US06CCHE21

UNIT – III

(A) SYNTHETIC DYES (B) EXPLOSIVES (C) PESTICIDES

(A) SYNTHETIC DYES

Synthetic Dyes: Classification of Dyes – Anionic and Cationic Dyes. Mordant and Vat Dyes.Reactive and Dispersed Dyes.Synthesis of Alizarin, Malachite Green, Indigo, Congo Red and Eosine

Dyes :A dye is acoloured organic compound or mixture that may be used for imparting colour to a substrate such as cloth, paper, plastics or leather in a reasonablypermanent fashion.

Classification of dyes:

Dyes are classified according their **chemical constitutions** or 0n the basis of their **application on fibers**.

a) Chemical classification:

The chemical constitution of dyes are so varied that it is difficult to classify them into distinct groups. The colour index classifies as under (in some cases a particular dye can be placed in one or other group)

Type of dye	Chromophore present
Nitroso –	– N = O
Nitro –	O ← N = O
Azo –	– N = N –
Anionic –	$-SO_3^-$
Cationic –	$-C=N^+$
Stilbene –	– CH = CH –

Anthraquinone, Diaryl Methane, TPM (triphenylmethane)Xanthene, Quinoline, Acridine, Sulfur, Thiazole, Thiazine, Indamine, Azine, Oxazine, Lactone, Indigoid, Phthalocyainetc.

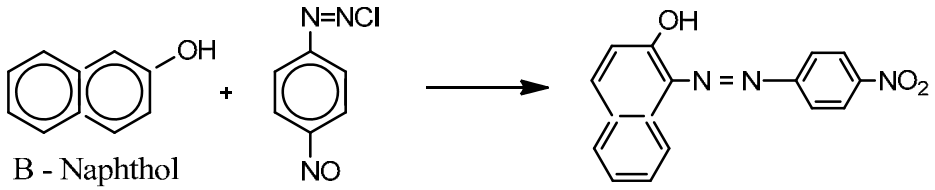
b) Classification according to application:

The method of application of dye on fiber depends upon the nature of the fiber and the dye.

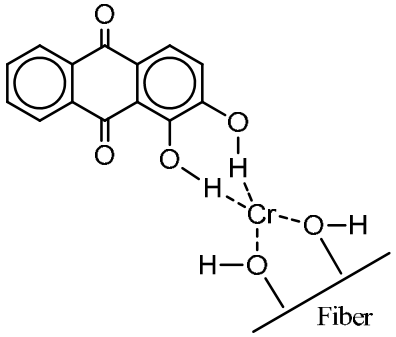
1) **Acid dyes:**These are sodium salts like $-SO_3^-Na^+$, $-COO^-Na^+$ and applicable to wool, silk, polyamide fibers and acrylic fibers.
2) **Basic dyes:**They are salts of colour base

$$\underset{\text{(Colourless)}}{\text{Leuco Base}} \underset{[H]}{\overset{[O]}{\rightleftharpoons}} \underset{\text{(Colourless)}}{\text{Colour Base}} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} \underset{\text{(Coloured)}}{\text{Dye}}$$

3) **Azoic dyes:**They are insoluble azo dyes which are prepared in situ (mainly applied to cellulose fibers) also called ingrain dyes e.g.

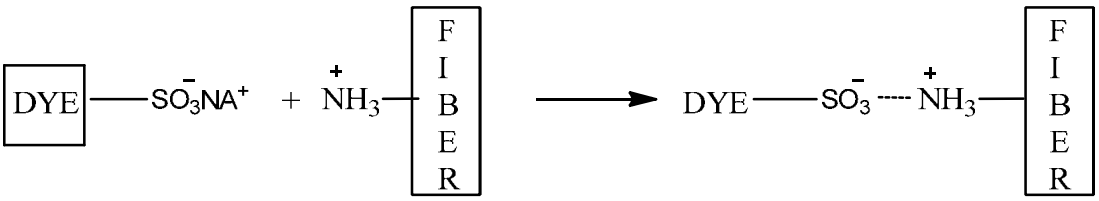


4) **Mordant dyes:**They require mordant for dyeing e.g. alizarin.

