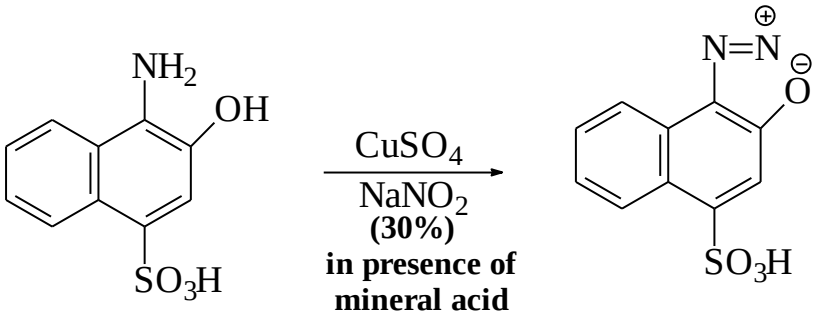
The presence of acidic group e.g. SO_3H make diazotization occur after dissolving amino sulphonic acid in $NaHCO_3$ solution and $NaNO_2$ is added to aqueous solution of aminosulphonic acid then diluted acid is added to make diazotization (this method is called reversed diazotization).

3- In case of aminophenol and aminonaphthol:

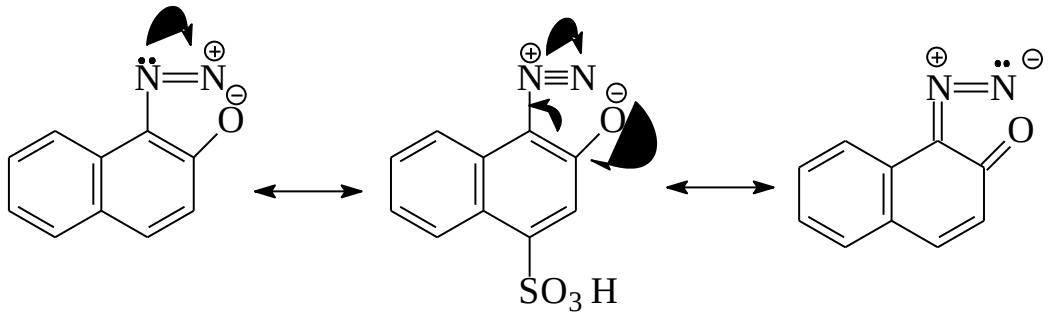
Amino phenol and amino naphthol in which NH_2 and OH are in position 1,2 or 1,4 for each other forming diazoxides.

- **1,3-aminophenols don't form diazo-oxides**

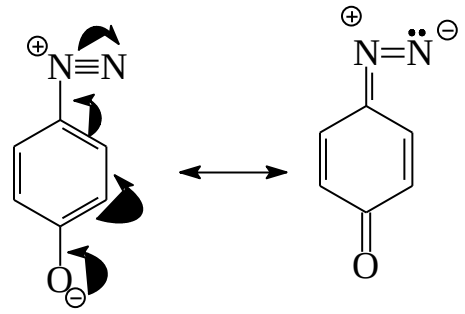
e.g.



- **Diazo–oxide is more stable than diazonium salt due to resonance e.g.**



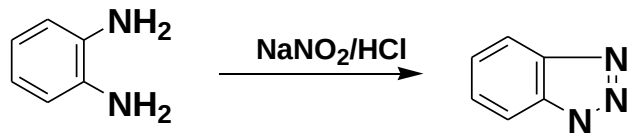
Also 1,4 aminophenol



1,2 aminohydroxyl compounds are used in manufacture of metal azo complex

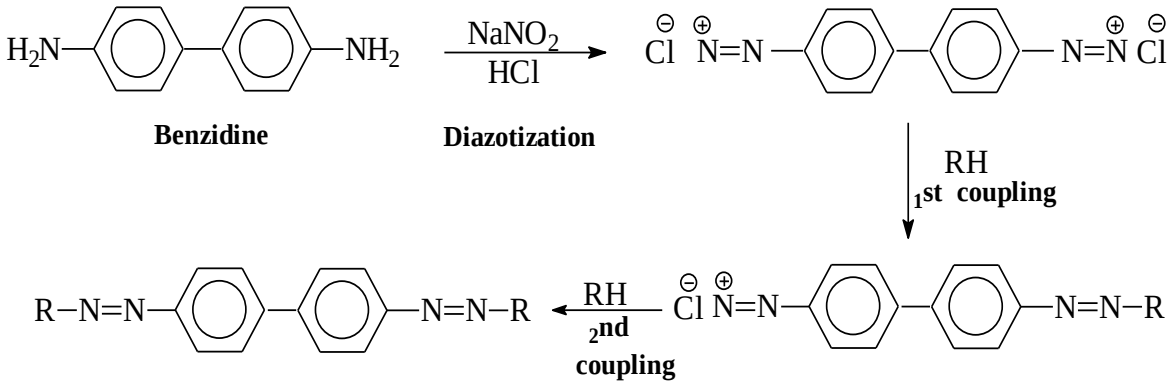
5- for diamines:

A) If two amino in o- position, no coupling occur due to ring closure.



O-Phenylenediamine **1*H*-Benzotriazole**

B) if two NH_2 are not in *o*- position diazatization occur.



Benzidine **Diazotization**

The 2nd coupling occurs slower than 1st.

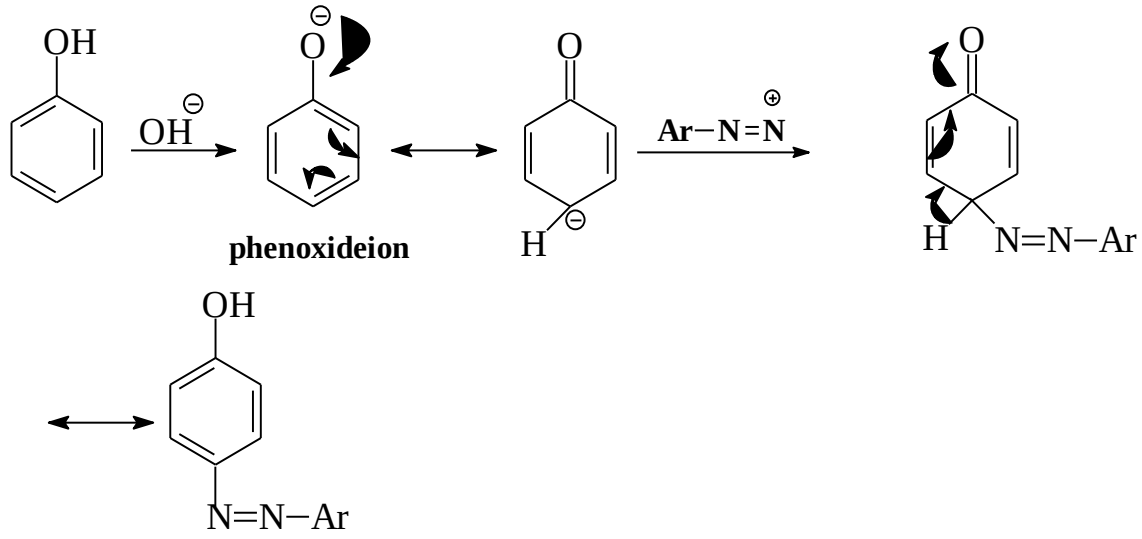
Diazo coupling

***Diazo coupling is electrophilic substitution by diazonium cation.**

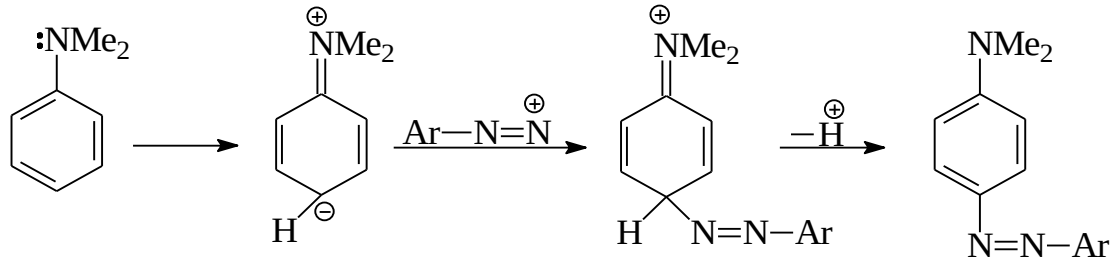
***It occurs often in para-position.**

***Coupling occurs for phenols in alkaline medium and for amines in slightly acidic medium.**

Mechanism of Diazo coupling of phenols:



Mechanism of Diazo-coupling of aromatic amines:



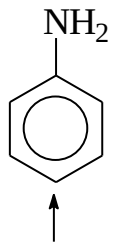
Coupling component:

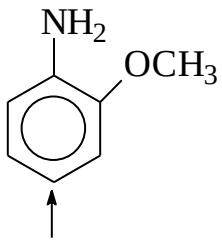
1) Benzene derivative:

A) Amines:

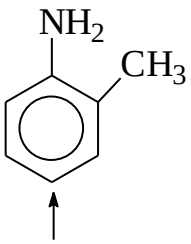
- **Medium of coupling: acidic medium**
- **Position of coupling: para-position of amino group.**

i- Primary amines:

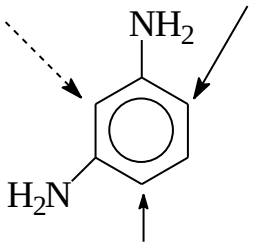




o-Ansidine



o-Toludine

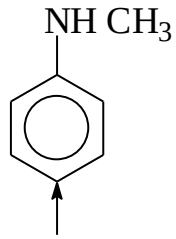


m–phenylenediamin

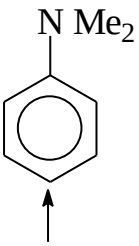
The arrow indicates the coupling position.

The arrow ⇢ indicate the less reactive position

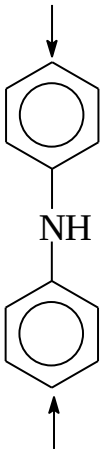
ii- Secondary and t–amines:



N–methyl aniline



N,N dimethyl aniline

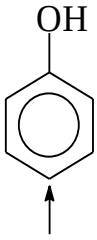


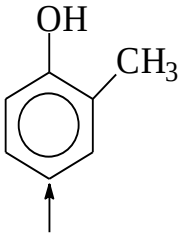
diphenyl amin

B) Hydroxy derivatives:

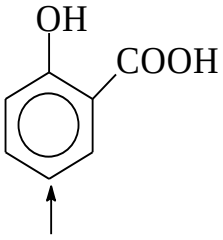
Medium of coupling: alkaline medium.

Position of coupling: para-position of –OH

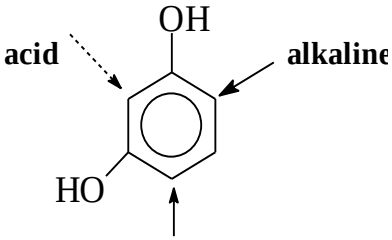




o- Cresol



Salicylic acid



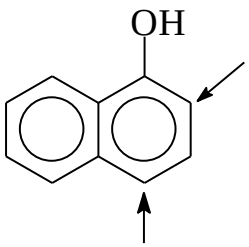
alkaline resoricnol

2) Naphthalene derivatives:

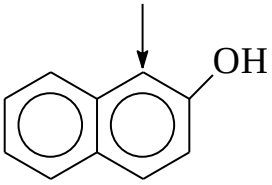
A) Naphthols:

Medium of coupling: alkaline

Position of coupling: usually p-position of 1-Naphthol and position 1 for β-Naphthols



1 Naphtholor α–Naphthol

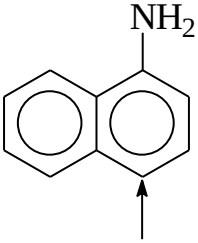


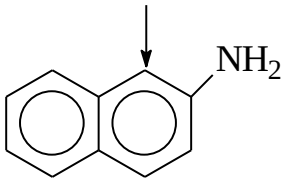
2-Naphthol or β-Naphtho

B) Naphthyl amines:

Medium: acidic

Position: position 4- for 1- Naphthylamine and position 1- for 2-naphthylamine.

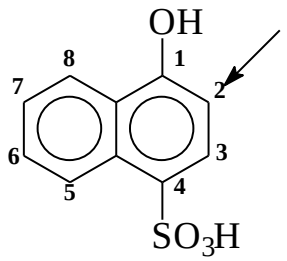




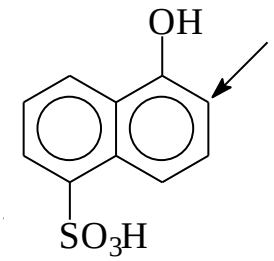
C) Naphthol sulphonic acid:

Medium: alkaline.

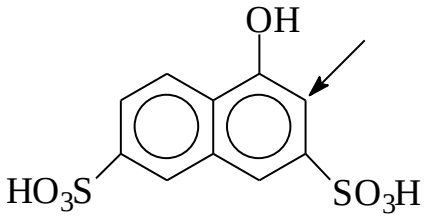
Position of coupling: ortho-position of OH.



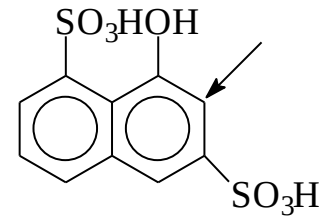
1-Naphthol-4-Sulphonic acid



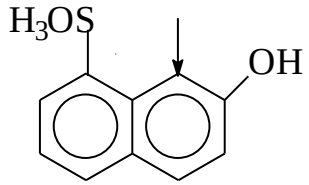
1-Naphthol-5-Sulphonic acid



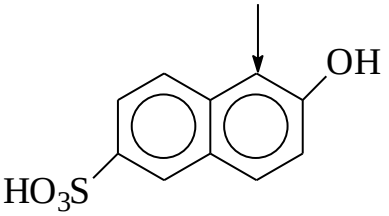
1-Naphthol-3,6-diSulphonic acid

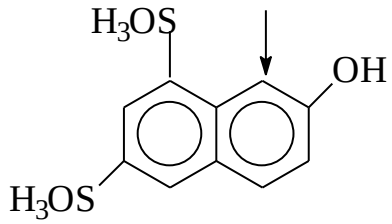


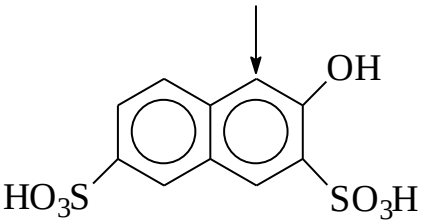
1-Naphthol-3,8-diSulphonic acid



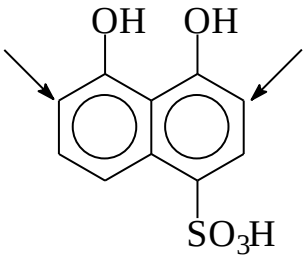
2-Naphthol-8-sulphonic acid

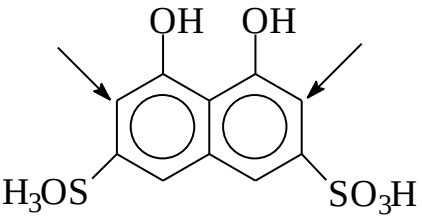






For dihydroxy naphthalene sulphonic acids





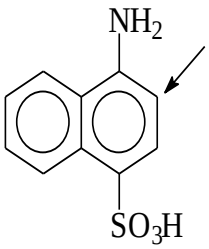
4,5 dihydroxy Naphthalene
1- sulphonic acid

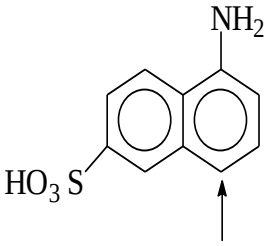
D) Naphthyl amine sulphonic acids:

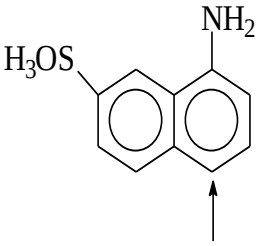
Medium: acidic

Position of coupling: position 4- for 1-Naphthylamine

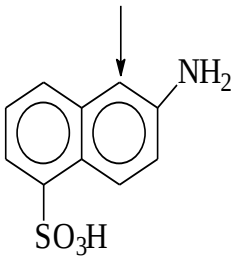
Position 1- for 2-Naphthylamine



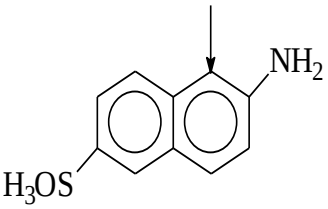




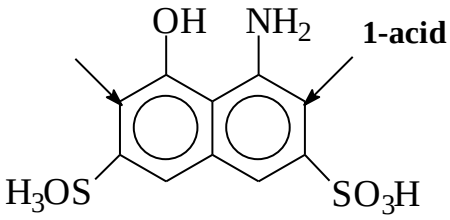
1-amino-7-Naphthalensulphonic acid ac



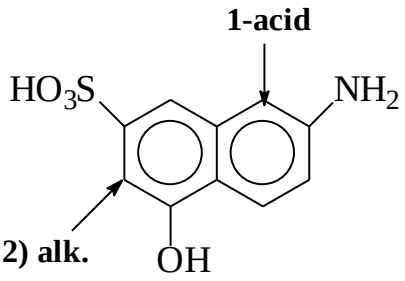
2-amino 5-Naphthene sulphonic acid



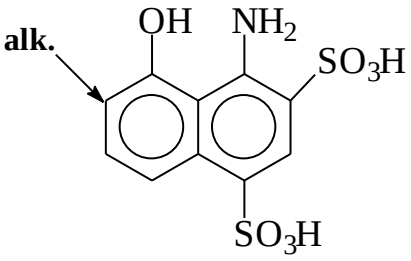
E) Amino naphthol sulphonic acids:

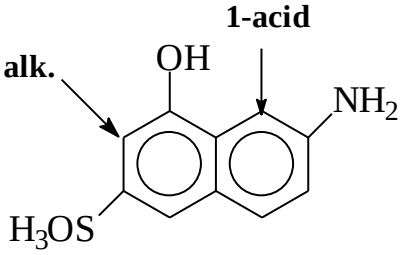


1- amino- 8-Naphthol 3,6 disulphonic acid



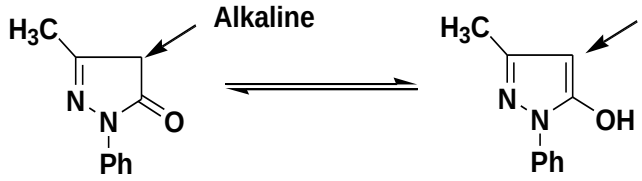
2-Amino-5-hydroxy-7-Naphthlene Sulphonic acid



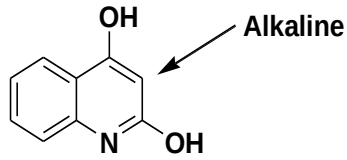


Active methylene component

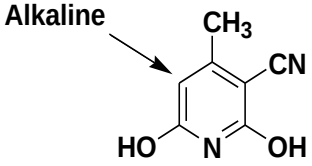
A) Hetero cyclic



3-Methyl-1-phenyl-2-pyrazoline-3-one

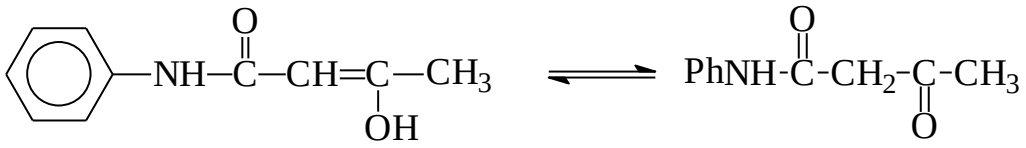


2,4-Dihydroxy-quinoline



2,6-Dihydroxy-4-methyl-nicotinonitrile
Or 3-Cyano-2,6-Dihydroxy-4-methyl-pyridine

Other example of active methylene acetoacetanilide



e.g of direct and acid dye

Questions

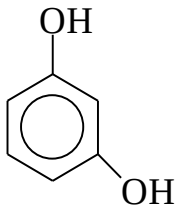
1- Give structure of Azo dyes prepared from aryl diazonium cation (ArN_2^+) and the following coupling agent.

a- Acetoacetanilide.

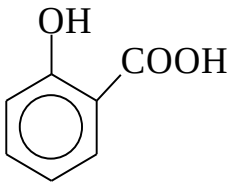
b- 1- amino–8-naphthol-3, 6-disuphonic acid.

c- 3- methyl-1-phenyl-2-pyrazolin-5-one.

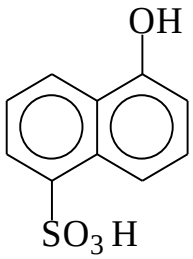
2- Give the structure of the following azo dyes which could be obtained from the interaction of diazonium cation (ArN_2^+) with the following coupling component



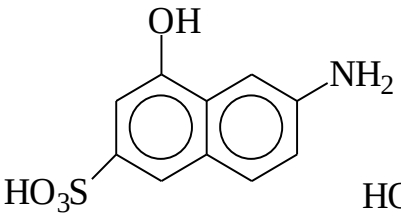
(1)



(2)



(3)



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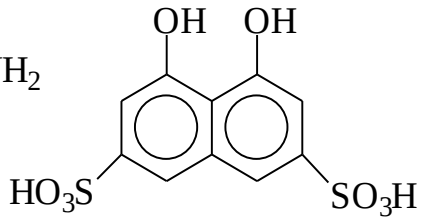

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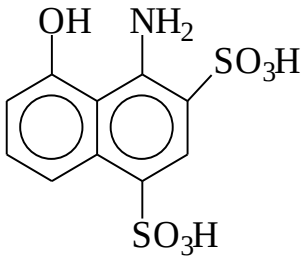

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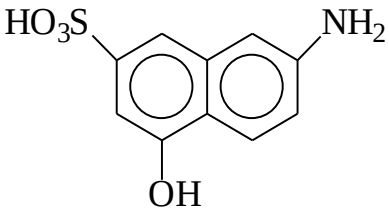
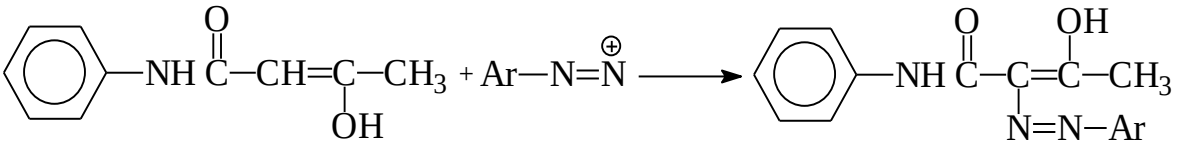


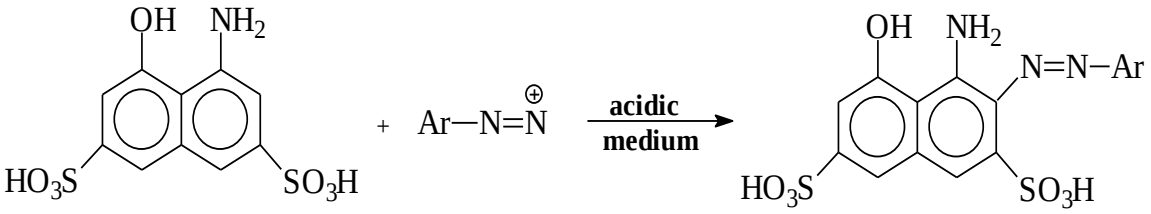
(7)

Answer of first question

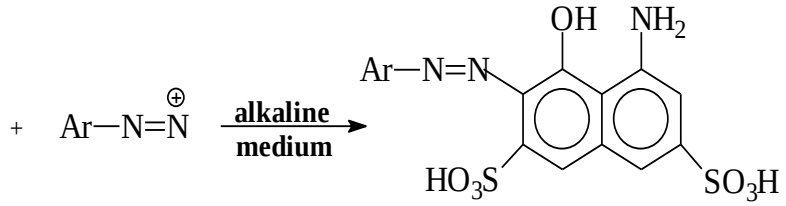
1) Acetoacetalide:



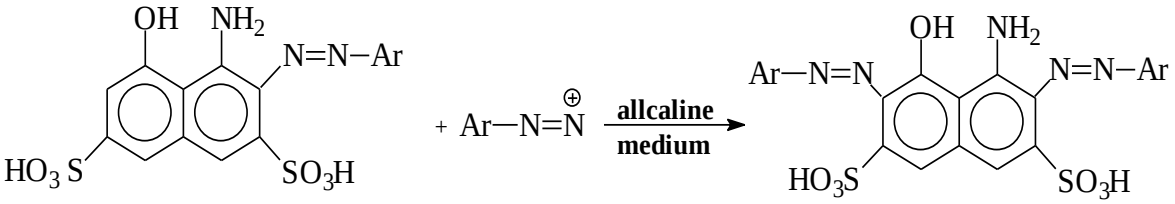
2) 1-amino–8-naphthol–3,6-disulphonic acid:



2-Arylazo-1- amino
8- naphthol-3,6 disulphonic acid

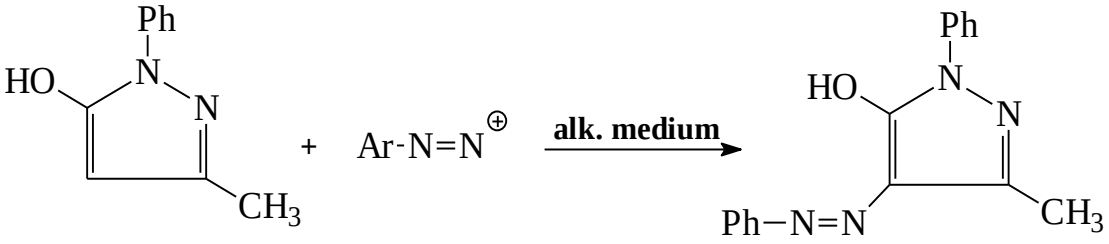


7-Arylazo-1- amio
-8-naphthol- 3,6 disulphonic acid



2,7 diarylazo-1- amino
-8-Naphthol-3,6 disulphonic acid

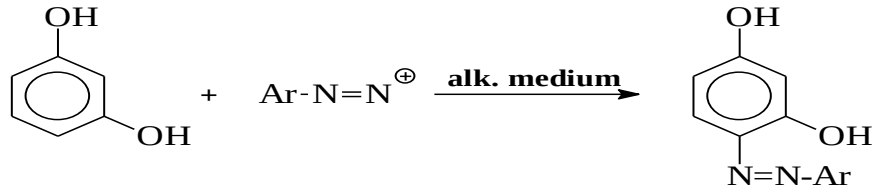
3) 3-methyl-1-phenyl-2-pyrazolin-5-one:



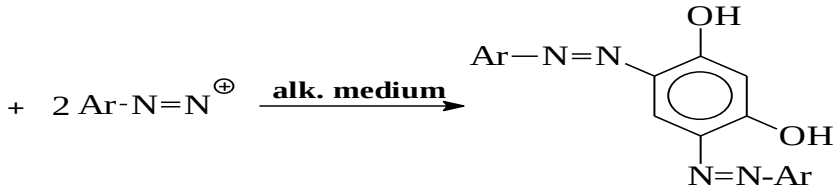
4-arylazo-3-methyl-1-phenyl 2- pyrazolin-5-one

- إجابـــــــــــــــــة الســـــــــــــــــؤال الثـــــــــــــــــاني

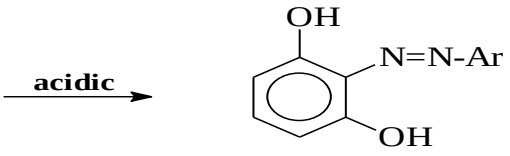
(1)



Resorcinol **4-arylazo resorcinol**

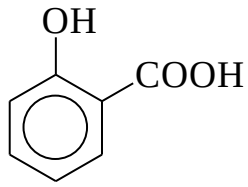


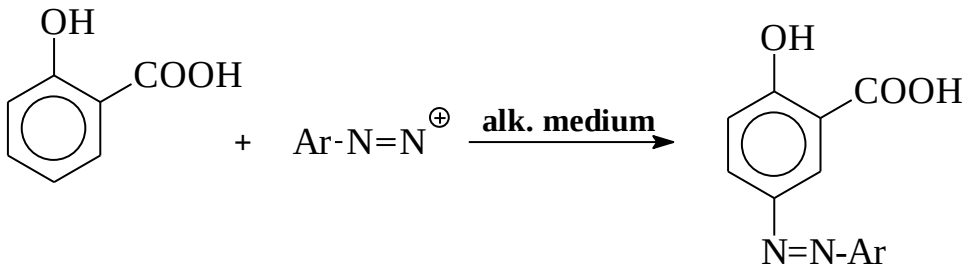
4,6-arylazo resorcino



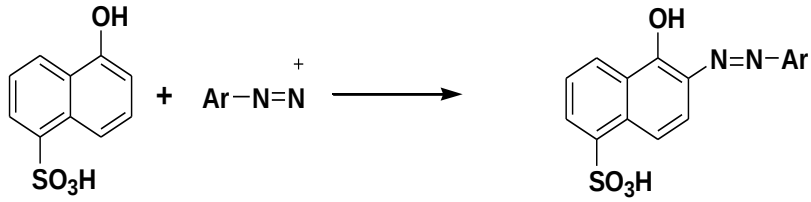
2-arylazo resorcinol

(2)





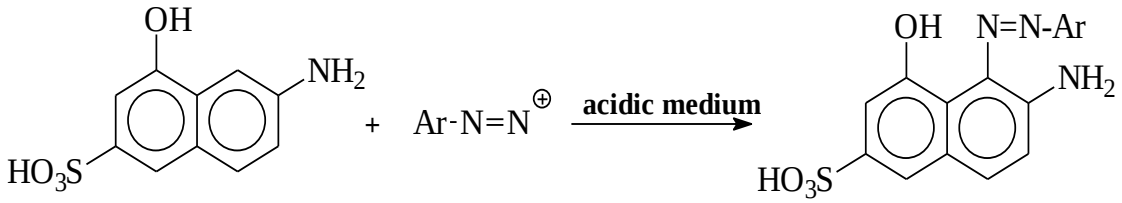
4-arylazo salicylic aci



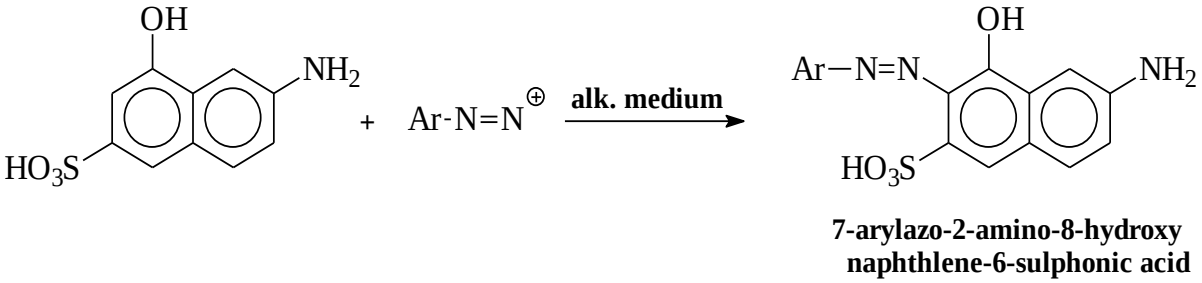
5-Hydroxy-naphthalene-1-sulfonic acid

2-Aryazo-5-Hydroxy-naphthalene-1-sulfonic acid

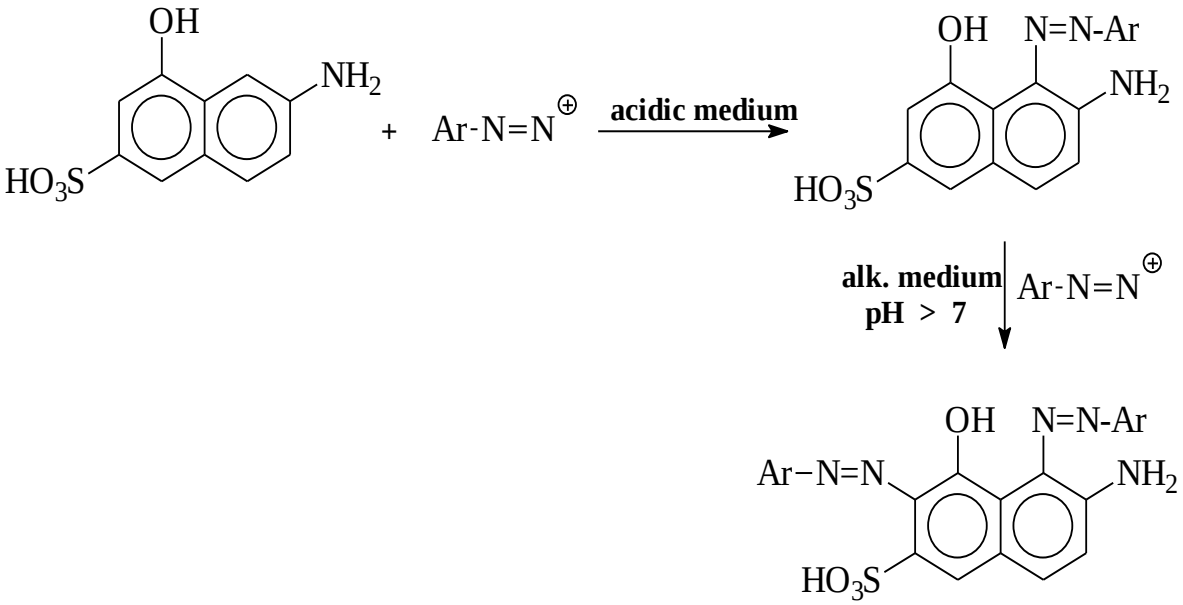
(a)



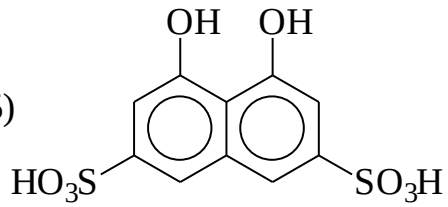
1-arylazo-2-amino-8-hydroxy naphthlene-6-sulphonic aci

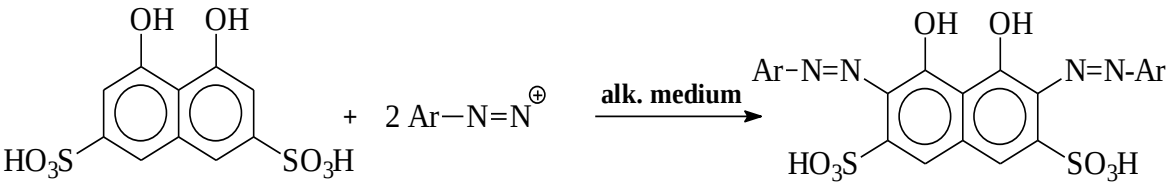


7-arylazo-2-amino-8-hydroxy naphthlene-6-sulphonic acid



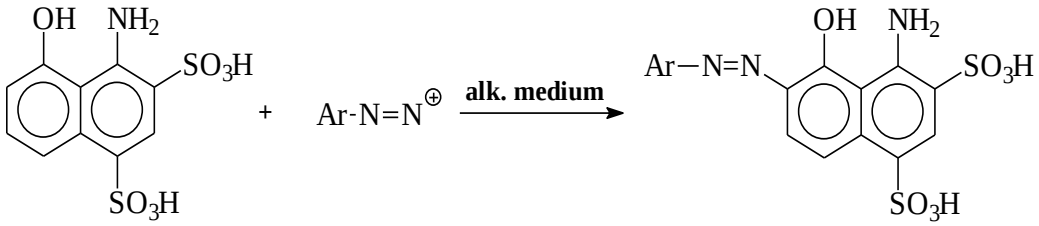
(5)





2,7-diarylazo-1,8-dihydroxy naphthalnene 3,6-disulphoric aci

(6)



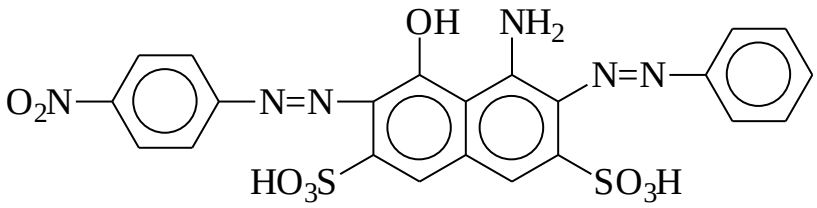
7-arylazo-1-amino-8-hydroxy naphthalnene 2,4-disulphoric aci

(7) Like (4).

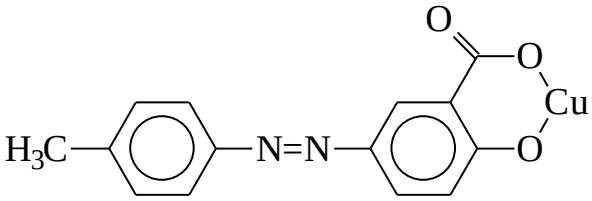
Question:

Synthesis of the following dyes:

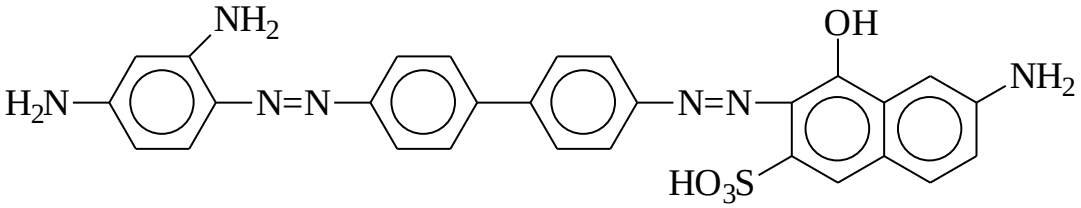
(1)



(2)

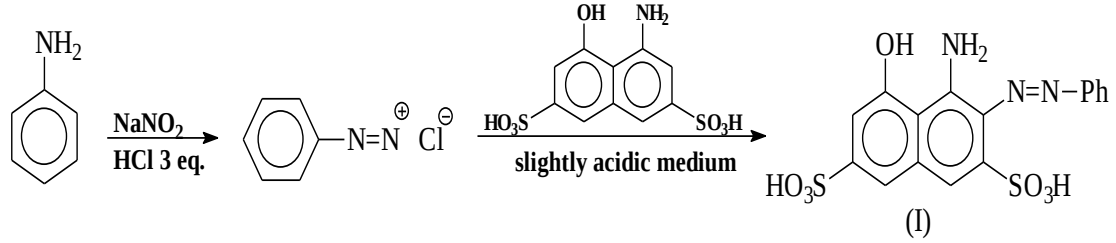


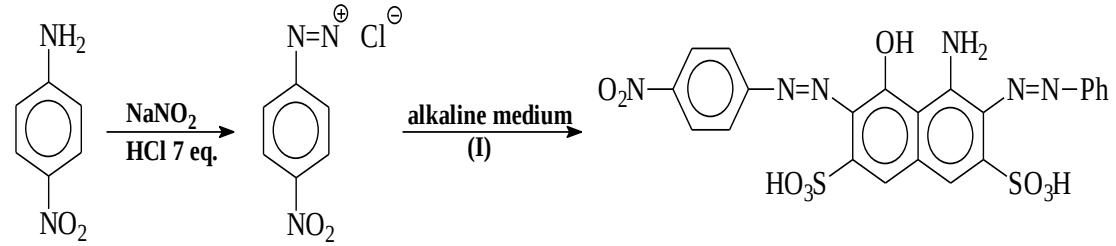
(3)



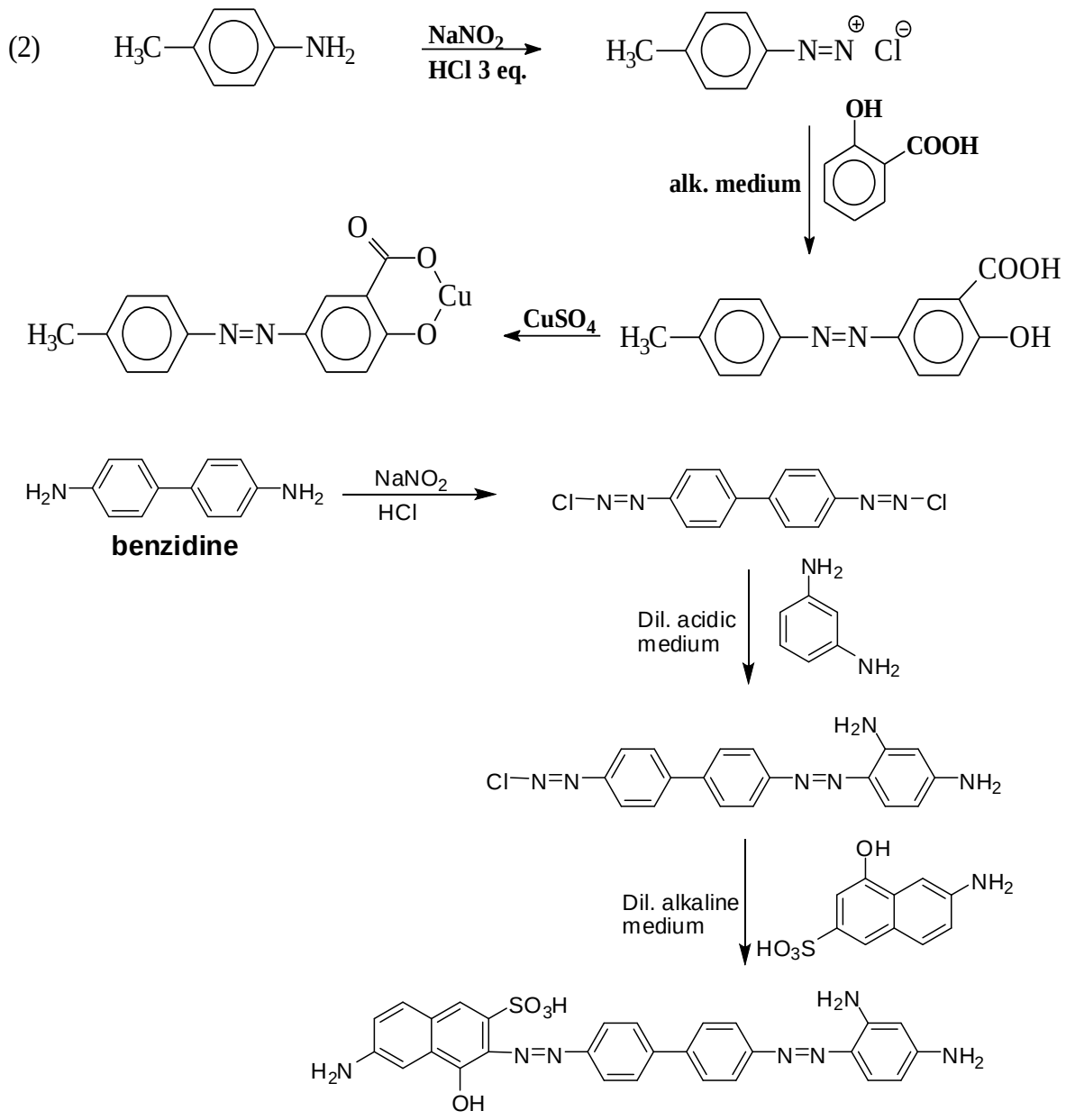
Solution:

(1)



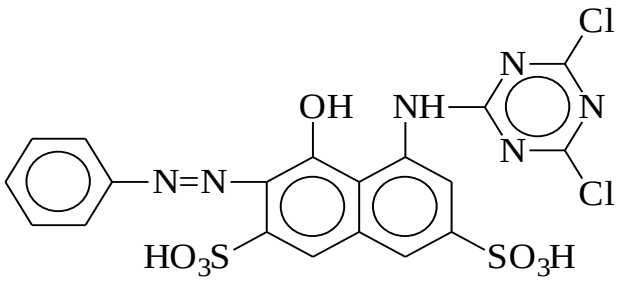


(2)

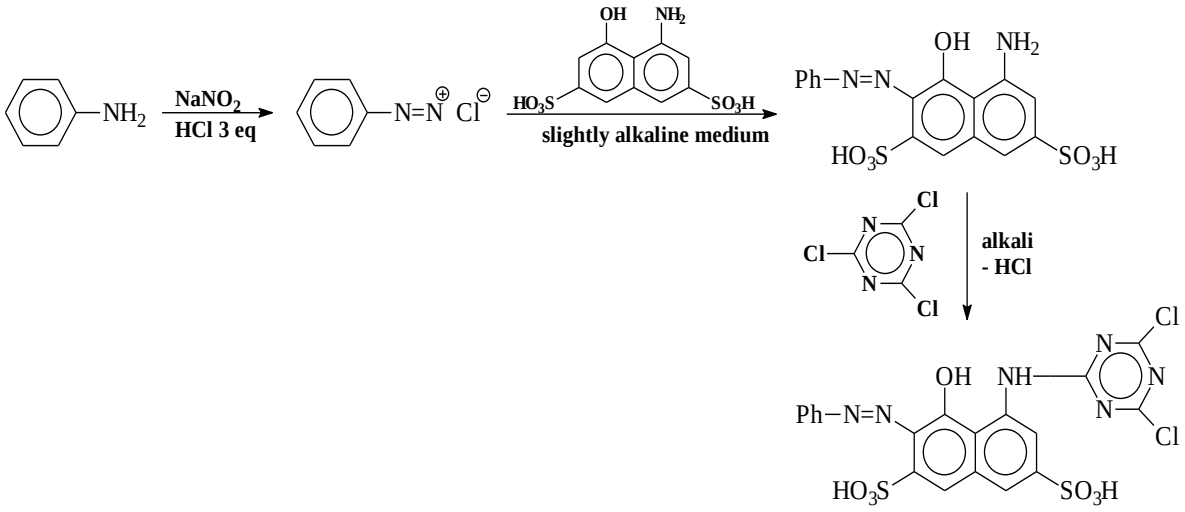

NaNO2
HCl 3 eq.
alk. medium
CuSO4
NaNO2
HCl
benzidine
Dil. acidic medium
Dil. alkaline medium

Question:

Synthesis



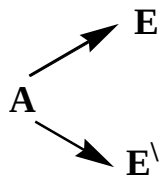
Solution:



Types of Disazo dyes

- **There are four types of Disazo dyes**

  1. **A→ E→ E\ or A→ M→ E**

2. 

3. **A→ E← A**

4. **A→ E.X.E ← A**

   Where A is diazo component (amine)

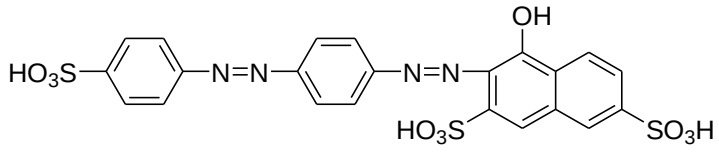
   E is coupling component

   X is agent used for binding two amines

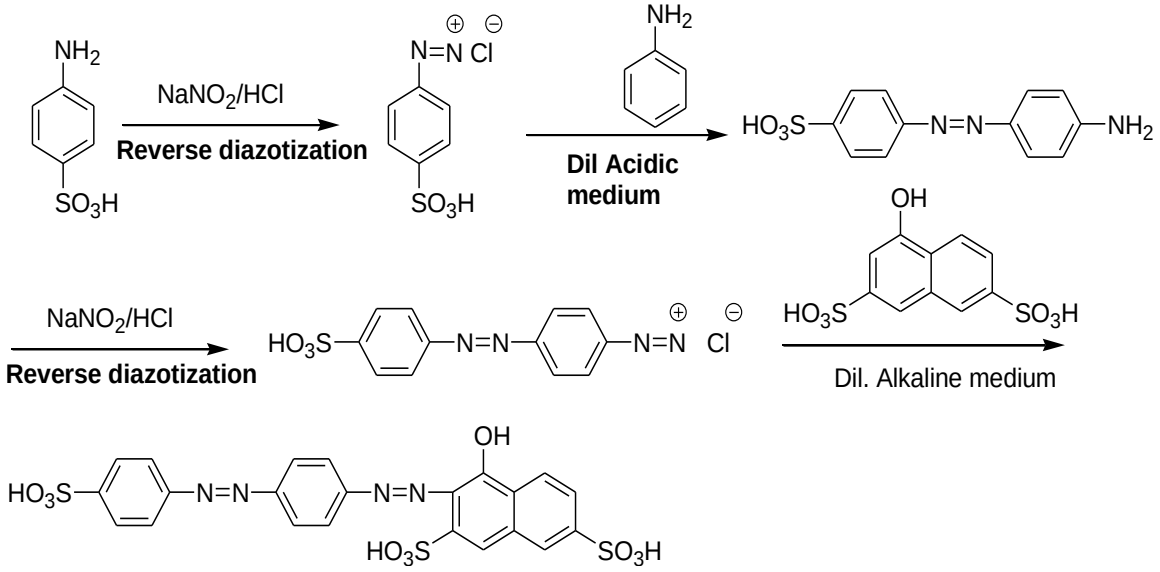
5. **<u>Type 1</u> A→ E→ E\ or A→ M→ E**

- **In this type we use diazonum salt to couple with amine, the resulted dye is used as amine for second coupling**

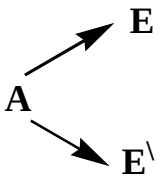
  <u>e.g.</u>



  <u>Synthesis</u>

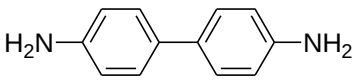


Type 2

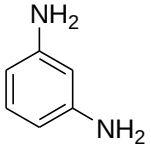


- **In this type we use Diamine as benzidine and couple it with two coupling component**

A as

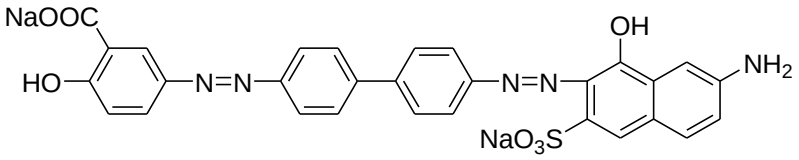


Benzidine

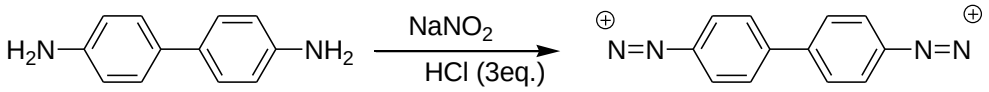


m-phenylenediamine

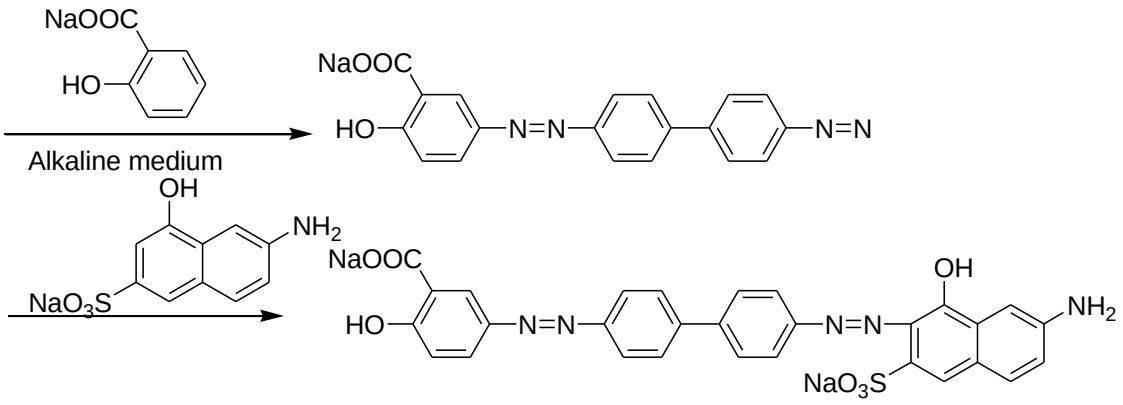
e.g.



Synthesis

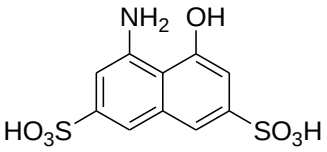


Benzidine



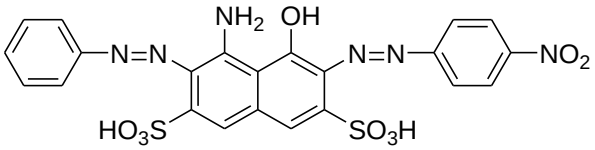
Type 3 A→ E← A

- **In this type, we use coupling component of more than one position of coupling and couple it with two amines**
  - **The best example of E in this case is**



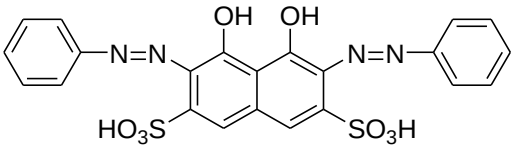
4-amino-5-hydroxynaphthalene-2,7-disulfonic acid

e.g.



See synthesis page 20

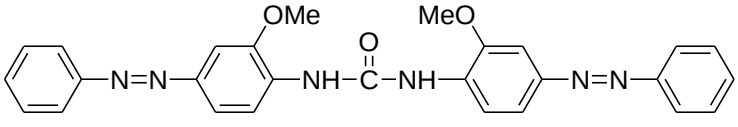
Example of A→ E← A



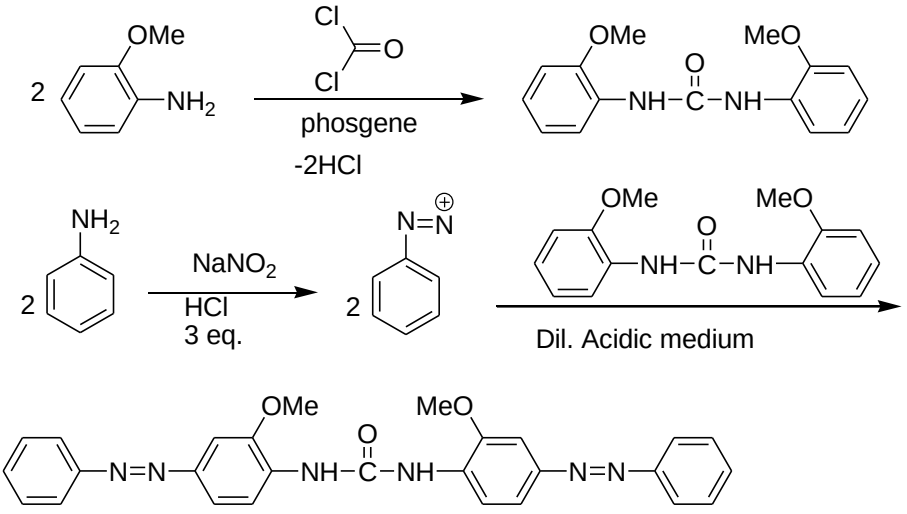
Type 4

- **In this type, we link two amines by using phosogene and then couple the products with two diazonium salts**

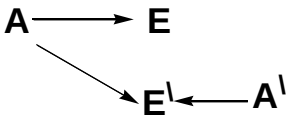
E.g.



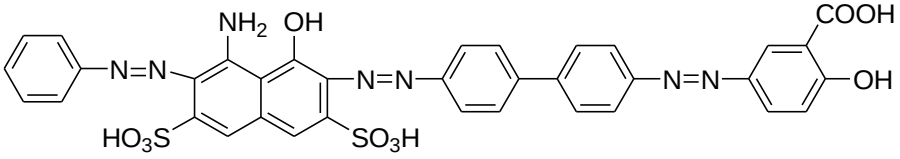
Synthesis



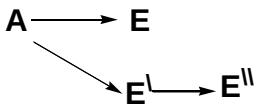
1. Triazodyes



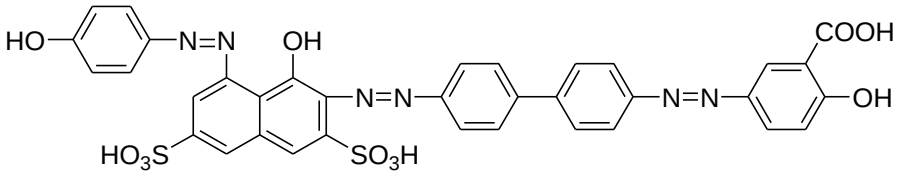
- **Like 3 but we introduce other coupling component on E**



2.

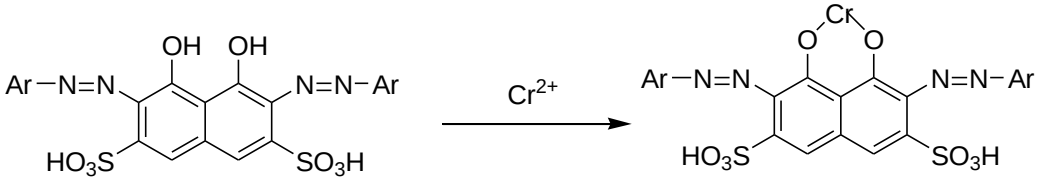


- **$E^{\backslash}$ must contain NH_2 which can be converted into diazonium salt can couple other coupling component**



<u>Metalazo compounds</u>

- **This dyes are azodyes usually contain OH groups ortho to azo group so can form stable complexes with metals. e.g.**



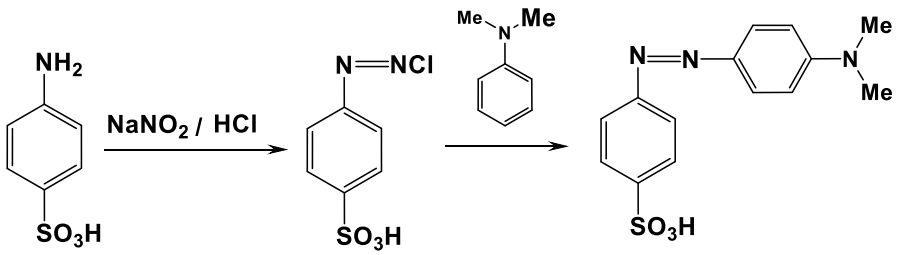
Some notes

- **The diazonium salt produced from diamines such as benzidine are called tetrazonium salt and the dye produced is called bisazo dye**

Different example of azo dye:-

1-methyl orange.

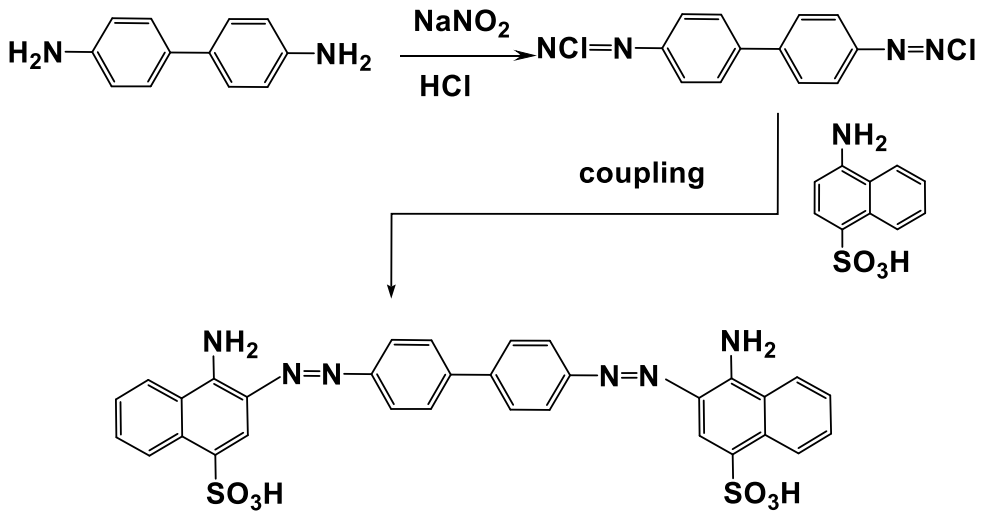
Used in dyeing wool and silk with orange color but it Can't fix on fibers so it is used only as indicator.



2-Congo red.

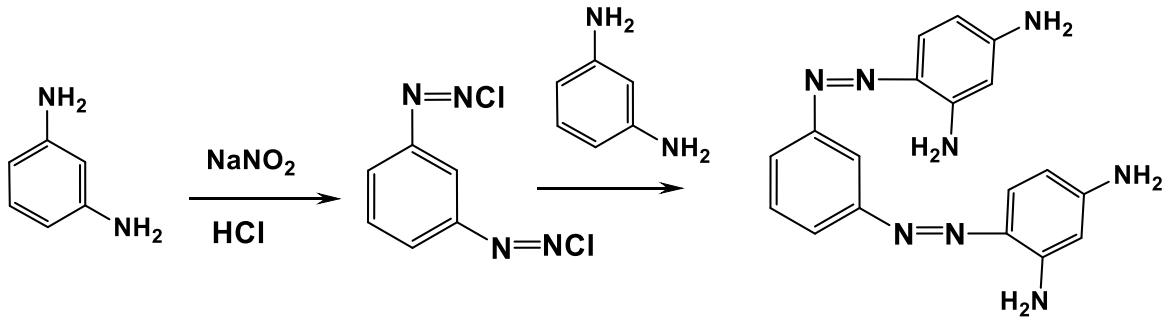
the sodium salt of 3,3′-([1,1′-biphenyl]-4,4′-diyl)bis(4-aminonaphthalene-1-sulfonic acid).in water yielding red colloidal solution. Used for dyeing cotton and as indicator (Due to a color change from blue to red at pH 3.0–5.2)

In histology and microscopy, Congo red is used for staining in amyloidosis, and for the cell walls of plants and fungi, and for the outer membrane of Gram-negative bacteria.



3-Bismarck brown.

Bismarck brown Y stains mast cell granules brown. It can be used with live cells. It is also used to stain cartilage in bone also Used in dyeing cotton and painting wood with brown color



Mordant Dyes
(Triphenyl methane dyes)

-are dyes that do not adhere to fabrics directly these need a chemical intermediate, known as a mordant, to attach themselves to the fabric. In this process, the mordant is applied to the fabric and then the dye is applied, which then bonds to the mordant. In this experiment, we will use tannic acid as a mordant to dye a sample of cotton with malachite green dye.

Example of mordent used :-

tannic acid, alum, chrome alum, sodium chloride, and certain salts of aluminium , chromium, copper, iron, iodine, potassium, sodium, tungsten, and tin.

Iodine is often referred to as a mordant in Gram stains, but is in fact a trapping agent.

Triphenyl methane dyes

Triphenyl methane dyes are obtained by introduction of NH_2, NHR, NR_2 or OH groups in para-position of two rings at least of three phenyl groups.The compounds obtained are colorless (leuco-base) on oxidation converted into t-alcohol (color-base), which forms quinoniud structure in the presence of acid.

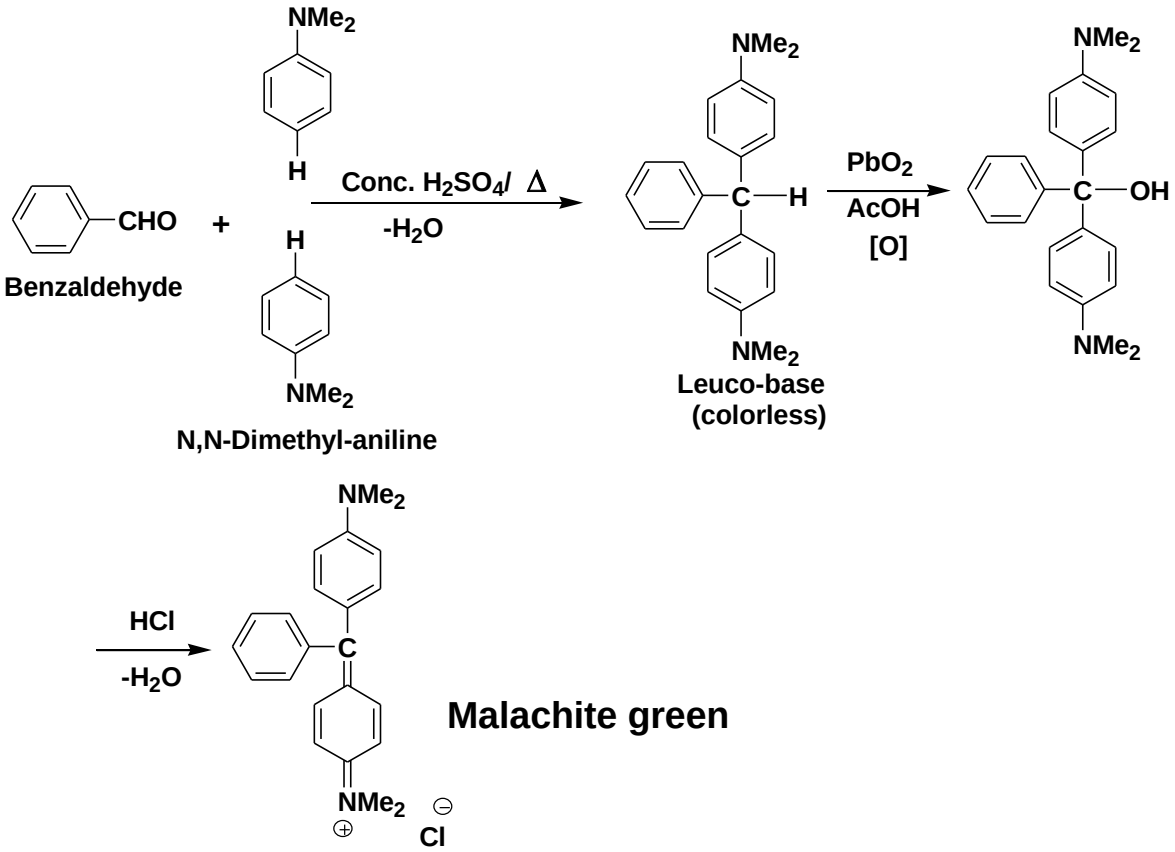
- **Triphenyl methane dyes are classified into:**

1- Base Dyes or cationic dyes.

2- Acid Dyes or anionic dyes.

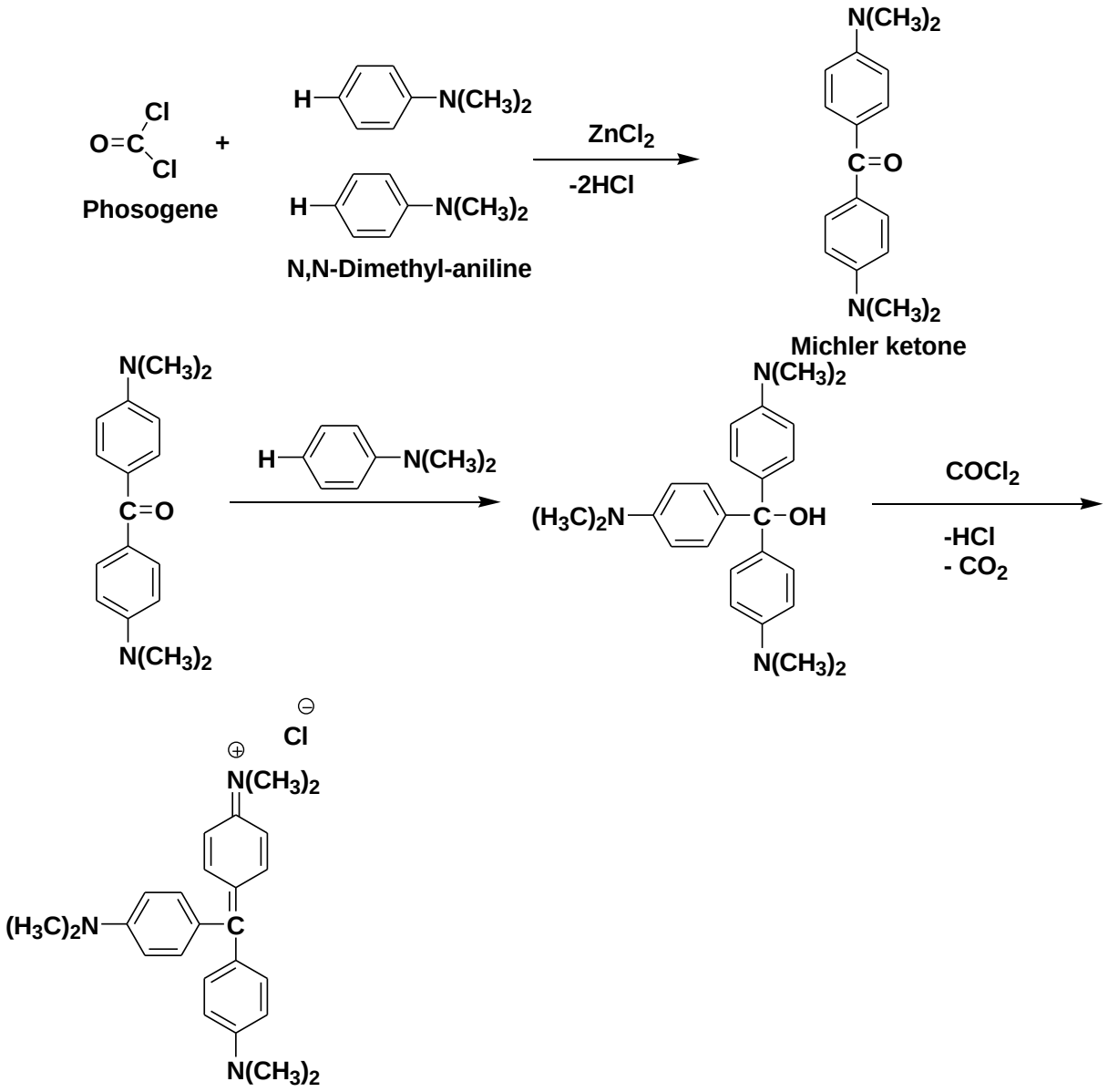
1) Base Dyes or cationic dyes

A) Malachite green

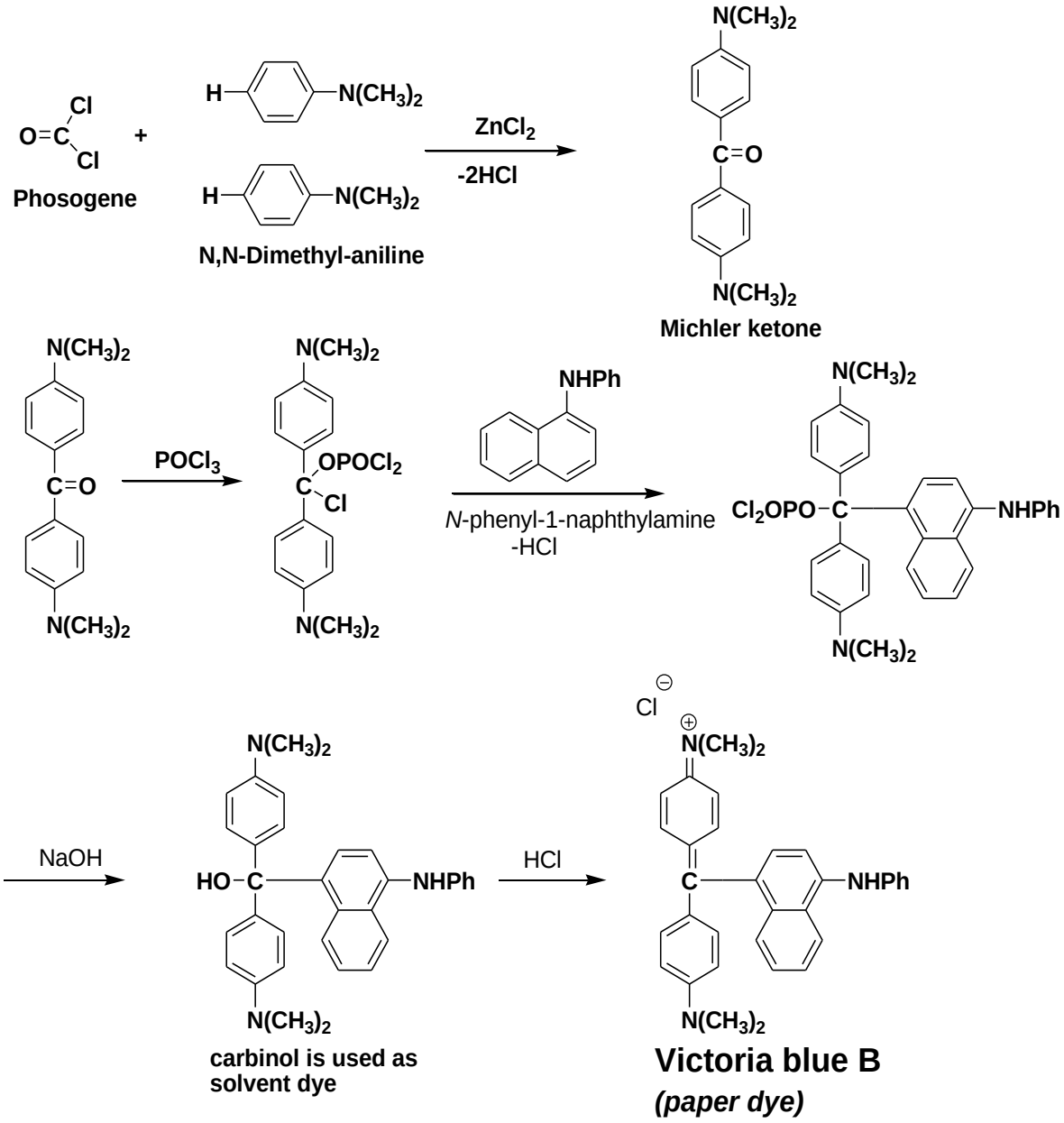


- ***Malachite green is used for dying cotton and polyacrylonitrile***

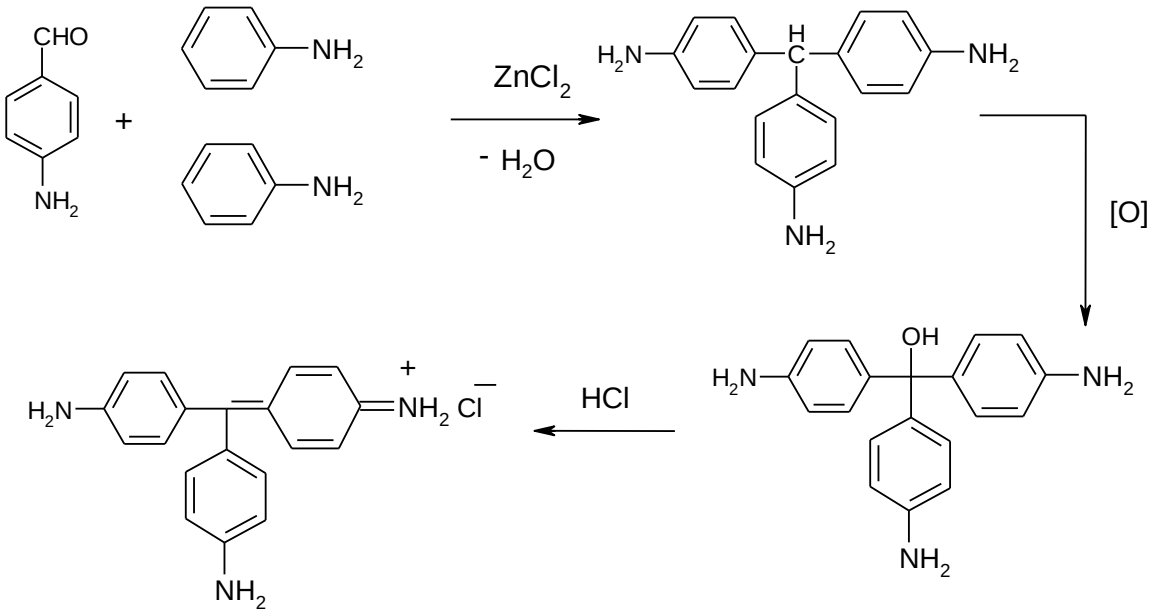
B) Crystal violet



C) Victoria blue B (paper dye)