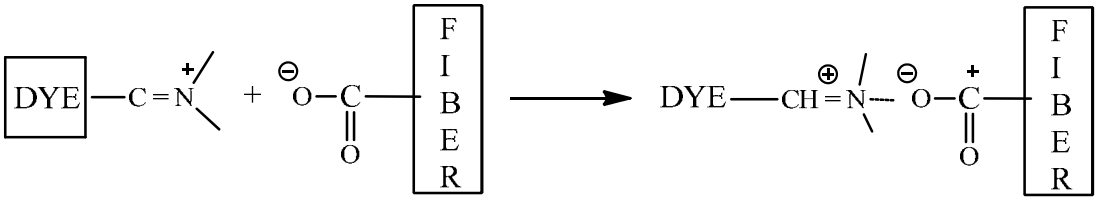


5) **Vat dyes:**Used in reduced from and the oxidized on fiber (e.g. cotton fiber) e.g, indigo dyes.
6) **Sulfur dyes:**Mainly used for cellulose fibers
7) **Dispersed dyes:**Insoluble in water and are dispersed with suitable reagents before application to the fiber.
8) **Fiber reactive dyes:**Directly combine with cellulosic fibers.
9) **Organic pigments:**Water soluble dyes.

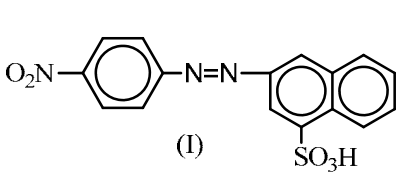
1) **Anionic (acid) and cationic (basic) dyes:**Anionic dye contains a carboxylic acid group or a sulfonic acid group which interacts with the acidic ($-NH_3^+$) group in the fiber, nylon is usually dyed by anionic dyes because it is amide fiber.



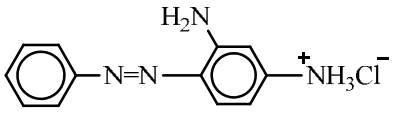
Tetrazine an Azo dye is an important yellow acid dye (anionic dye) for wool and silk, methyl orange acid base indicator, orange (II) etc. are anionic dyes.



Cationic dyes interact with the acid group of the fibers



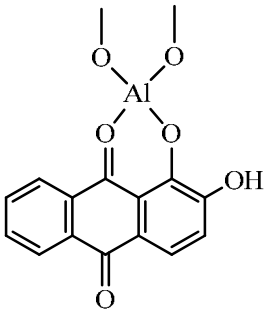
(I)



(II)

Acid red (I) and chrysodine (II) are examples of cationic dyes.

2) **Mordant dyes:**They do not fix on a fiber directly but they require a mordant. For acidic dyes a metal hydroxide is used as mordant while for basic dyes tannin (tannic acid) is used as mordant. Metal salts such as Cu, Cr, Fe, Sn, Al etc. from chelate after treatment with mordant.



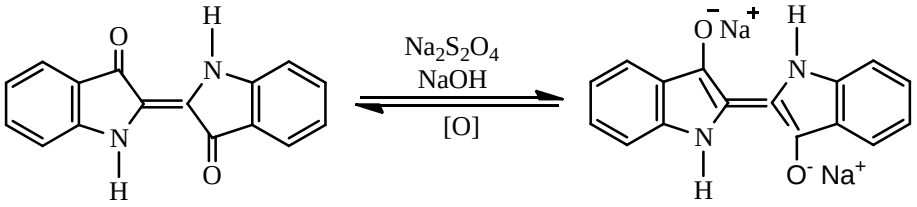
Alizarin

For a dye to be fast while using mordant the complex formed should be very stable.

The most important mordanting metal is chromium

The fiber is mordented by boiling with $K_2Cr_2O_7$ usually with a reducing agent such as formic, lactic or oxalic acid

3) **Vat dyes:**A type of dyes which can be used for all fibers, both natural and synthetic is the vat dye. They are usually water soluble in their reduced form but when oxidised become insoluble. Indigo is a insoluble blue vat dye. When reduced by sodium dithionate (sodium hydrosulfite) to leuco indigo a soluble form is obtained which is colourless.