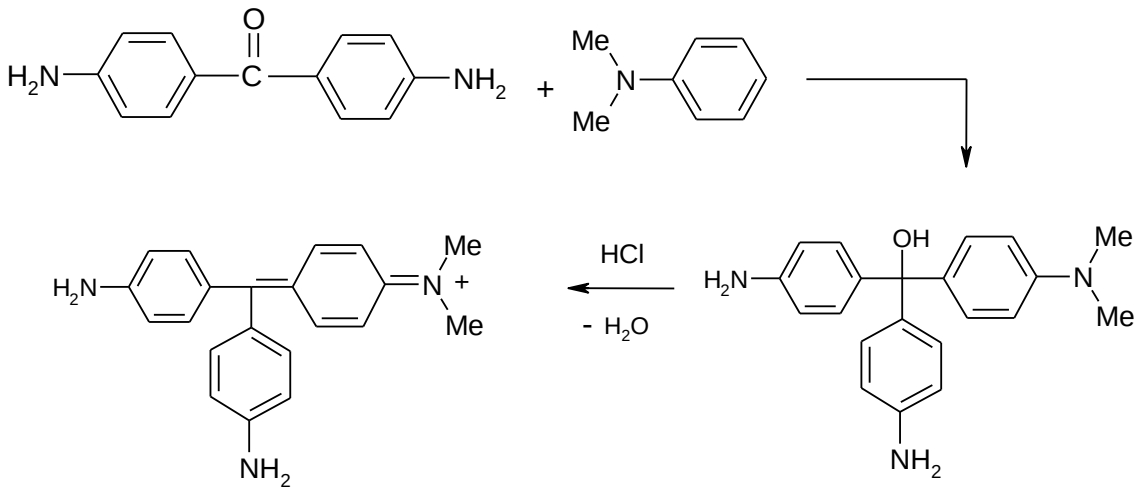


D)-Para rose aniline dye



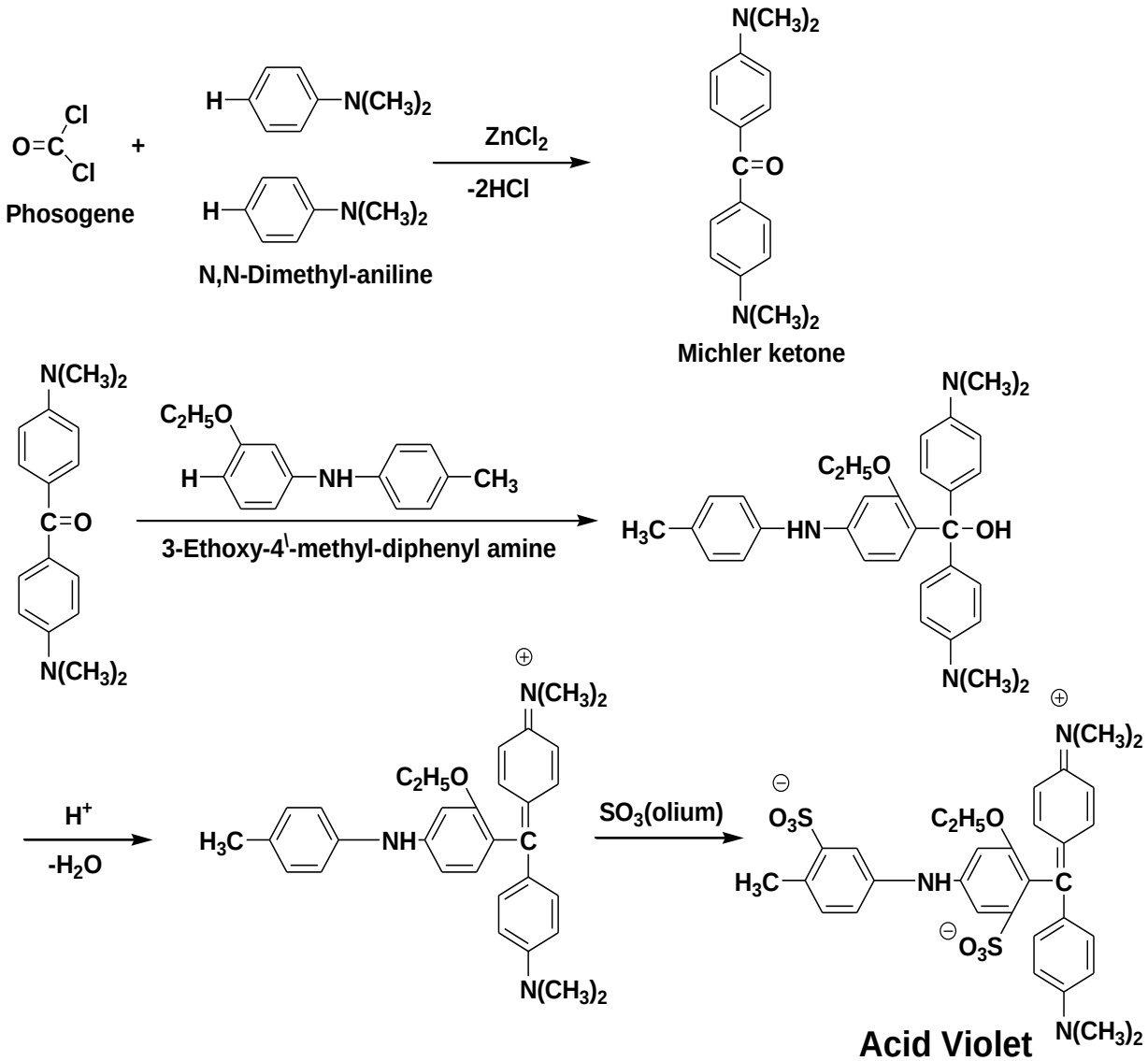
E) Gention violet dye

Used as antiseptic

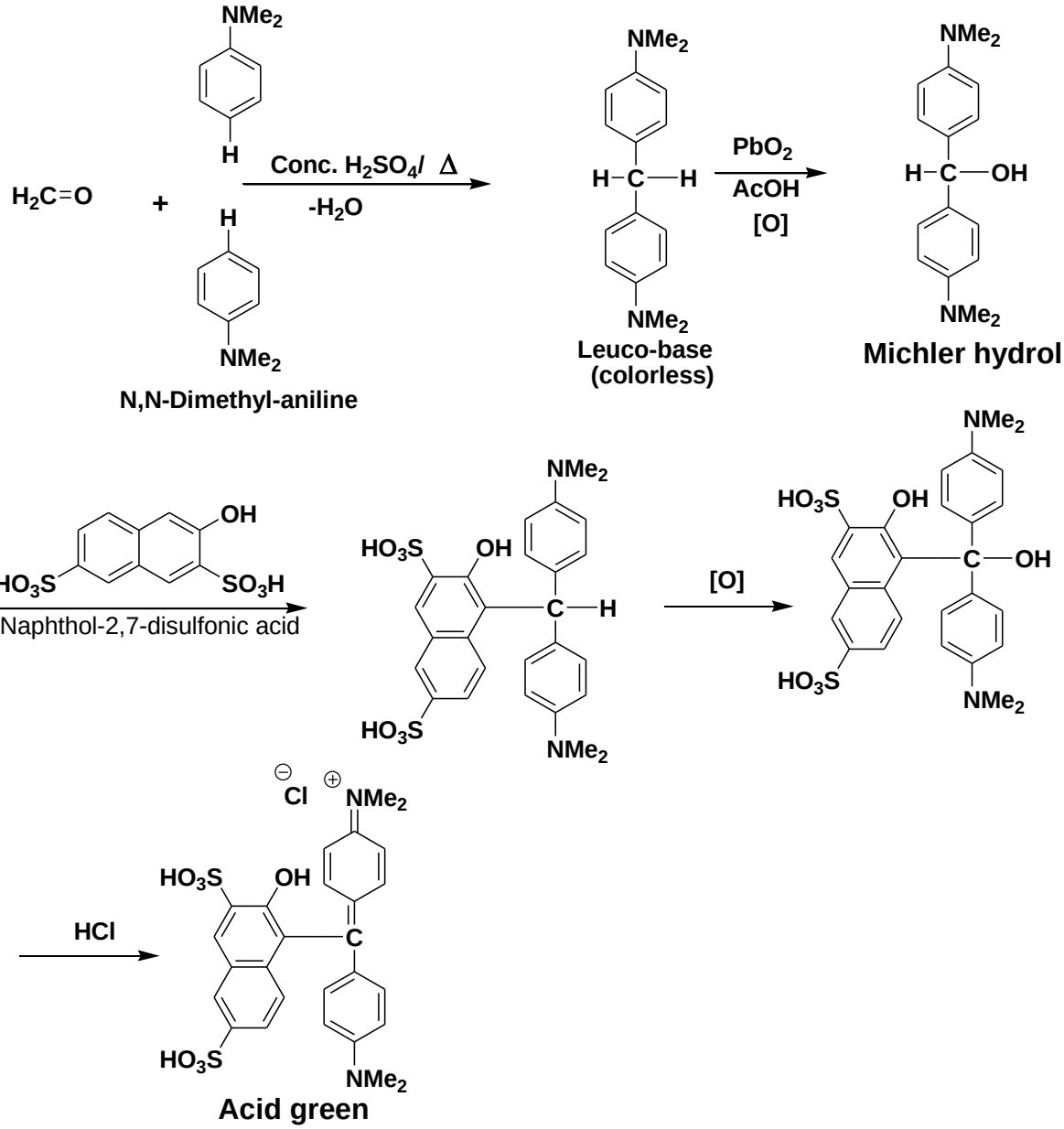


Acid dyes

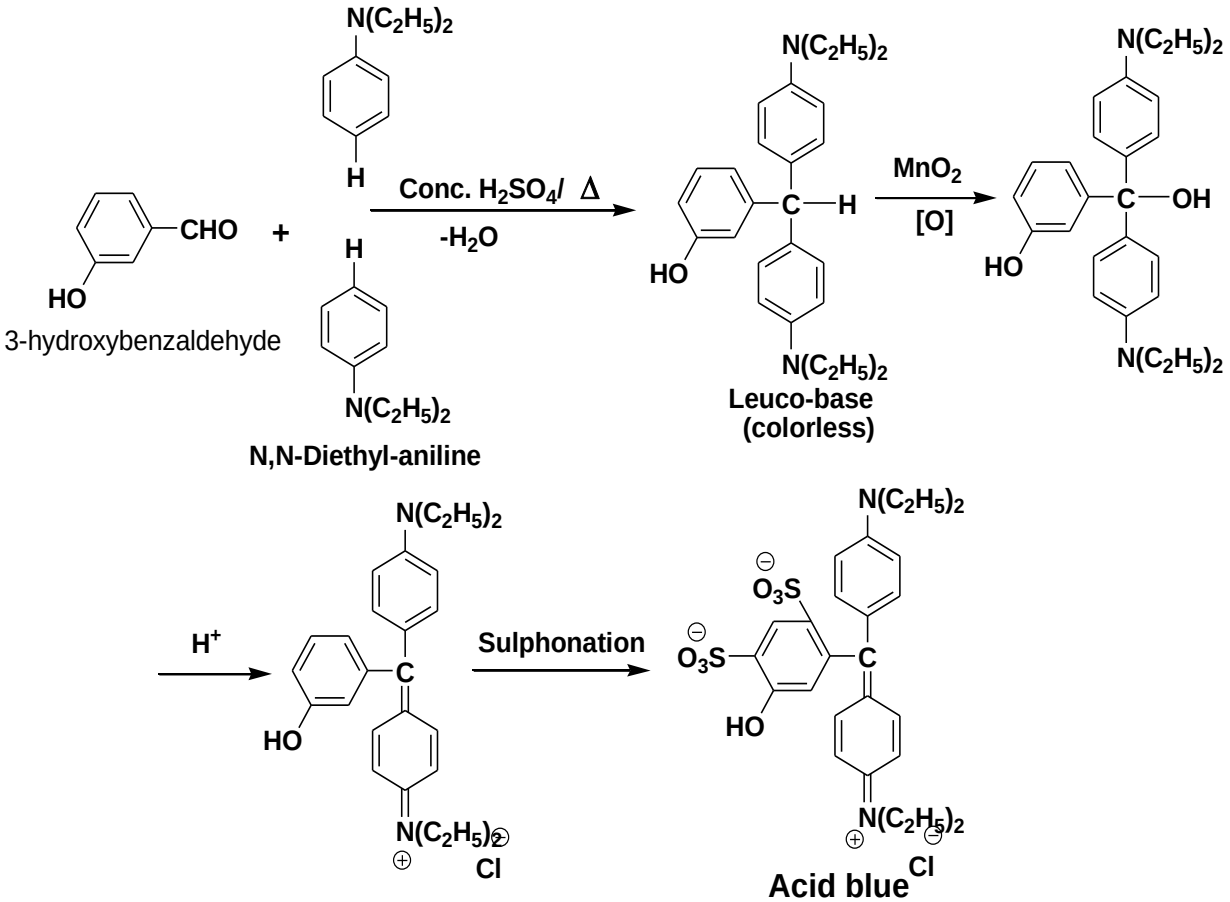
1) Acid violet :- used for **staining fingerprints and shoeprints .**



2) Acid green (wool green):

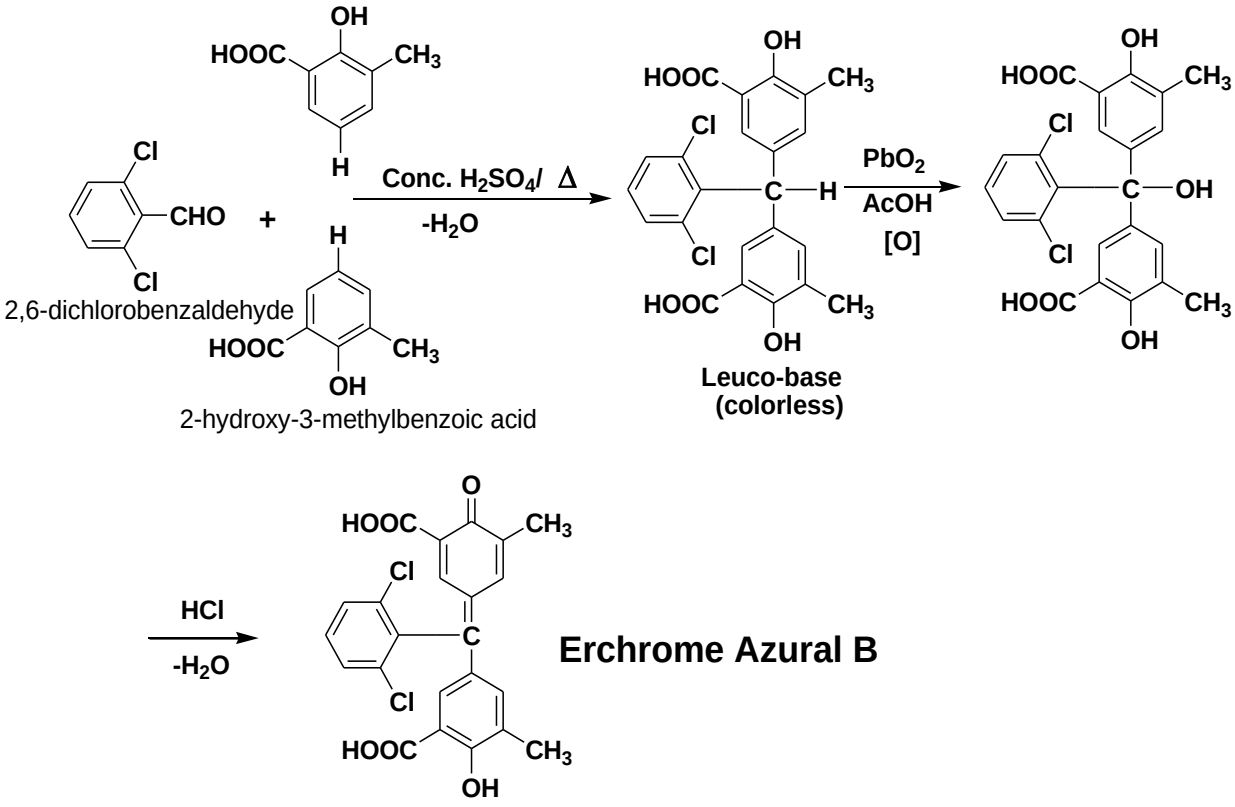


2) Acid blue (patent blue): patent blue is used for marking lymphatic vessels and arterial territories as well as for sentinel lymph node prior to biopsy in patients with operable breast cancer. Patent blue is also used in the textile, paper, agriculture and cosmetic industry

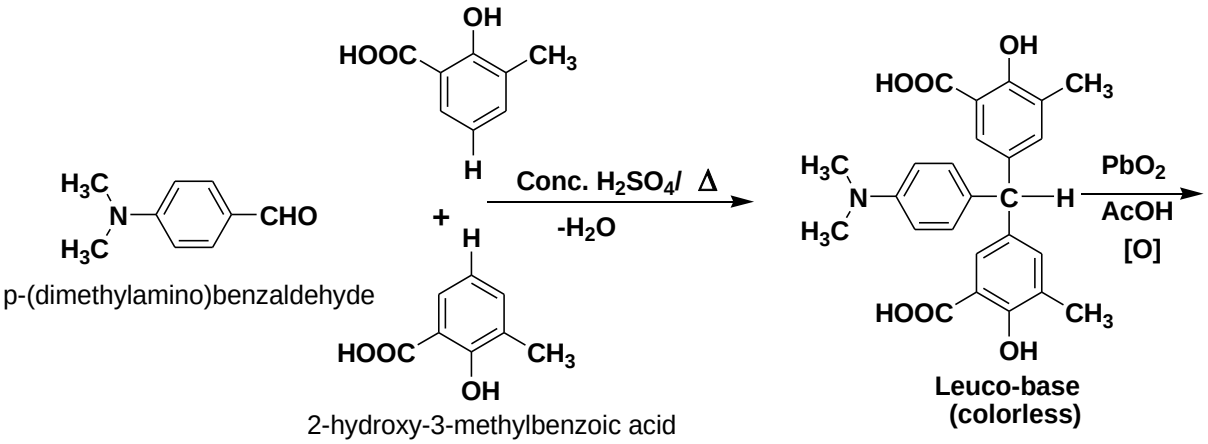


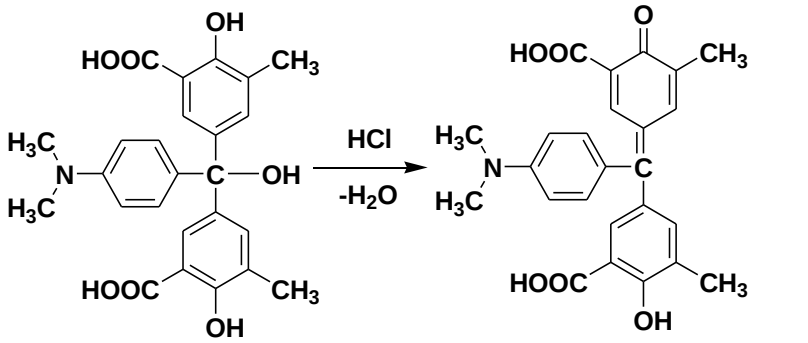
Hydroxy triaryl methane dye

1-Erichrome azurol B:



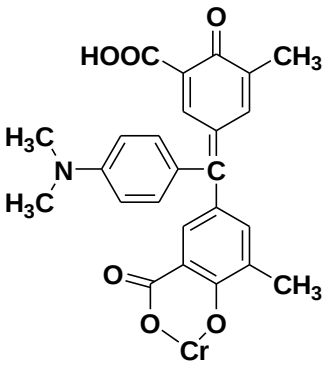
2-C.I Mordant violet Dye





C.I. Mordant violet

- **This dye is used for dying wool after treatment by Cr with bright blue shade.**


O
HOOC
CH3
H3C
N
H3C
C
O
CH3
O
O
Cr

Xanthene dyes

- The general skeleton:

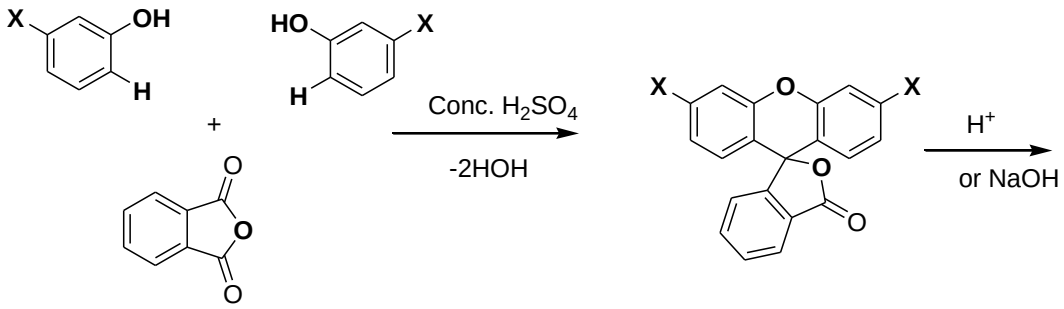
X = auxochromes (NH_2, NHR, NR_2, OH).

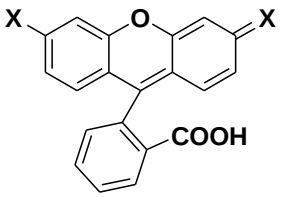
X must be in para-position to CR_2

- The color is due to formation of quinoid structure.

Xanthene dyes

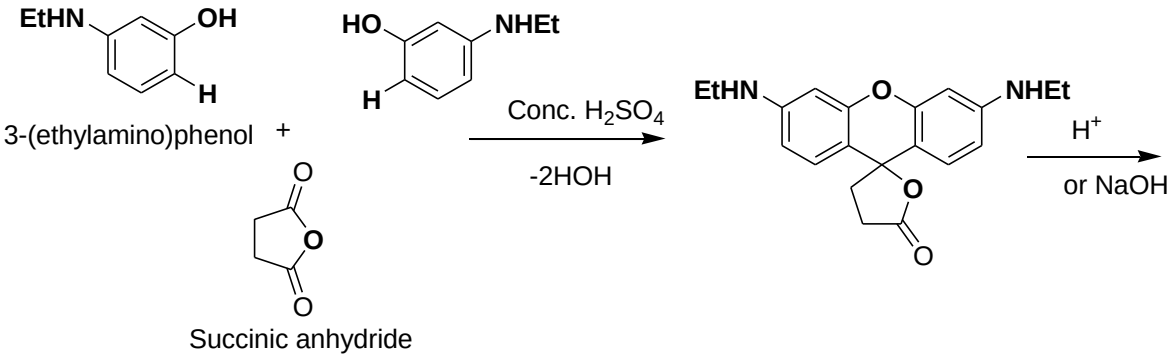
General procedures

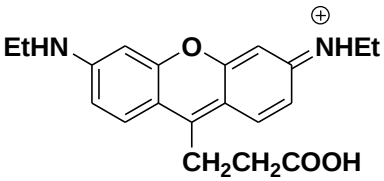




Where X = NH_2 or NHR or NR_2 the dye is called rhodamine

1- C.I. Basic red

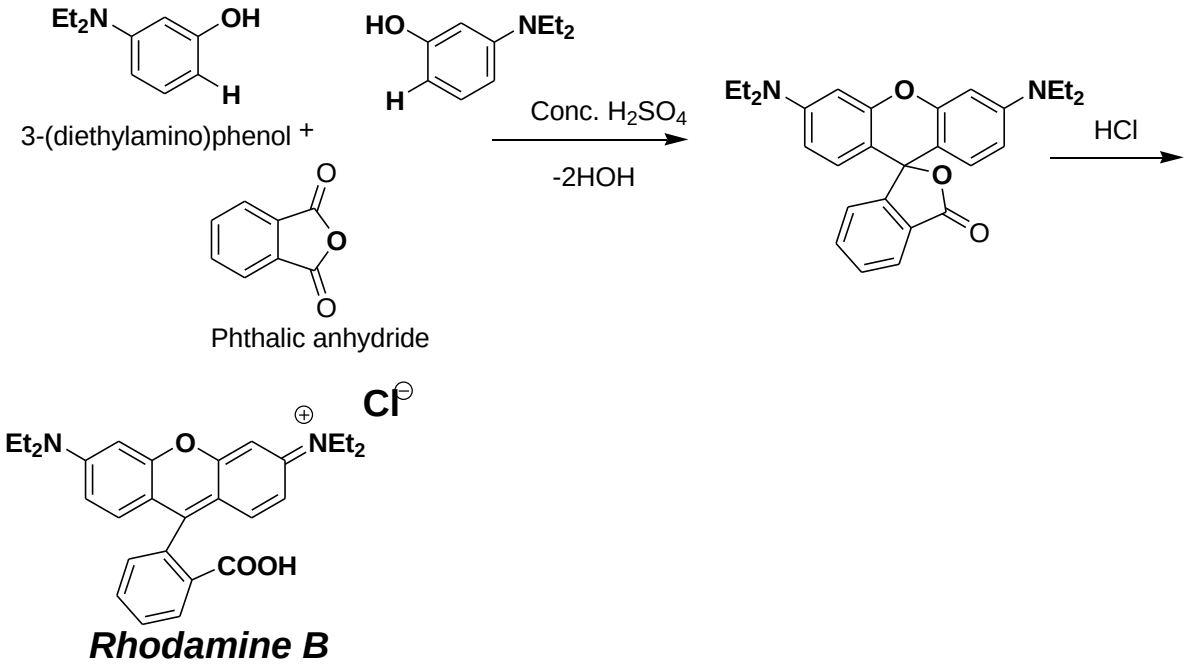




C. I. Basic red

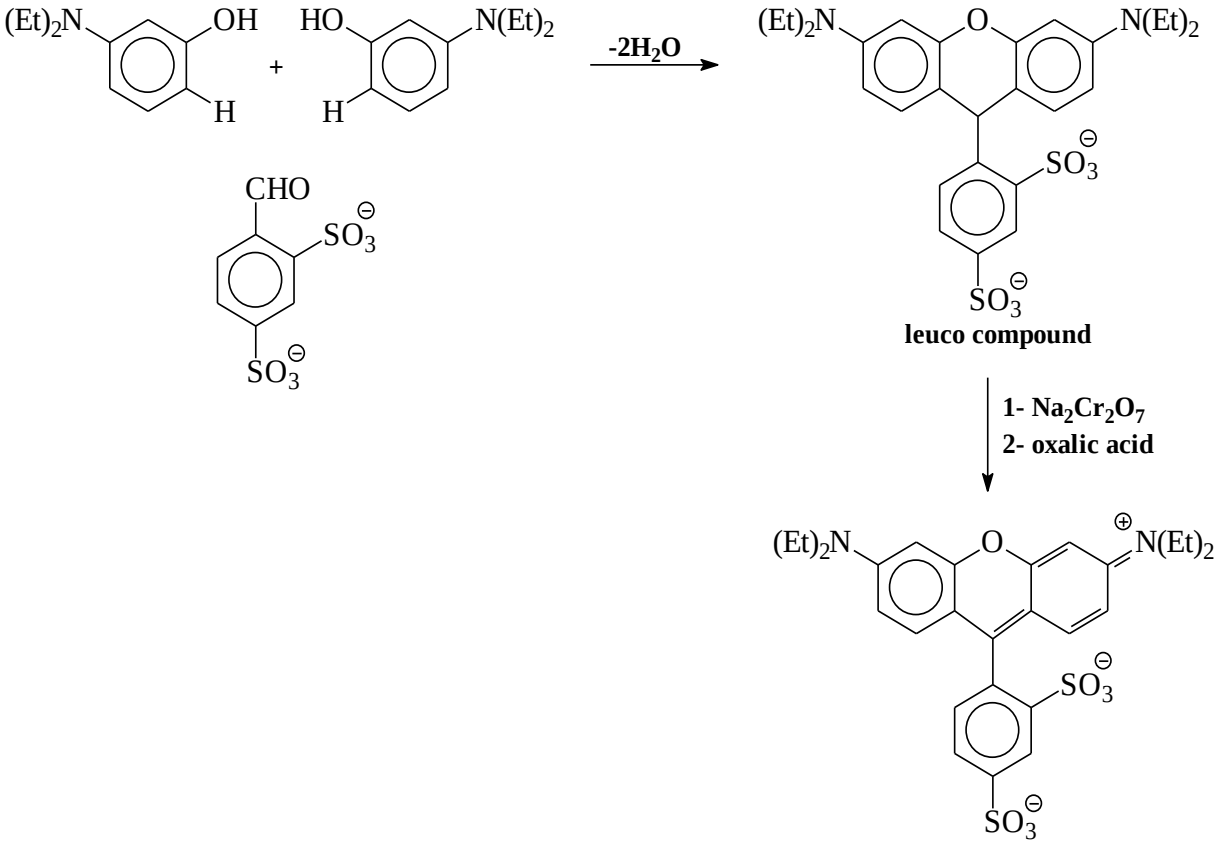
3) Rhodamine B

Rhodamine B (RhB) is widely used in industrial purposes, such as **printing and dyeing in textile, paper, paints, leathers** etc. However, the organic dyes will cause serious environmental and biological problems, even capable to induce irritation to the skin, eyes**.** Rhodamine dyes are also used extensively in biotechnology applications such as fluorescence microscopy, flow cytometry, fluorescence correlation spectroscopy.

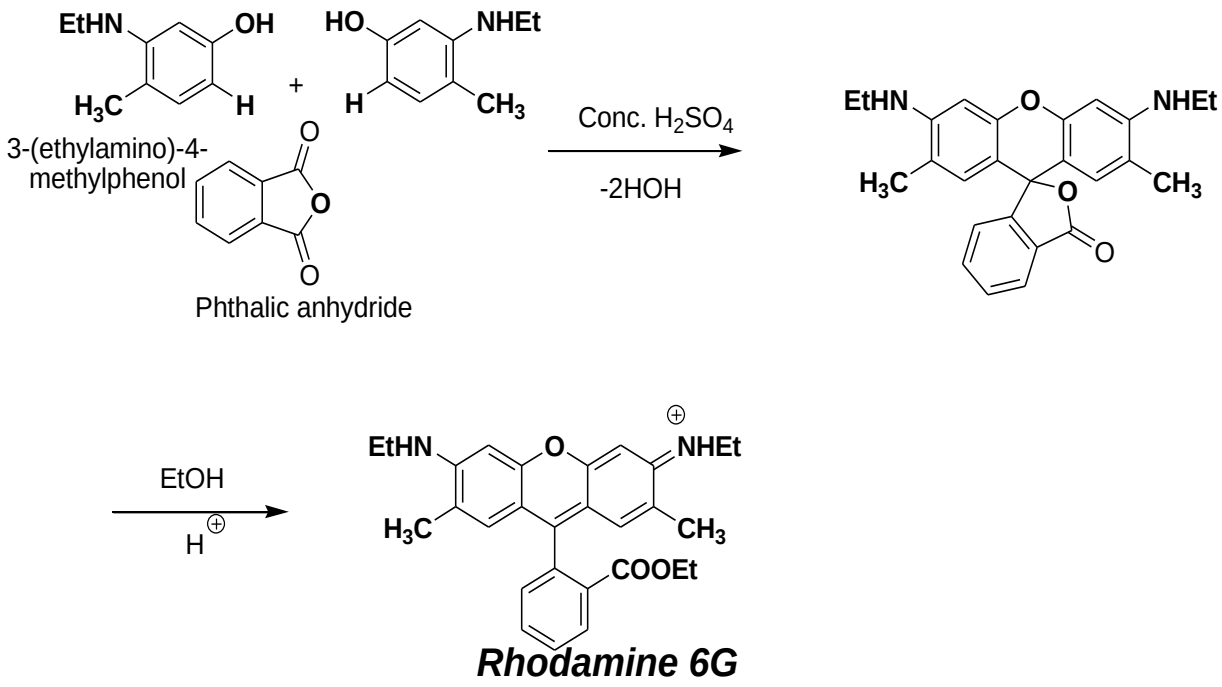


Rhodamine B

3) Sulphorhodamine (Rosamine dye)

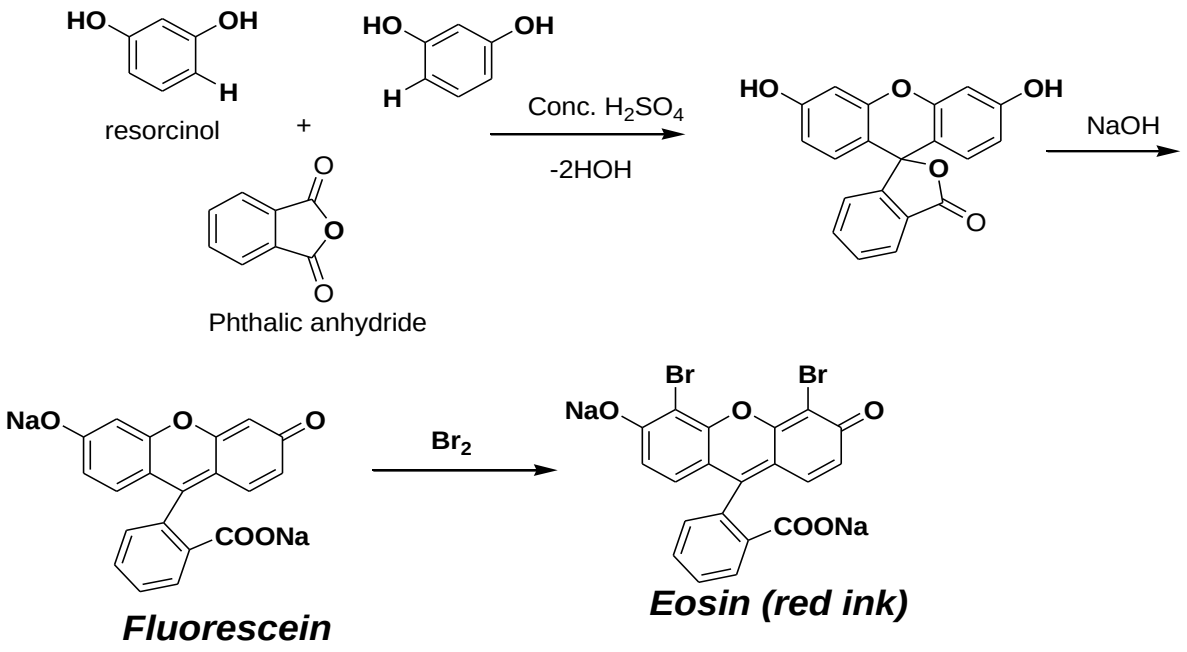


4) Rhodamine 6G



Rhodamine 6G

5) Fluorescein dye and its derivative (Eosin)



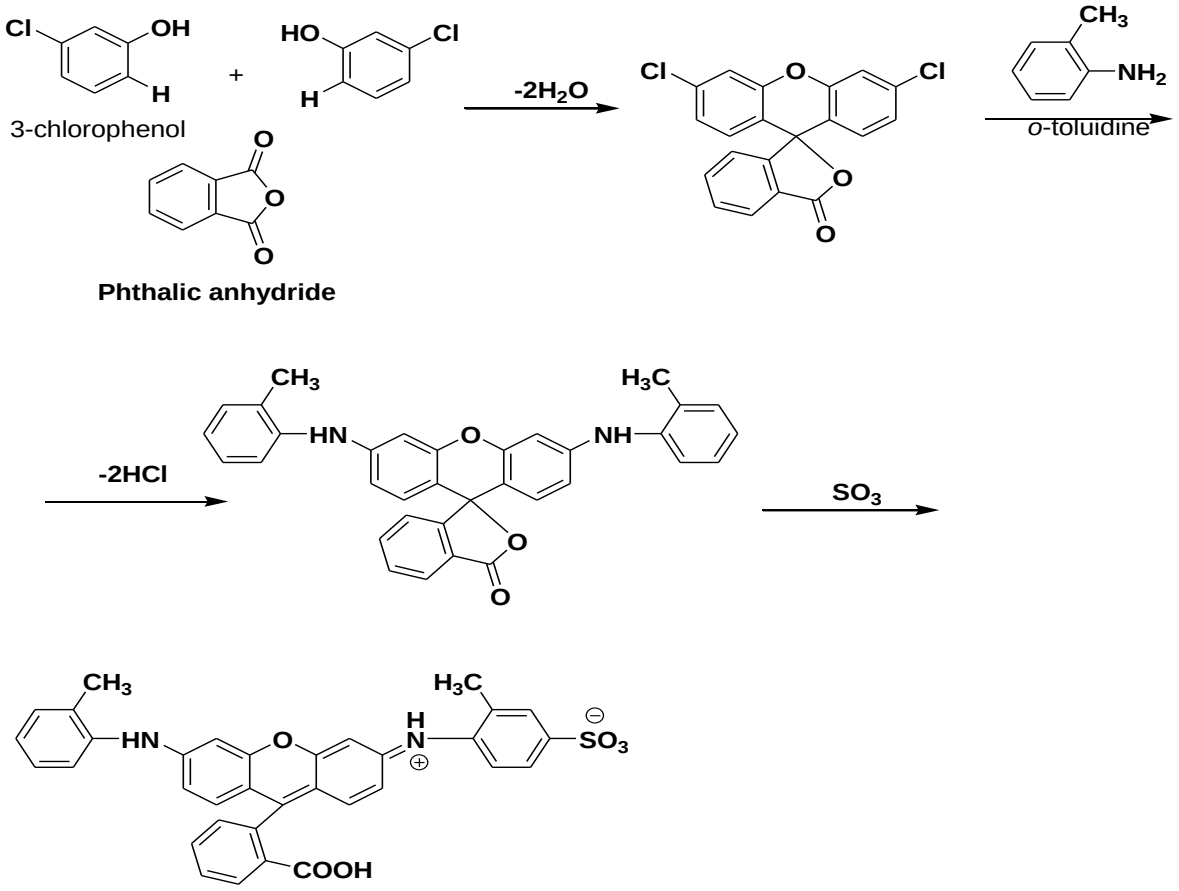
<u>3-Kiton fuchine A_2R:</u>

It is wool dye.

It is reddish violet dye with good fastness.

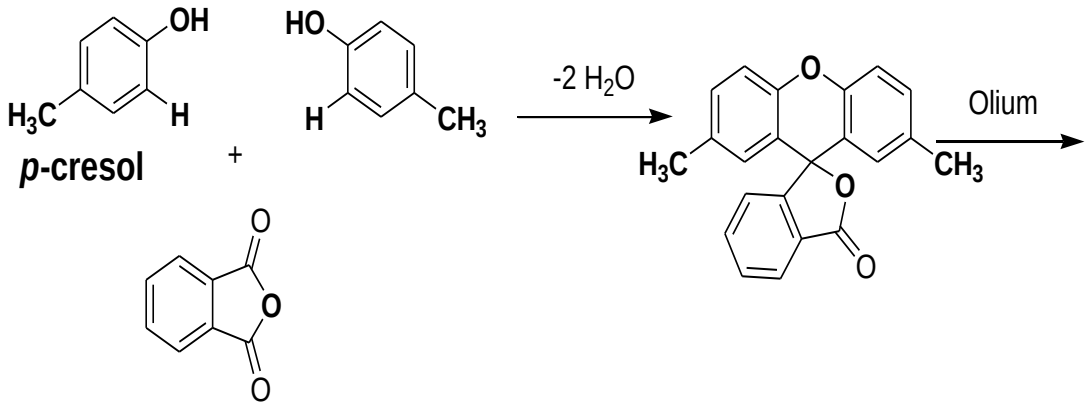
It can be used for paper coloration.

It can be prepared as follow.



4-Fluorol 5-G: (Coloring mineral oil)

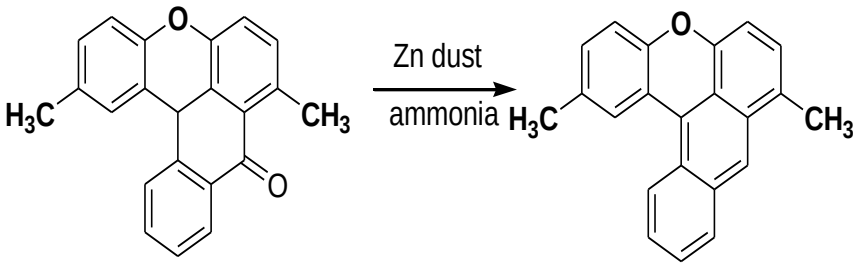
Fluorol Yellow 088 is a polyaromatic organic dye used to stain cells of suberin lamellae in plant tissue



***p*-cresol**

+

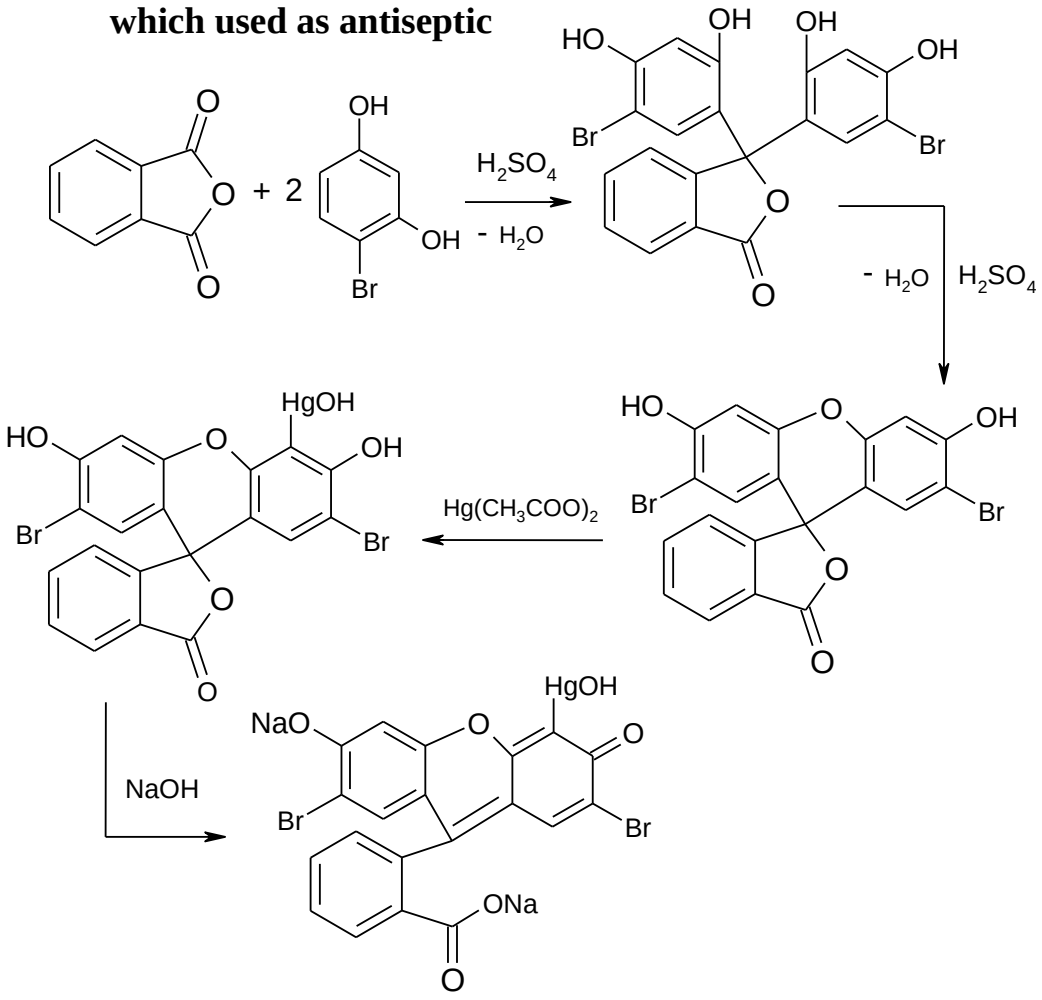
Phthalic anhydride



Fluorol 5G
Coloring mineral oil)

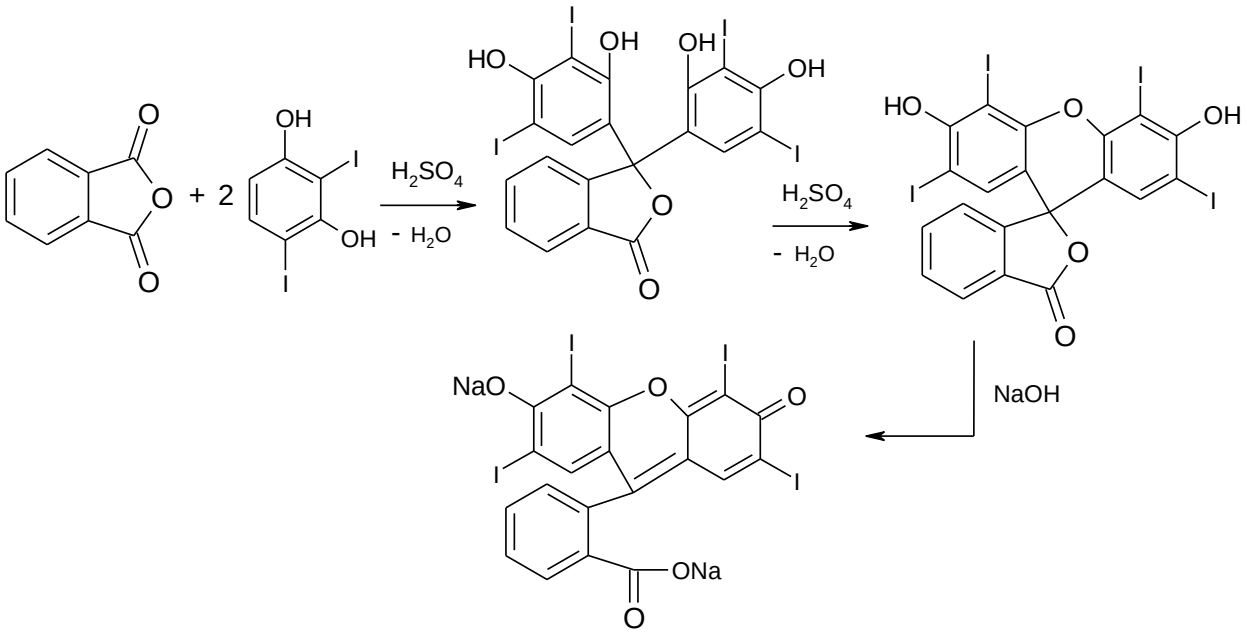
5- Merchrochrom dyes:

which used as antiseptic



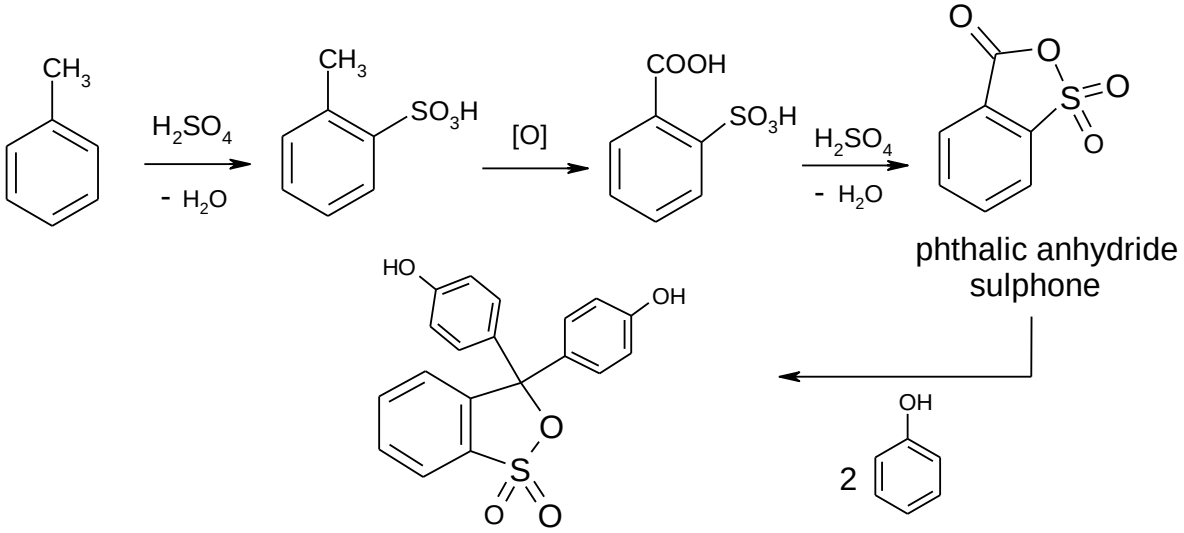
6- Erthorocine:-

It does not used in dyeing processes but it can be used in manufacture of medicine and in coloring of food with yellow color



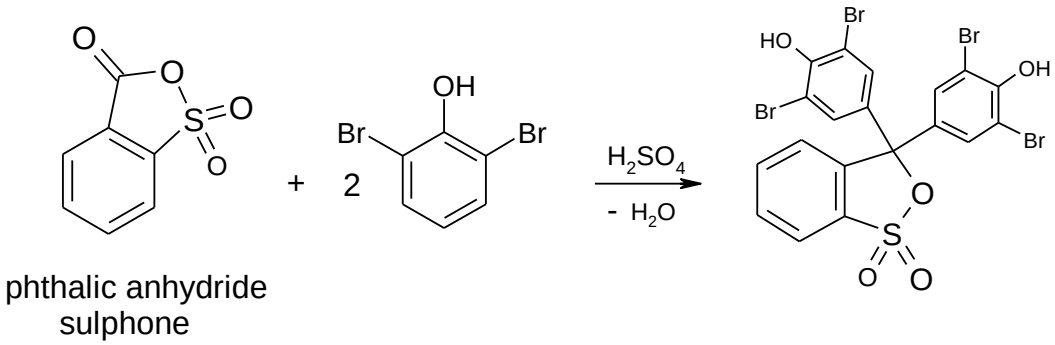
phthaleine sulphone dyes (phenol red)

Used in medicine and it has a red color.