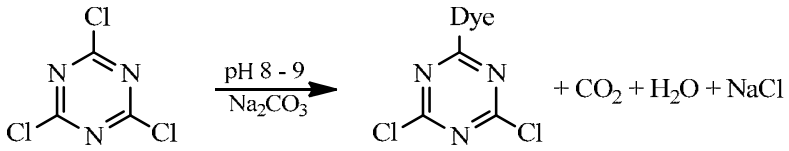


Indigo
(Blue Insoluble)
(Oxidised form)

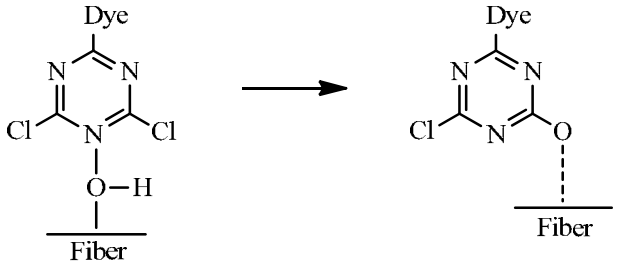
Leuco-Indigo
(Colourless soluble)
(Reduced form)

In the vat process for indigo the fiber is soaked in a hot solution of leuco indigo in a vat. It is then allowed to dry in air when it is oxidized to blue indigo form.

4) **Reactive dyes:**The main class of fiber reactive dyes in procion dyes (water soluble used for cellulose fibers) are based on cyanuric chloride (chloro – 1, 3, 5 – tetrazine).If a dye with a good nucleophilic group is allowed to react with cyanuric chloride in basic solution the dye becomes bound to it by covalent bond and a procion dye is produced.

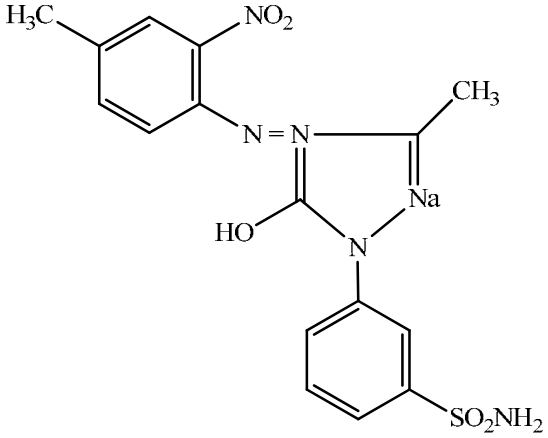


General the dye molecule should contain groups like –OH, $–NH_2$ etc. to replace chlorine from cyanuric chloride molecule.

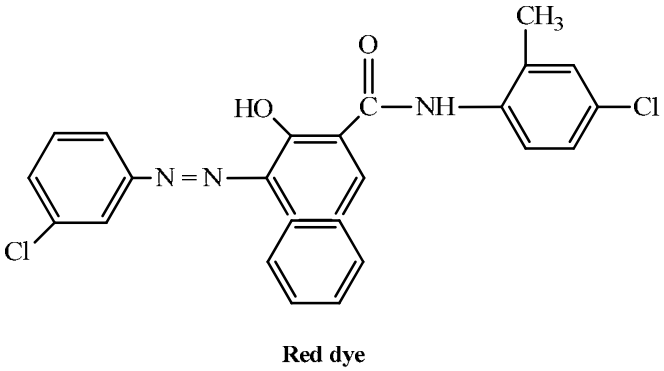


The –OH or $–NH_2$ group fiber replaces the other chlorine atom and the dye is fixed on fiber.

5) **Dispersed dyes:**Fibres like dacron, acetate etc. are hard to dye, hence organic solvents are used to disperse the dye in the fabric. They becomes trapped within the fiber only because it is water insoluble. It is not bonded to fiber. Terylene is dyed dyes e.g. a pyrazolone derivative which is yellow dye (I) and the other azo dye is red in colour.

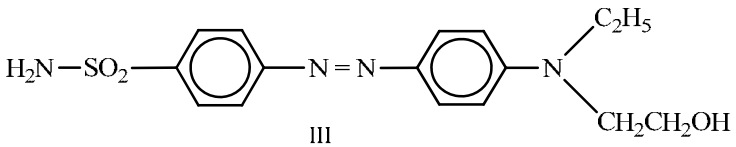


Pyrazolone yellow

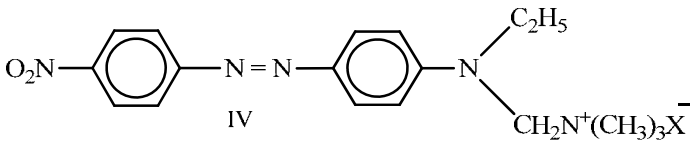


Red dye

Nylon may be dyed with acid disperse dye like (III) and polyacrylonitrile may be dyed with basic dispersed dye like (IV) as under.