B-Tetrabromo phthaleine sulphone

Bromophenol blue , is used as a pH indicator, a color marker, and a dye



phthalic anhydride sulphone

Vat dyes

are insoluble in their colored form. They are reduced by another chemical and converted to a soluble form .

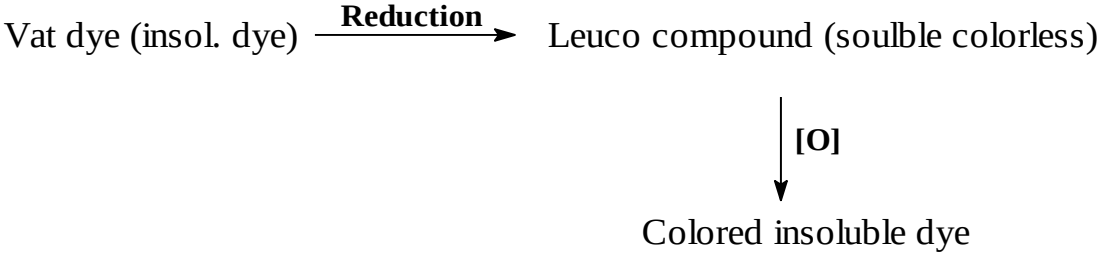
The reduced dye is applied to the fabric, and then exposed to the air which oxidizes he dye back to its colored form .

In this experiment indigo dye will be used to dye a sample of cotton fabric. Indigo is the dye used to make blue jeans

It classified into two types:

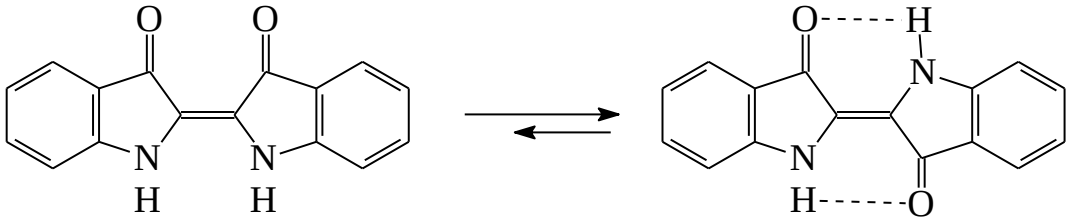
1- **Indigo dyes.**

2- **Anthraquinone dyes.**



Structure of indigotin:

Indigotin can exist in both cis and trans form.

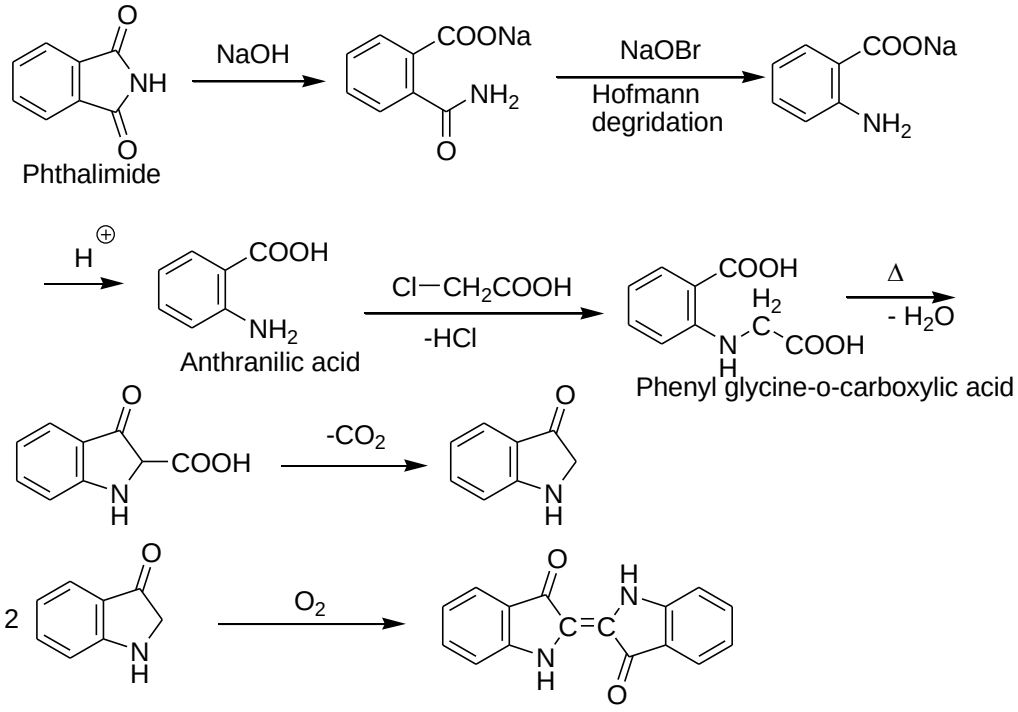


cis form
less stable

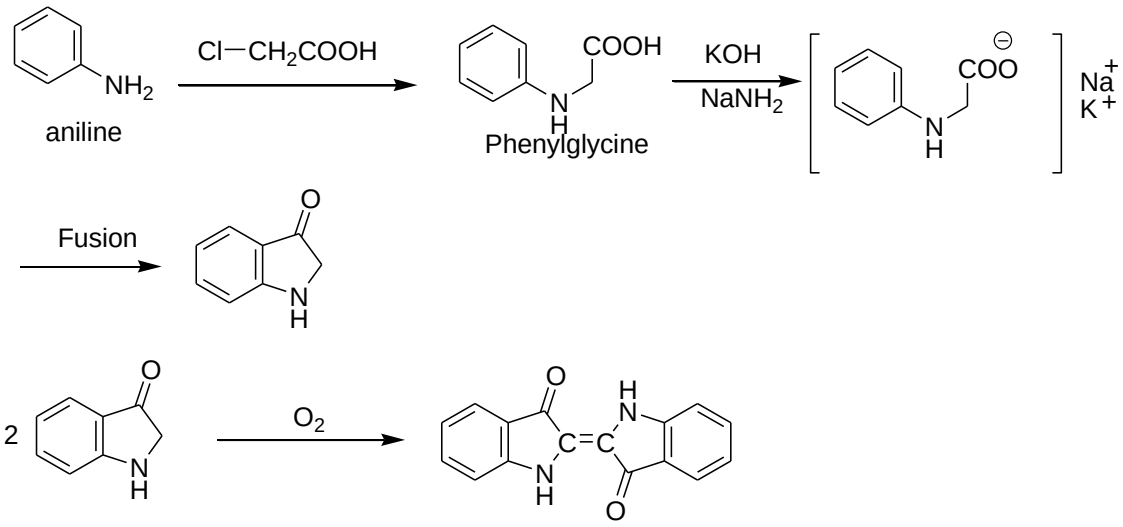
trans form
more stable due to
formation of H.b.

Synthesis of Indigo

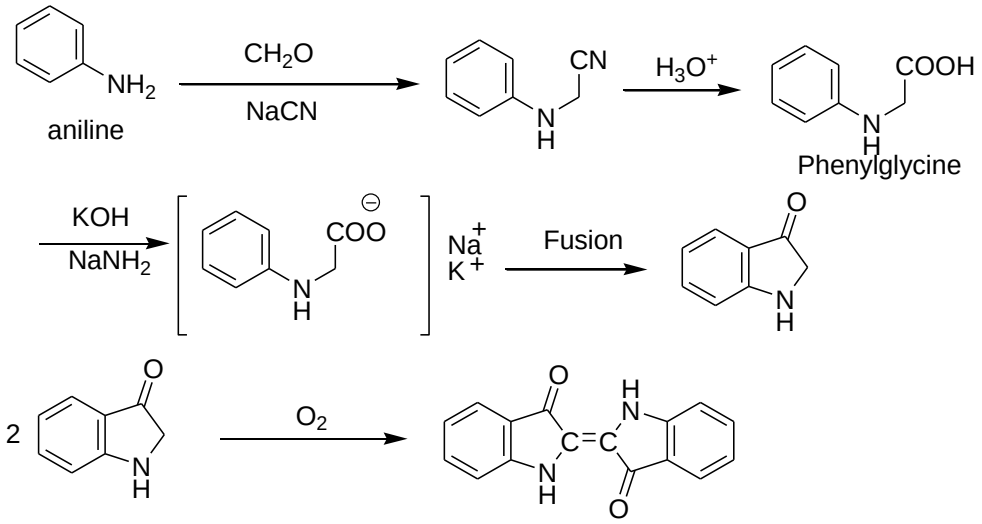
1. **Heumann process**



2. Sodamide process

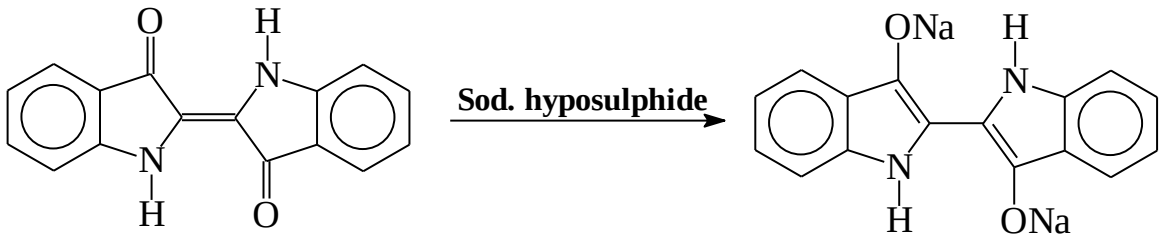


3. From aniline and sodium cyanide



Application of indigotin (vat dye) on cotton:

When indigotin paste is agitated with alkali in large amount, the indogotin is reduced to soluble leuco compound (colorless).



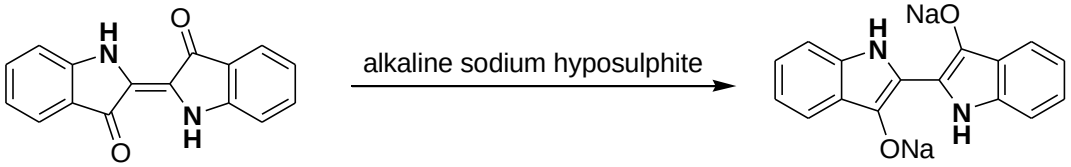
indigotin blue oxidized form water insol.

indigotin colorless reduced form water soluble

When cotton is to be dyed is soaked in the alkaline medium and then exposed to air, where upon the original blue dye is regenerated in cloth.

Indigotin derivatives

1) Indigotin white

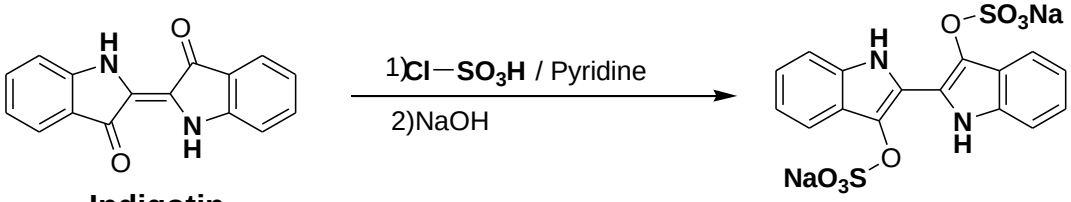


Indigotin
dark blue
water insoluble

White Indigotin
colorless
water soluble

2) Indigosol O

- **It is used for dying wool**



Indigotin

Indgosol O
Water soluble

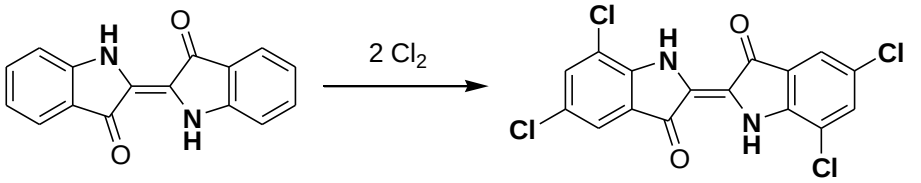
$NaNO_2/H^+$
oxidizing agent

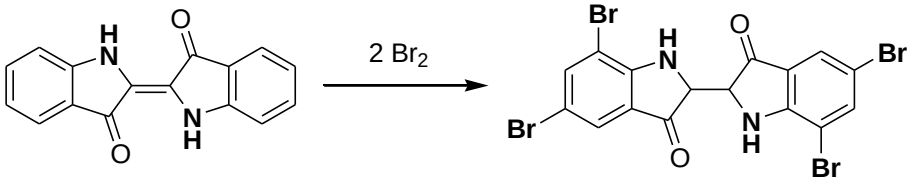
Indigotin

Application of Indigosol on fibres

Indigosol O is applied on both animal and vegetable fibres by soakin the fabic in the solution, and then oxidizing the indigosol O in acid solution (with $NaNO_2$) to the original insoluble vat dye.

3) Brilliant indigo B and Brilliant indigo 2B



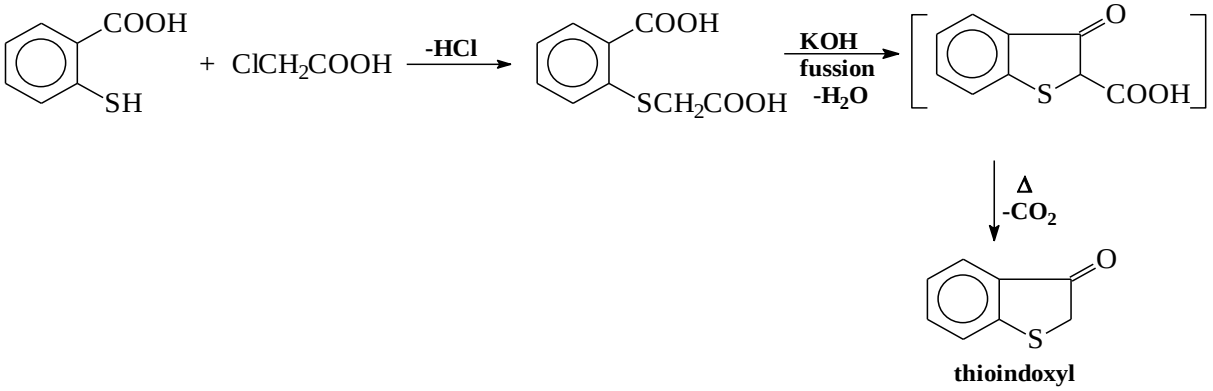


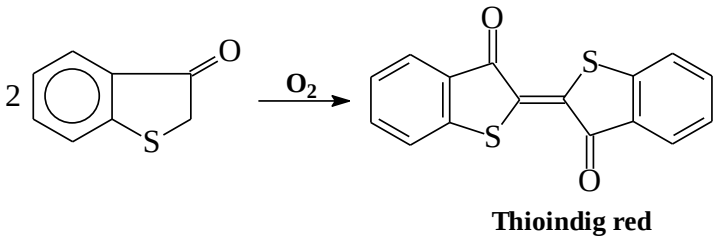
5,5',7,7'-tetrabromo Brilliant Indigo 2B

Preparation of thio-indigo:

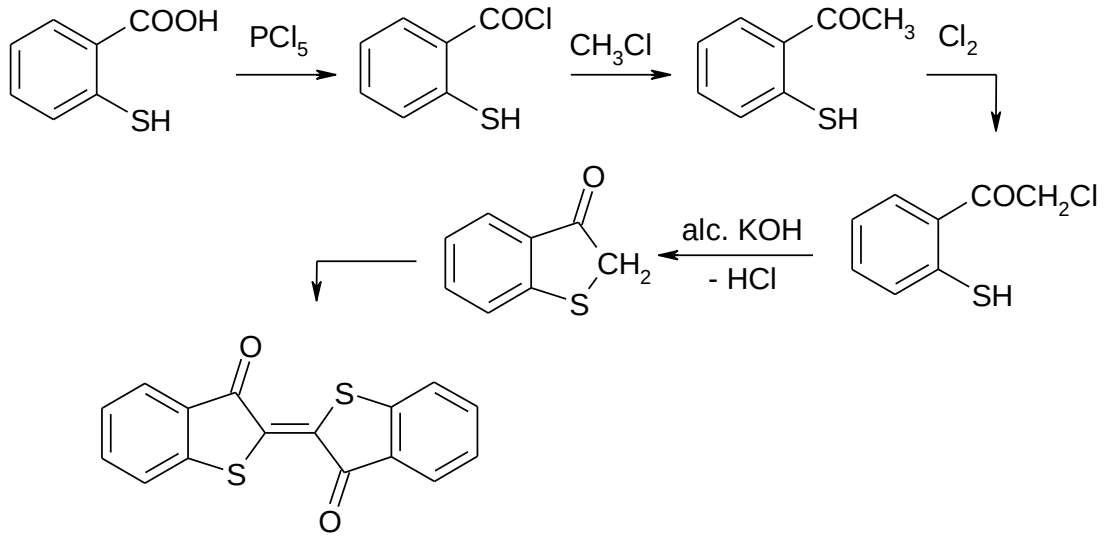
thioindigo is an organosulfur compound that is used **to dye polyester fabric**. A synthetic dye, thioindigo is related to the plant-derived dye indigo, replacing two NH groups with two sulfur atoms to create a shade of pink**.**

First method

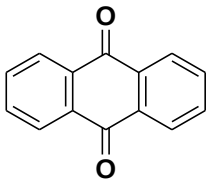




Second method

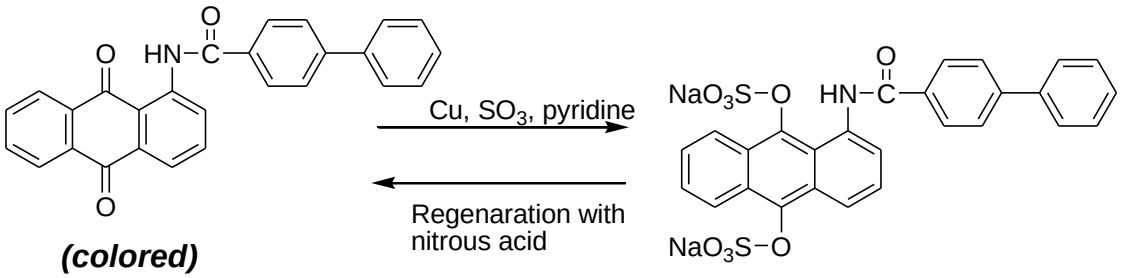


Anthraquinone dyes:



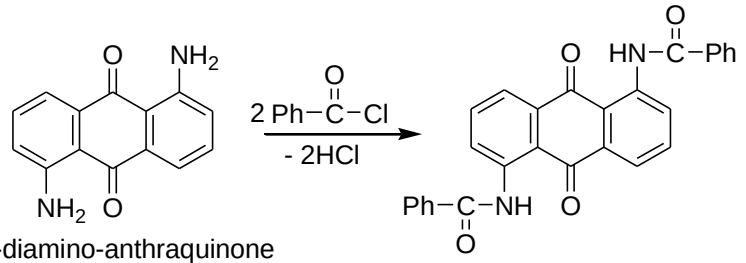
Anthraquinone

- **The application of anthraquinone dye, where it is used as leuco form and the color regenerated on fibre by nitrous acid as shown**



1) Indanthrone dyes:

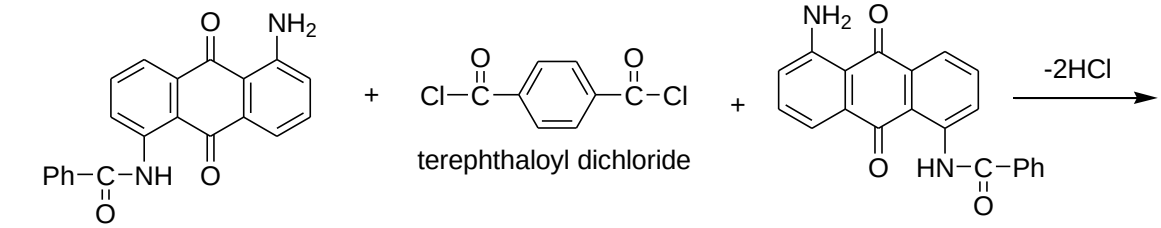
Synthesis of C.I vat yellow(cibanone yellow FGK), (Indanthrene yellow GK)



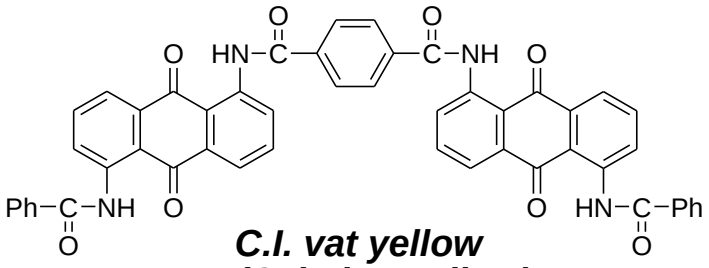
1,5-diamino-anthraquinone

C.I vat yellow(cibanone yellow FGK), (Indanthrene yellow GK)

Synthesis of C.I vat yellow (Caledon yellow)