III

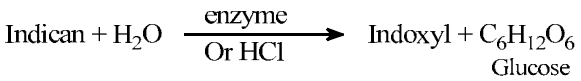


IV

❖ SYNTHESIS OF INDIGO:

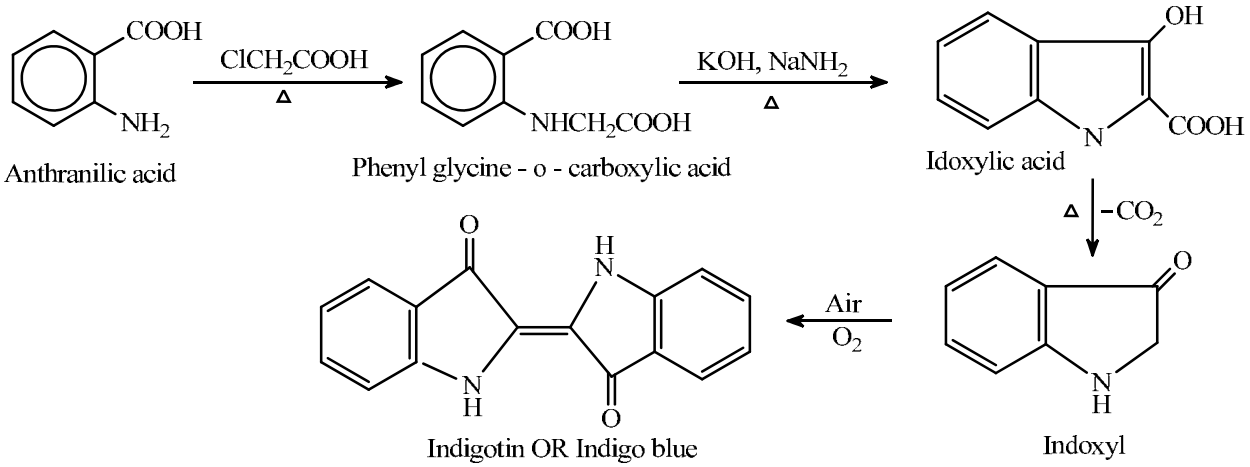
Indigo is an example of the type of dyes which contains carbonyl chromophore. Indigo dye is an organic compound with a distinctive blue colour.

Indigo was a natural dye extracted from the leaves of some plants of the indigofera genus, in particular indigoferatinctoria.
Indigo dye is a dark blue crystalline powder.
Indigo is insoluble in water, alcohol and ether.
Indigo is soluble in DMSO (Dimethyl Sulfoxide), Chloroform, Nitrobenzene and concentrated Sulfuric acid.
Indigo is found in the stems of the indigo plants (indigoferatinctoria) with glucose as indican.



$$\text{Indoxyl} + O_2 \rightarrow \text{indigo} + 2H_2O$$

Indigo from anthranilic acid:



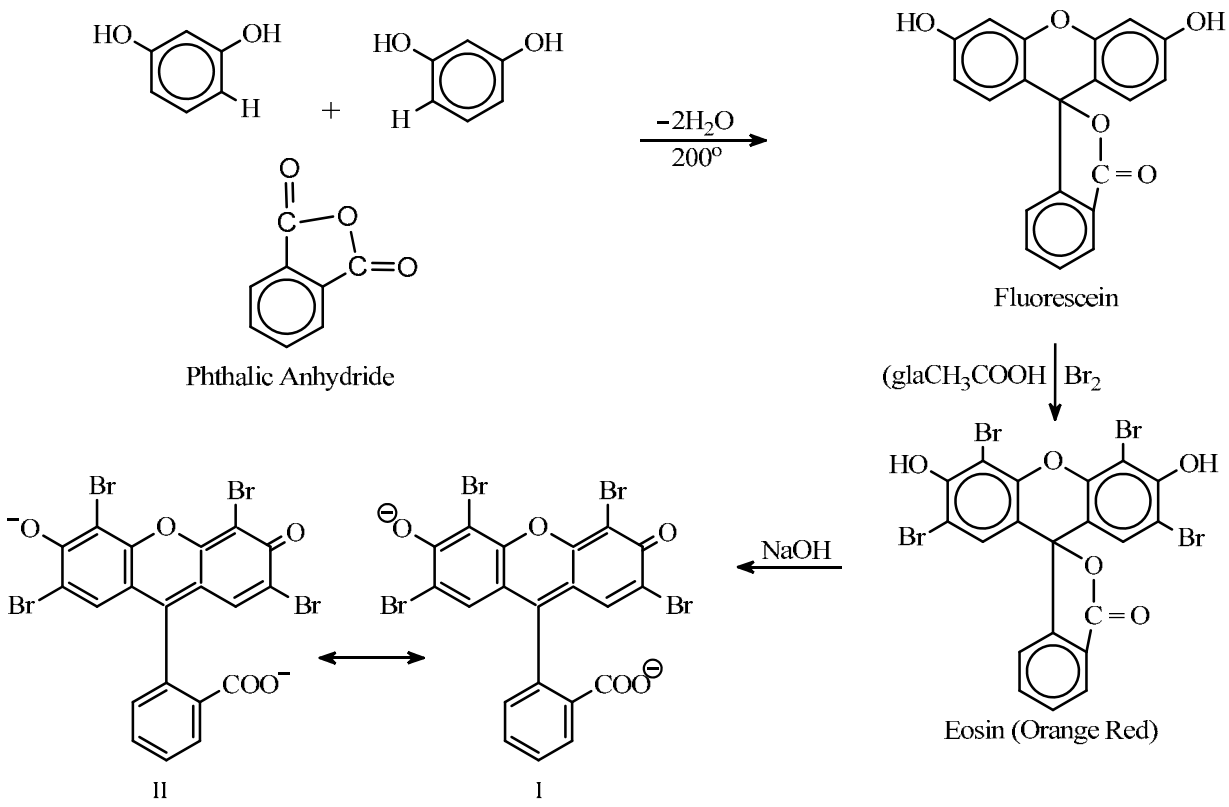
Uses:

It is an important vat dye

It is used for dyeing cotton by the Vat process.

❖ **SYNTHESIS OF EOSIN:**

It is xanthene dye.
Eosin is tetrabromofluoresceinand is obtained by the action of bromine on fluorescein in glacial
Fluorescein is prepared by heating phthalic anhydride (1 mole) with resorcinol (2 moles) at 200°C as under.