1-Amino-5-benzoylamino-anthraquinone

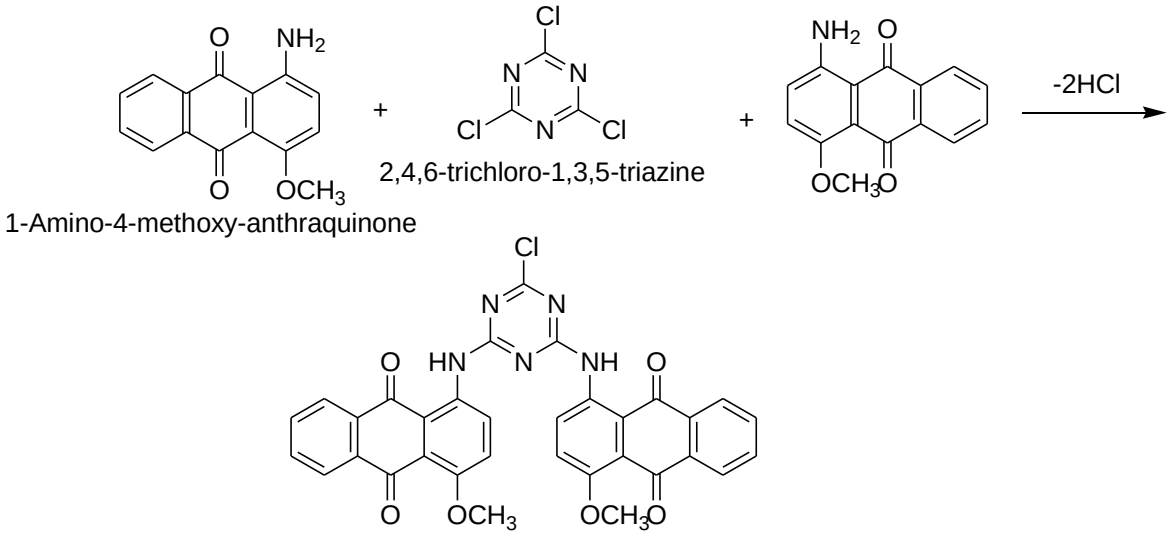


C.I. vat yellow (Caledon yellow)

Synthesis of C.I. vat orange (Cibanone Orange 6R)

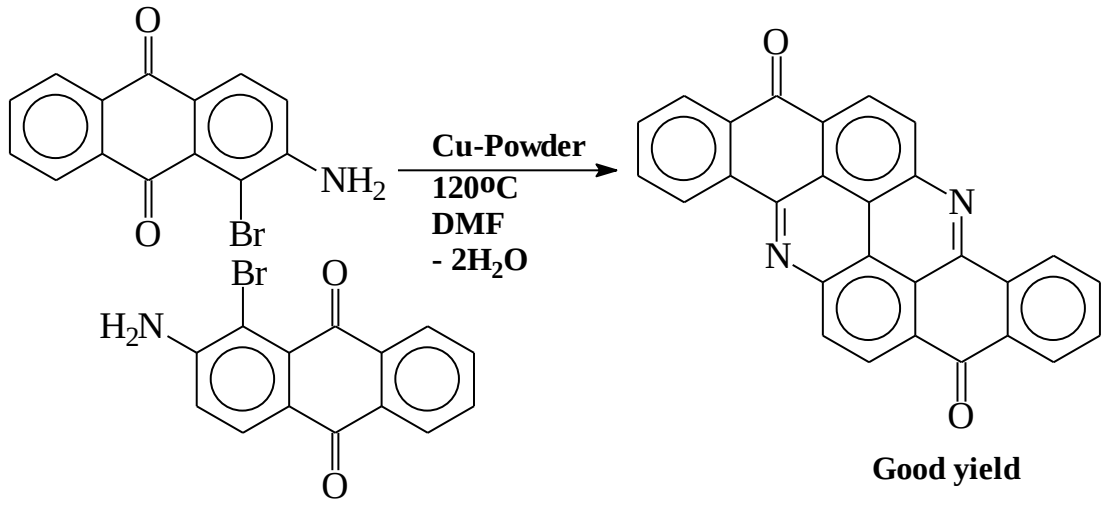
- **Cibanone Orange 6R is an example of reactive dye which is used for dying cellulosic fibres**

- **It is type of reactive dye**



C.I. vat orange
(Cibanone Orange 6R)

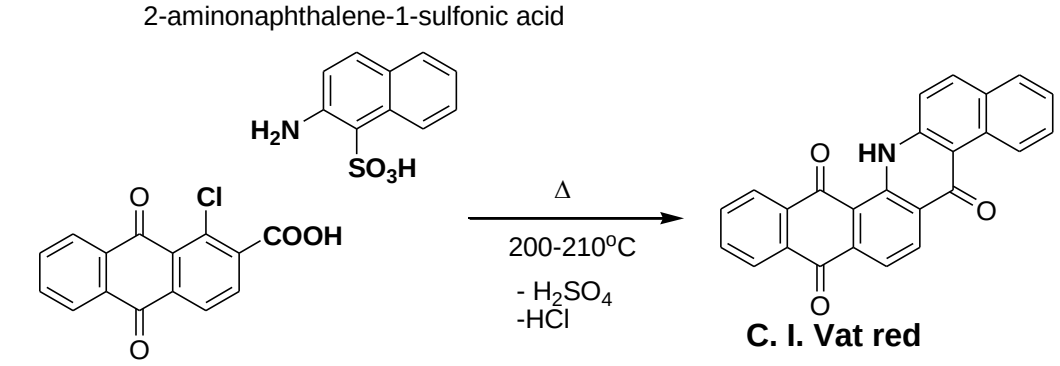
C) Flavanthrone (Indanthrone yellow G):



Good yield

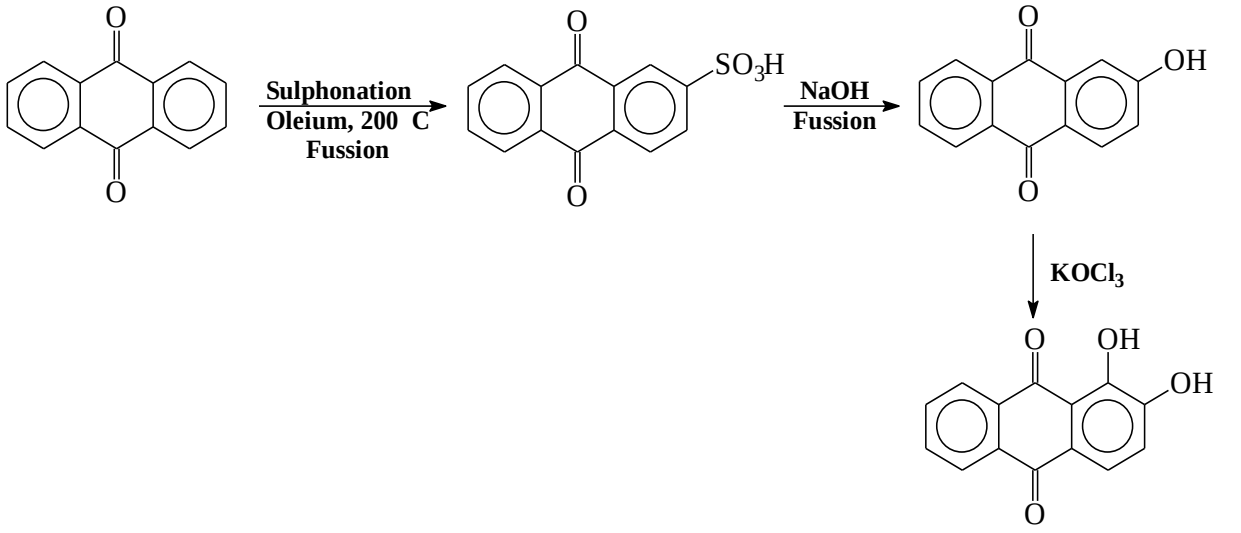
Anthraquinonacridine

Synthesis of C.I Vat red



1-Chloro-anthraquinone-2-carboxylic acid

Alizarine



Alizarin
1,2 dihydroxy 9,10 anthraquinon

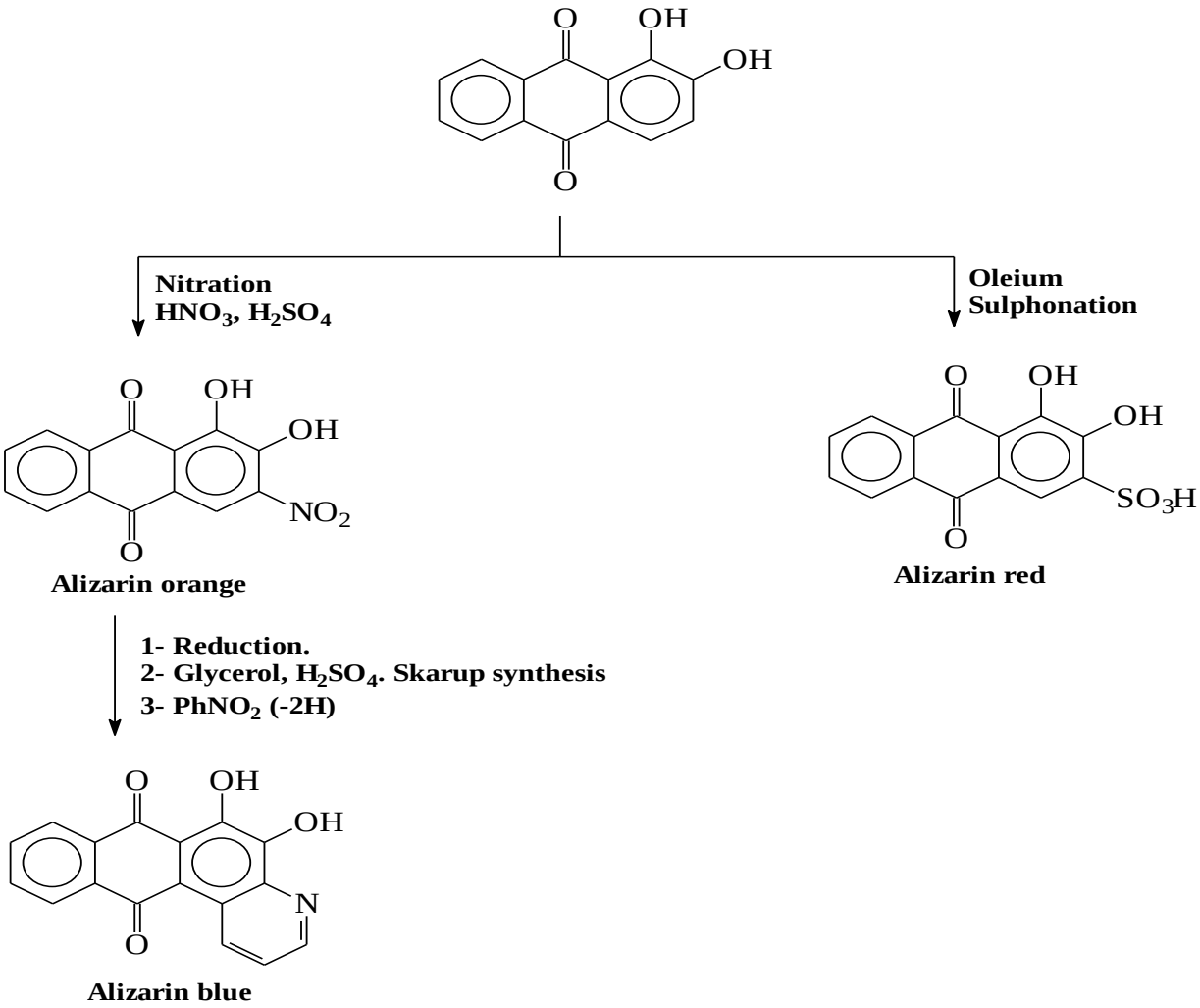
Alizarin is used to prepare:

a- Alizarin orange.

b- Alizarin red.

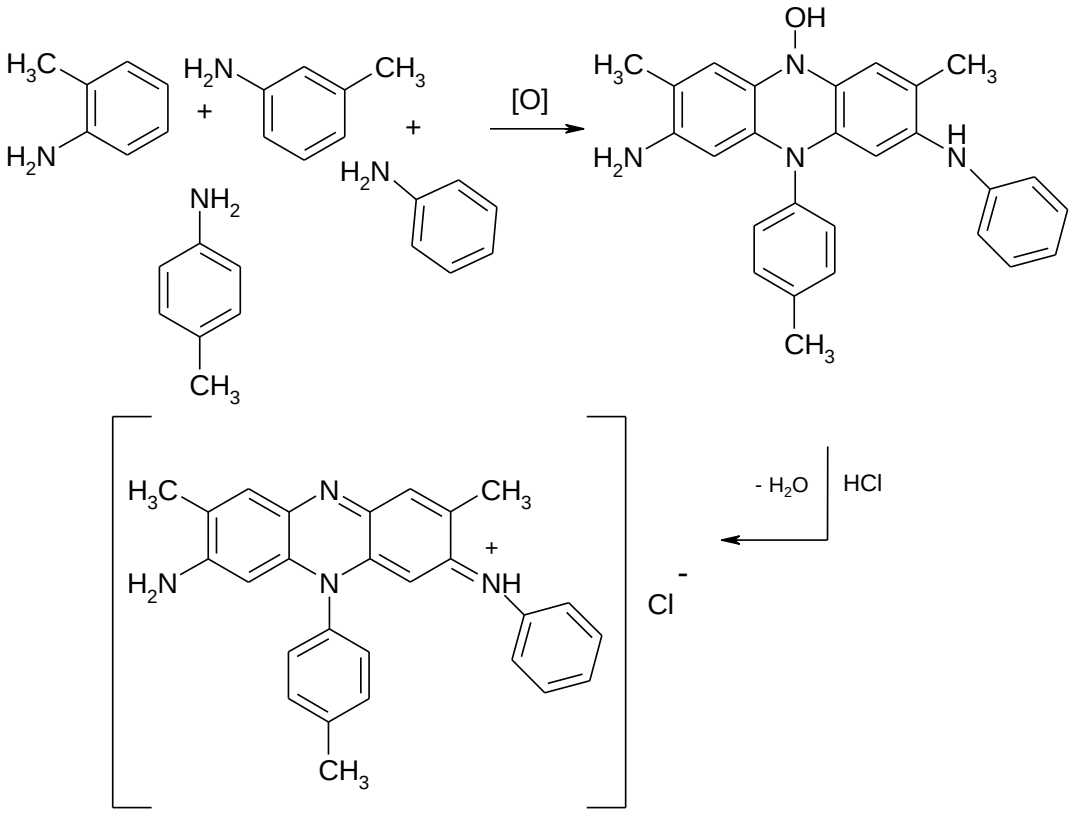
c- Alizarin blue.

As the following:

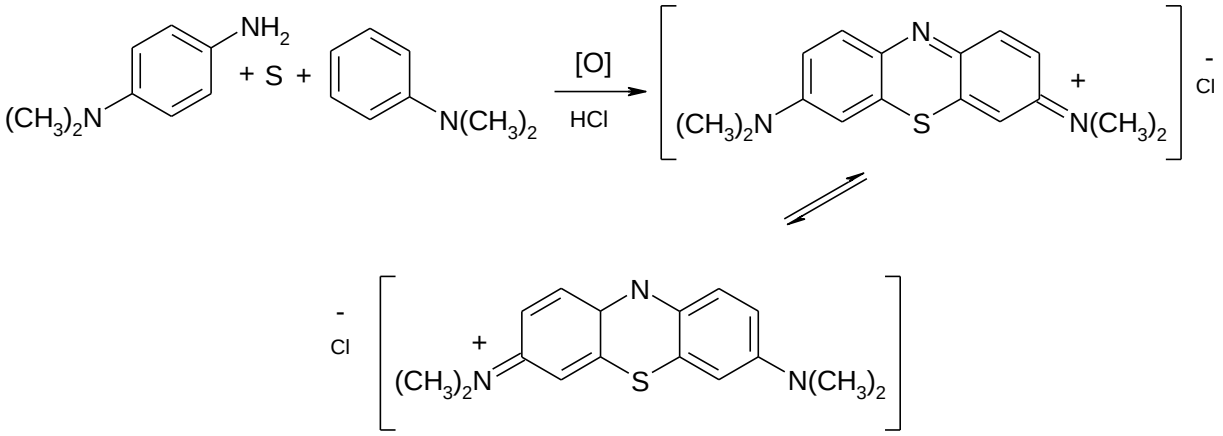


Azine dyes

1-mauvin dye:-Used in dyeing silk and cotton with reddish violet color.



3- methylene blue:- used in dyeing wool and silk with blue color.



Fiber

- Types of forces (bonds) by which dye molecule are bound to fiber:

1- Van der Waals forces:

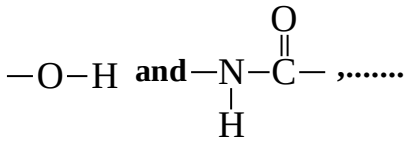
Vander Waal forces are due to interaction between π-orbitals of dye and fiber. The Van der Waal forces are effective in linear dyes i.e. long and flat. Van der Waal forces are very weak forces. It is present in certain wool dye and majority polyester and

2-Hydrogen bonding:

The hydrogen bonding is resulted as result of acceptance of hydrogen atoms of lone pair of electrons from an electron donor groups such as:

$-\ddot{N}H_2$ ， $-\ddot{N}=\ddot{N}-$ ，$-\ddot{O}H$

- Examples of electron acceptors are hydrogens of



- The hydrogen bond is weaker but stronger than Vander Waal forces.

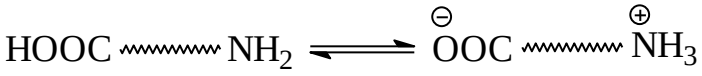
- Examples of fiber, which are bound by hydrogen bond, are silk, wool, synthetic Fibres.

-Not suitable for cellulose fibers because it forms hydrogen bond with water than with dye

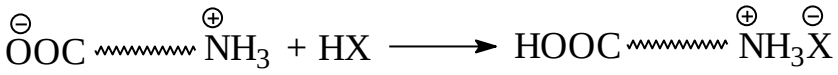
<u>3-Ionic bond</u>

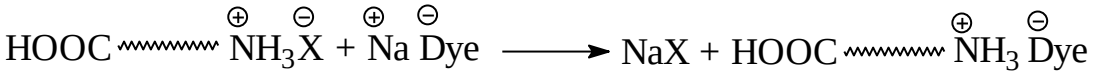
- It is interaction between -ve center of dye with +ve center of fiber and vice versa.

- Wool fiber is bound with ionic bond with sodium salt of dye. The ionic bond is formed when dyeing process occur in diluted acidic medium as follow:



wool fiber **Dipolar wool fiber**



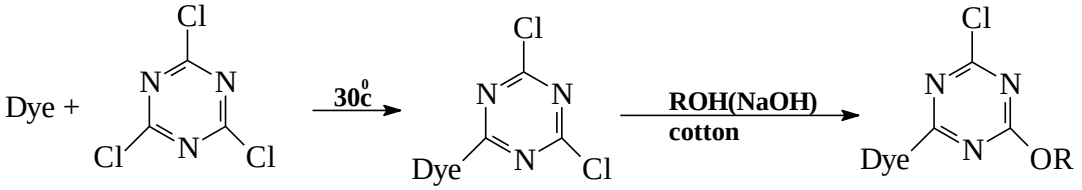


4- Covalent bond:

It is actual chemical bond between fiber and dye through crosslinkage agent such as 2,4,6-trichloro triazine.

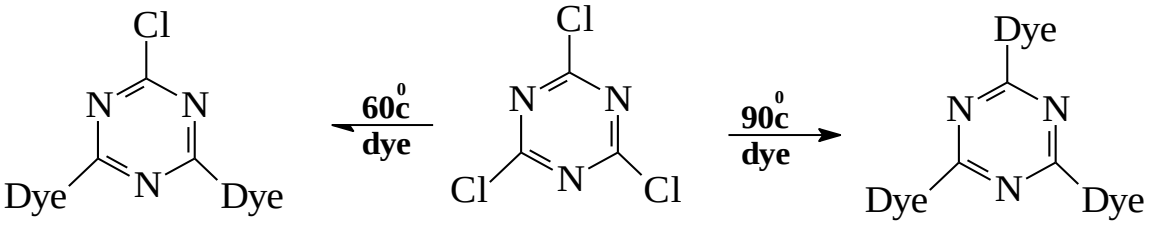
It is called reactive dye

Example of covalent bond of cotton (R-OH) and Dyes containing NH2 or OH



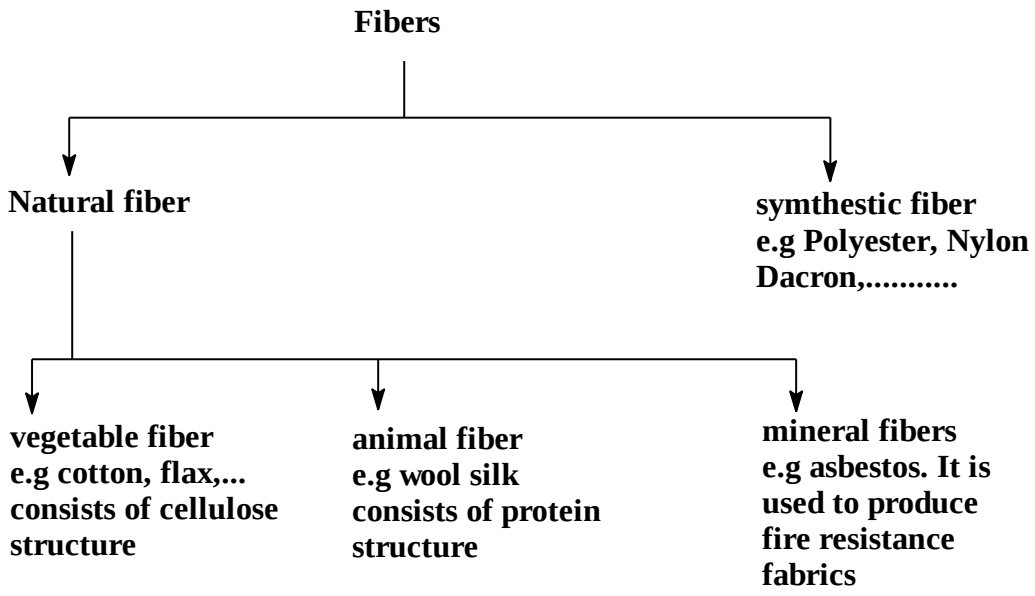
trichloro triazing **reacdive dye**

- The number of dye molecules is affected by temperature



not attach with fibr

- **Classification of fibers:**



plant fiber :

Plant fibers are generally composed of cellulose, often in combination with other components such as lignin.

Examples include cotton, hemp, jute, flax, sisal, ...

Animal fiber :- generally comprise proteins such as collagen, keratin like : wool –silk –goat hair (cashmere, mohair)

1- Structure of cotton:

-Cotton consists of 88-96% of pure cellulose. Cellulos is a long-chain polymer of beta-glucose molecules joined together.

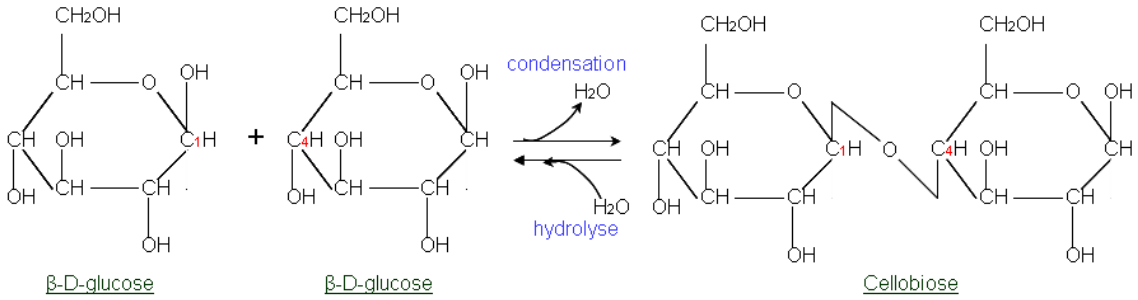
-consisting of 3,000 or more glucose units.

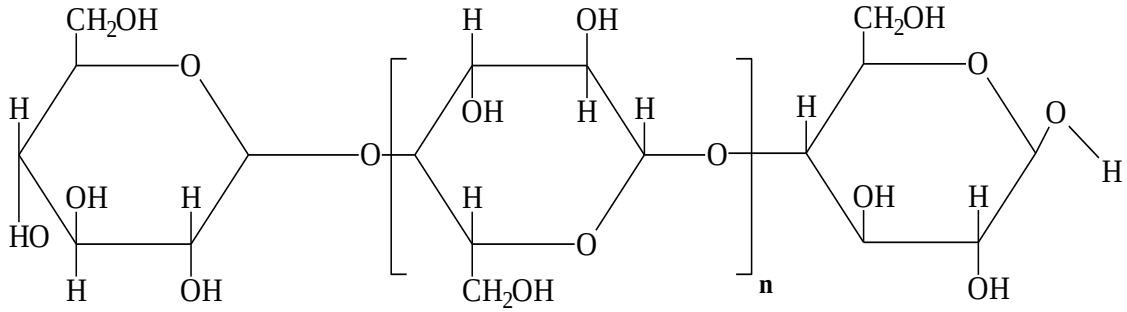
-Cellulose is an organic compound with the formula

-$(C_6H_{10}O_5)_n$, a polysaccharide consisting of a linear chain of several hundred to many thousands of β(1→4) linked D-glucose units.

-Cellulose is a straight chain polymer.

-Cellulose is an important structural component of the primary cell wall of green plants,


condensation
H2O
H2O
hydrolyse
β-D-glucose
β-D-glucose
Cellobiose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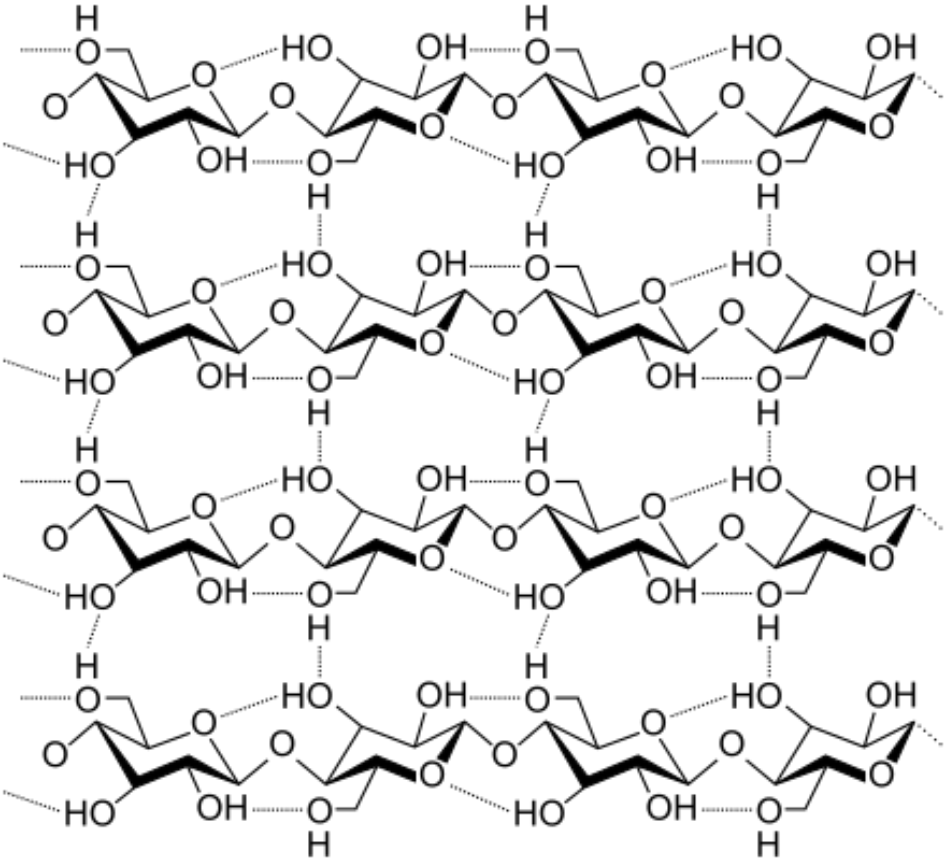


The dying of cotton depends on:

Presence of –OH, which give the hydrophilic character for cotton.

The size and configuration of glucose units.

The chemical composition of cotton:

Cotton consists of 88-96% cellulose and other components are protein, ash, wax, starch.

Modification of cotton:

(1) Mercerization of cotton:

- In mercerization process, cotton is treated with 50% NaOH, so cotton fiber will swell and shrinked.

- After treatment of cotton, the alkali is removed by washing with water.

$$\underset{\textbf{cotton 50\%}}{ROH} + NaOH \longrightarrow \underset{\textbf{mercerized cotton}}{RONa}$$

- Mercerized cotton has similar structure of cotton (both consists of glucose) but mercerized cotton has advantages than non-mercerized.

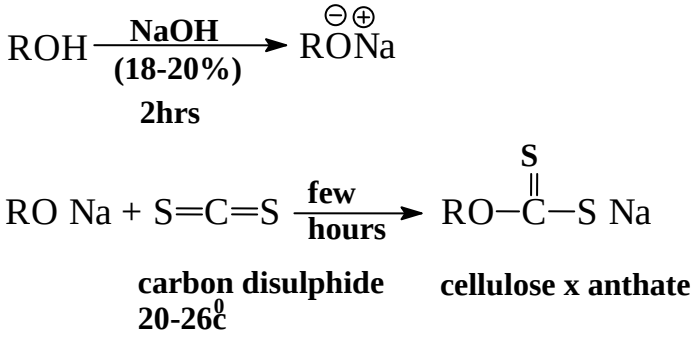
1- The fiber stronger.

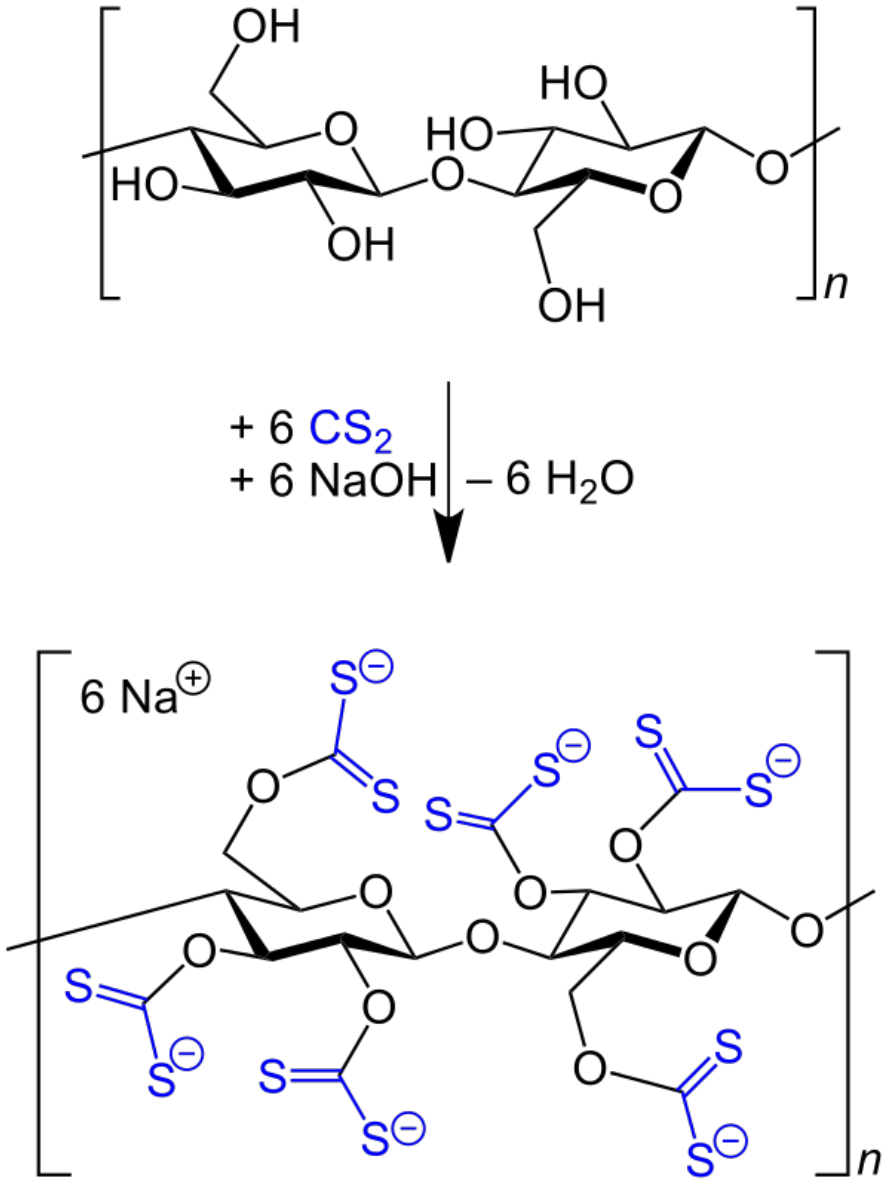
4- **The fiber has an increased affinity for dyestuffs أكثر قابلية للصباغة.**

artificial fibers

(1) viscose

Viscose **is a type of rayon fiber that is made from natural sources such as cellulose fiber. The molecular structure of natural cellulose is preserved in the process. The many types and grades of viscose fibers can imitate the feel and texture of natural fibers such as silk, wool, cotton, and linen. The types that resemble silk are often called artificial silk. The fibre is used to make textiles for clothing and other purposes**





(cellulose xanthate)

Cellulose xanthate is soluble in water forming viscous solution, which gives rayon fibers after purification.

Rayon is purified by washing with Na2S at first then by sod. Hypo chlorite dilute acid, NaOH and finally water

(2) Production of cellulose acetate:

Wood pulp لب الخشب or cotton linters القطن بعد عملية الحلج are used as raw materials in cellulose acetate production.

Variation in properties (advantages) of acetylated cotton than non-acetylated.

1- It is more resistance to degradation by heat.

2- More resistance to attack by microorganism and chemicals.

- Production of cellulose acetate occur as follow

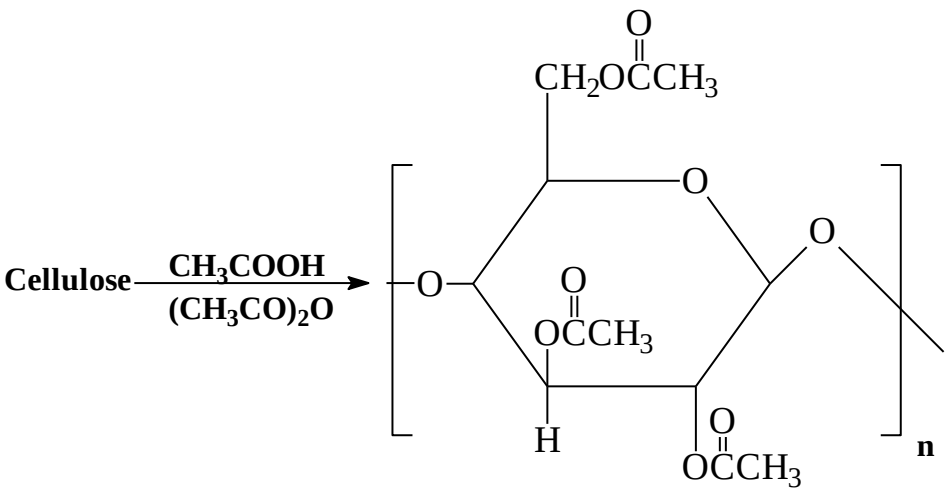
(A) Pretreatment:

The cellulose is pretreatment with acetic acid; this opens up the structure and makes the polymer more reactive.

(B) Acetylation:

- Acetylation is the chemical process by which H of –OH is replaced by CH3C=O gp.

- Acetylation occurs by mixing of cellulose with ACOH and AC2O in presence of catalyst.



cellulose triacetate

controlled alkaline hydrolysis

cellulose acetate contain 2-3 acetyl group per glucose unit

- Cellulose acetate is precipitated by adding H2O, the precipitate is washed, dried and it has white flakes shape قشور بيضاء الشكل

(C) Spinning الغزل

- The spinning solution is made by dissolving the cellulose acetate flake in acetone containing small quantity of H2O. This solution is filtered then pumped through spinneret (المغزل) to form filaments خيوط, which are solidified by passing current of worm water. Then, the filaments are stretched تمط, these produce continuous filaments.

Properties of cellulose acetate and cellulose triacetate:

Low moisture uptake

High melting point.

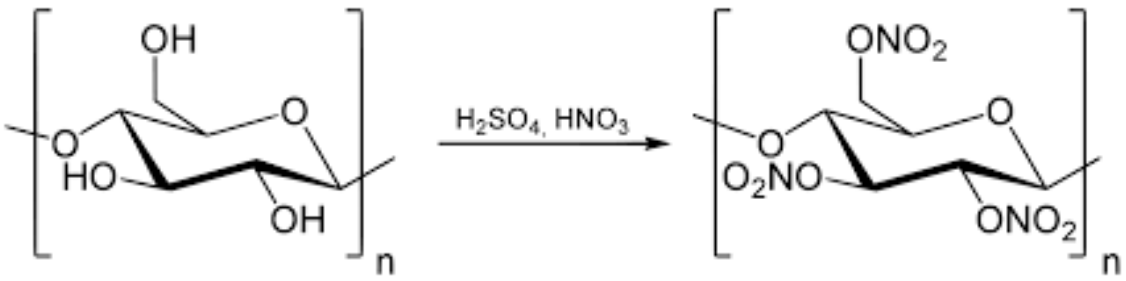
Good heat resistance

(3) cellulose nitrate silk :-

Nitrocellulose (also known as cellulose nitrate, flash paper) is a highly flammable compound formed

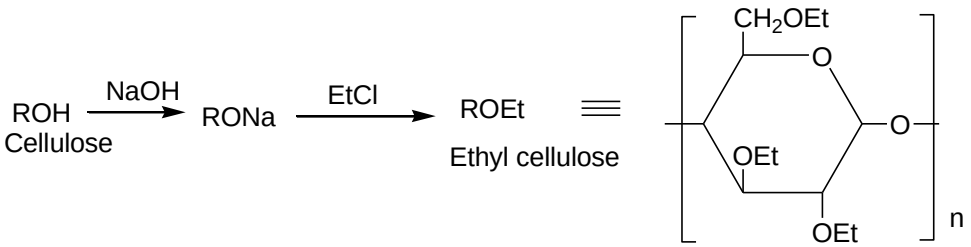
by nitrating cellulose through reaction of mixture of nitric acid and sulfuric acid.

-One of its first major uses was as guncotton, a replacement for gun powder as propellant in firearms.



(4) Cellulose ether:

- It is prepared by reaction of ethyl chloride on alkaline cellulose.



- Ethyl cellulose is used to manufacture صناعة films, coating and plastics.

(5) Cellophane

- It is produces in similar manner to rayon except the xanthate is extruded into the acid bath in thin sheets and at the end into glycerol bath way.

Animal fiber:

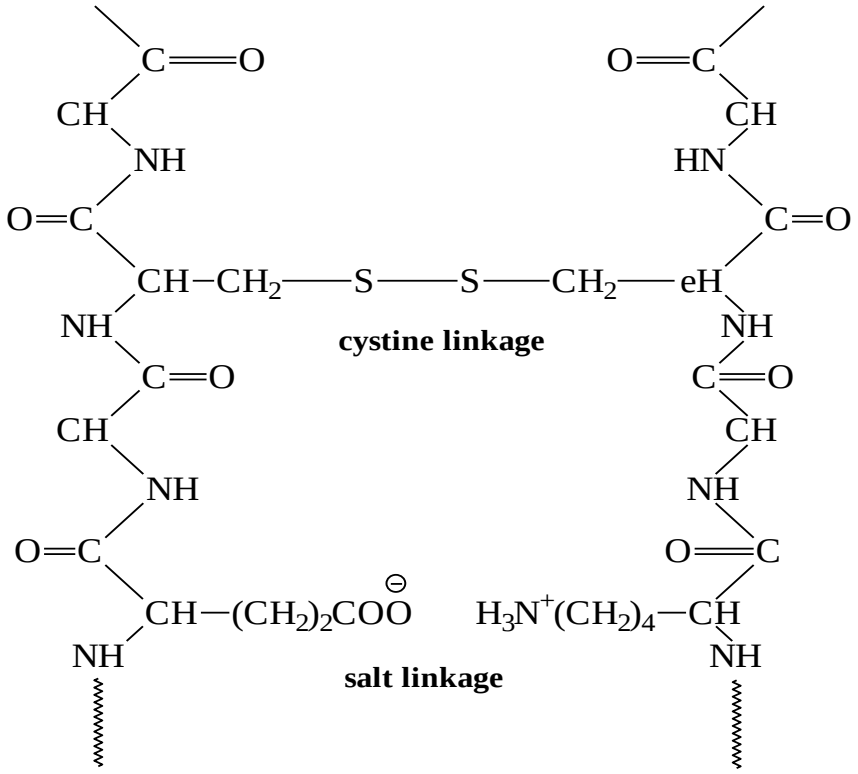
(1) Wool

Chemical structure of wool (Stedaman theory):

- Wool consists of two adjacent chains of amino acids linked together by two different types of linkage.

Cystine linkage (-S-S-) in narrow regions.

Salt linkage in wide region.



- The structure explain the resiliency مقاومة الضغط of wool fiber where stress is applied, the crimped المتعرجة positions of the carbon to carbon bonds can be straightened out when the applied stress is removed, these crimped positions return their original position, and the cross linkages will return its normal length, thus helping to forces the wool fiber.

properties of wool:

1-The characteristics of Wool fiber or protein fibers are as follows:

2-They are composed of amino acids.

3-They have excellent absorbency Moisture

4-They tend to be warmer than others.

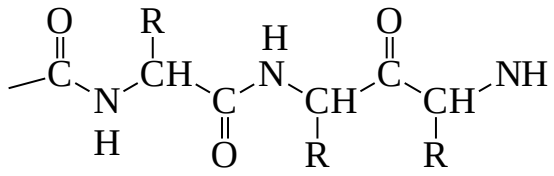
5-They have poor resistance to alkalis but good resistance to acids.

6-They have good elasticity

(2) Silk

Chemical structure of silk.

- It consists of α-amino acid linked together with peptide linkage.



- Silk does not contain –S-S- bond or salt linkage as in wool so this difference in chemical structure between wool and silk explain variation in properties between wool and silk.

- Silk molecules are closely packed together in certain area, so silk is strongly fiber but not elastic.

Weighting of silk (modification of silk):

- This process produces heavy and opaque معتم silk.

- The silk is immersed on tin chloride solution, it absorbs 50% of this solution, this leads to increase the intensity of silk and hence silk has good handle than non-modified silk. Weighted silk not strong as pure silk and are more sensitive حساسية to deterioration التلف by light and perspiration العرق.

Differences between cellulose, wool and silk:

- By burning test:

Cellulose → burn easily leaving gray ash رماد

Wool → burn with evolution of H2S

Silk → melting

Synthetic fiber

made from synthesized polymers of small molecules.

Nylon 6 6 :-

Nylon 66 (nylon 6-6 or nylon 6,6) is a type of polyamide or nylon. It, and nylon 6, are the two most common for textile and plastic industries. Nylon 66 is made of two monomers each containing 6 carbon atoms, hexamethylenediamine and adipic acid, which give nylon 66 its name.

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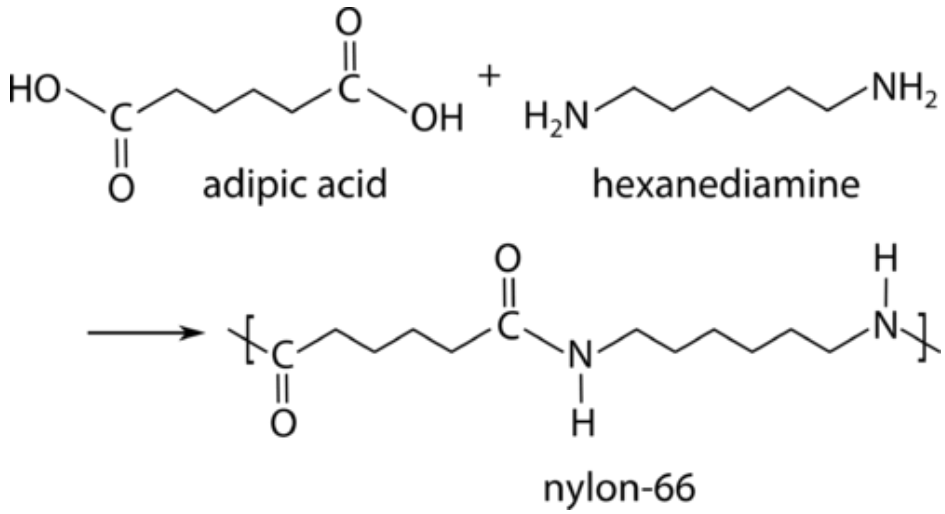
Nylon -6,6 is synthesized by polycondensation of hexamethylenediamine and adipic acid.



Used of nylone 66 :-

1-airbags, tires, ropes.

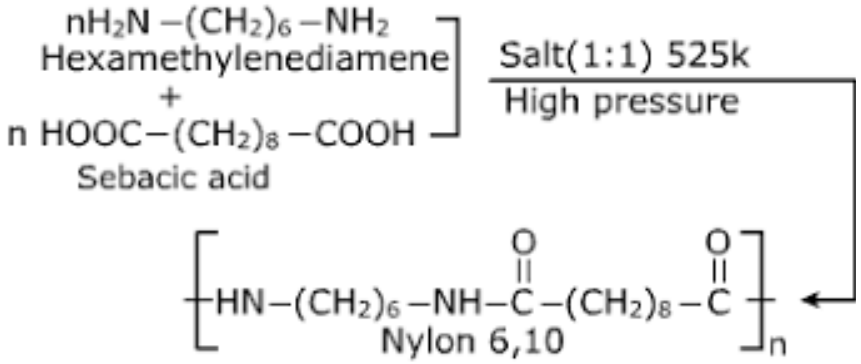
2-It is light material so it suitable to be used for parachutes

3-it is waterproof so it is used to make swimwear

4-it is resistant to electricity so it is used to make machine parts

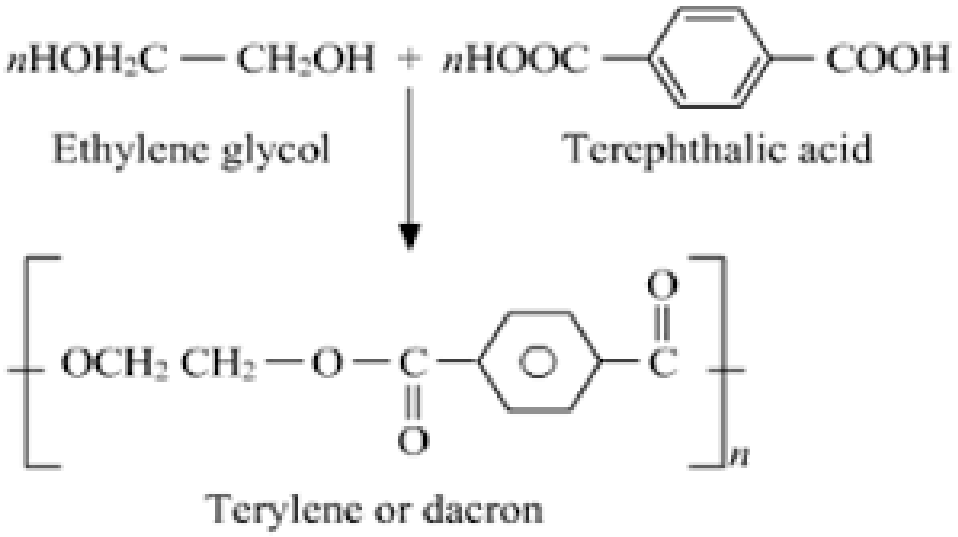
Nylon -6,10

Nylon-6,10 is semicrystalline polyamide commonly used in monofilament form in applications such as bristles and brushes. Due to its low moisture absorption compared to other nylons.



Dacron or Terylene

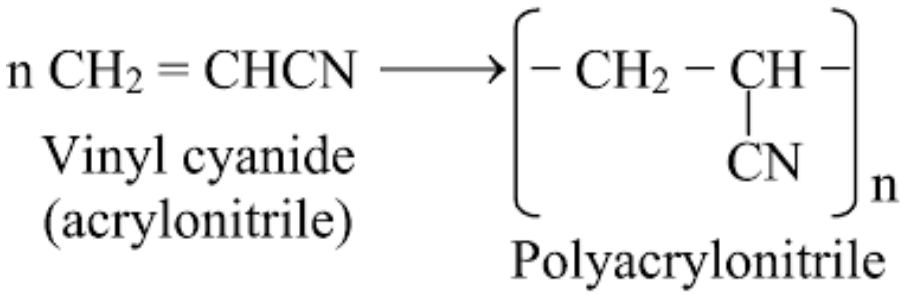
Polyethylene terephthalate commonly PETP common thermoplastic polymer resin of the polyester family and is used in fibers for clothing, containers for liquids and foods.



Terylene or dacron

Orlon

Acrylic fibers are synthetic fibers made from a polymer (polyacrylonitrile) with an average molecular weight of - 100,000, about 1900 monomer units.



Use of orlon :-

- **Orlon is resistant to sunlight and atmospheric gases, which makes it ideal for awnings and other outdoor uses.(tent –curtains)**
- **It is also characterized by stability, resistance to shrinkage, a soft, warm feel (blanket)**

- **it have a high tensile strength that is almost as good when wet as dry.(dresses)**
- **it have good elasticity and low moisture absorption. (sweaters)**

reference :-

1- Dyes and pigment book
2-The chemistry of synthetic dye book