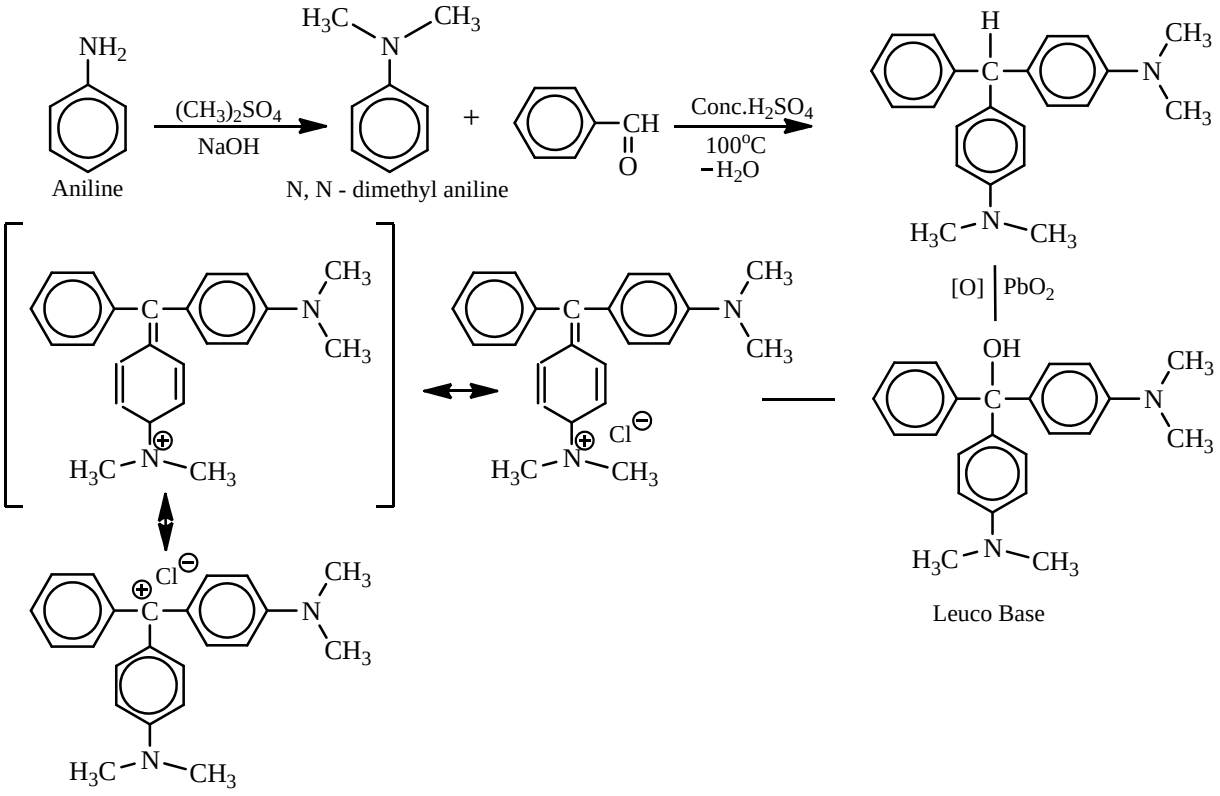
Eosin is red powder.
Alkaline solution of Eosin shows greenish yellow fluorescence.

Uses:

Eosin dyes wool and silk.
It is used in preparing poster printing colour.
Most red ink are the dilute solution of Eosin.

❖ SYNTHESIS OF MALACHITE GREEN:

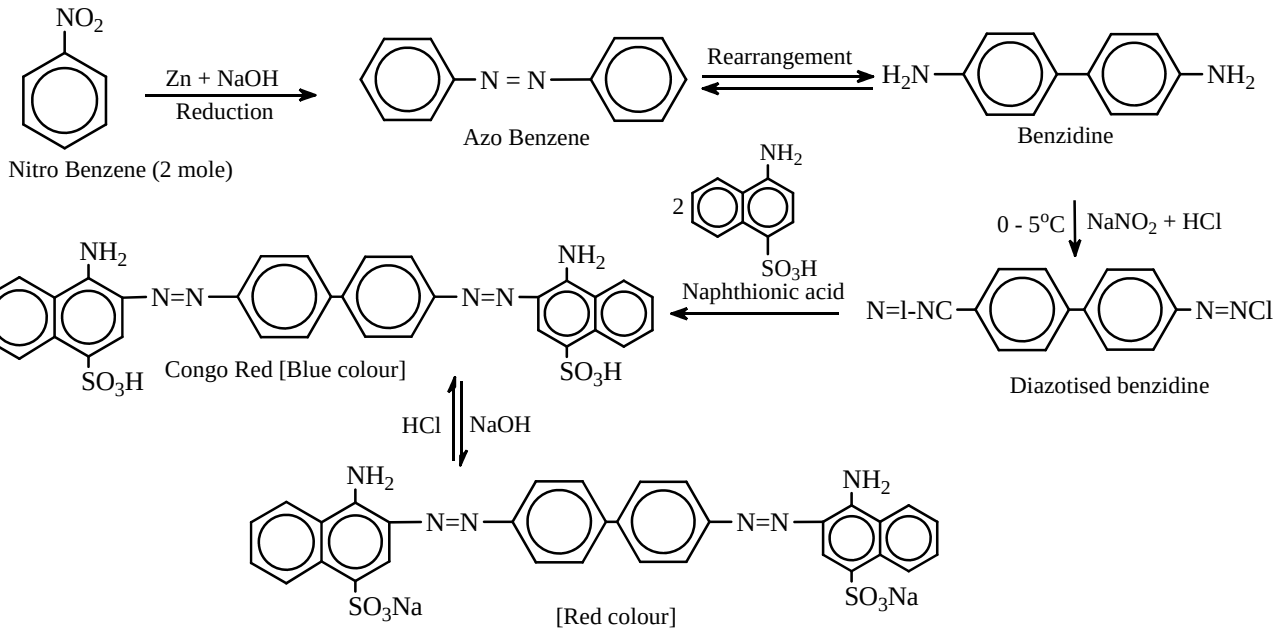
Malachite Green is a type of Triarylmethane (TPM) dyes in which a central carbon is bonded to three aromatic ring, one of which is in the quinoid form (the chromophore).In triarylmethane dyes auxochrome are– NH_2 ,– NR_2 and– OH.
Malachite green has a deep green – blue colour.
Although the colour fades in light.
Malachite green is obtained by treating benzaldehyde (1 mole) with n,n – Dimethylaniline (Two mole) in the presence of concentrated H_2SO to give Leuco Base (Gr. Leuco = colourless).
Oxidation of the leuco base with Lead oxide followed by treatment with HCl yields the Malachite green dye.



Uses: Malachite green is used as direct dye.
it dyes wool and silk directly, but cotton with mordant like tannine.

❖ SYNTHESIS OF CONGO RED:

Congo Red is a type of azo dye.
The azo dye contain one or more azo groups, (– N = N –) as te primary chromophore.
The common auxochromes are $–NH_2$, $–NR_2$, –OH, $–SO_3H$ etc.
Azo dyes from the largest and most important group of synthetic dyes. They are highly coloured and can be prepared by diazotizing an aromatic amine and subsequent coupling with suitable aromatic phenol or amine. By varying the substituents present in both the diazonium salt and the coupling compound a series of azo dyes can be produced with almost any colour.
Congo red contains two azo(– N = N –) groups.
Congo red is an example of tetra azo dye.
Congo red is prepared by coupling tetrazotisedbenzidine with two molecules of naphthionic acid.

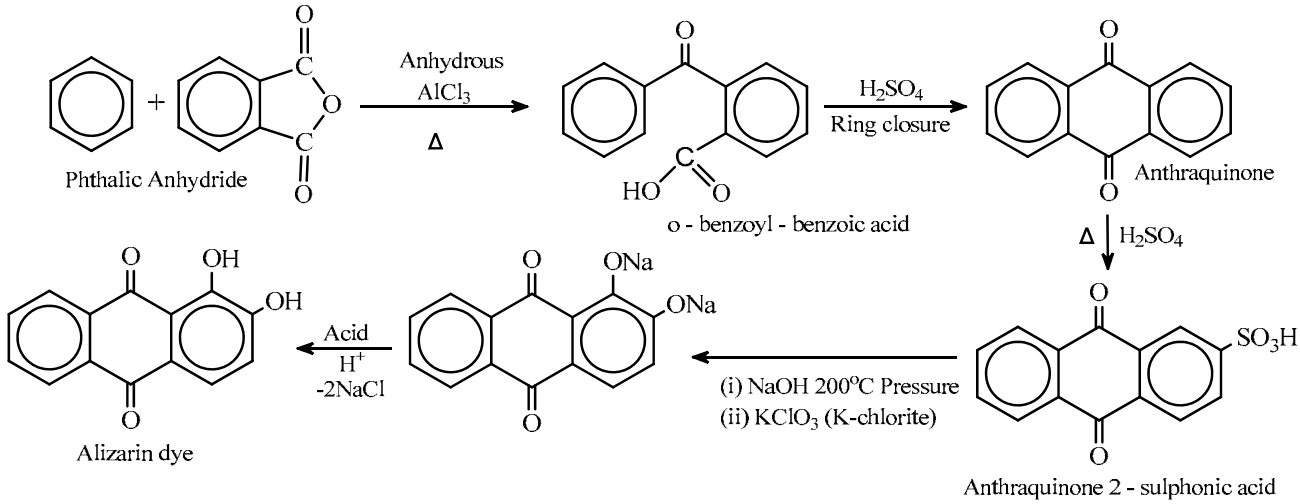


It is red in alkaline solution HCl and NaOH as sodium salt dyes.

Uses: Congo red is a direct dye and its sodium salt is used for dyeing cotton red from aqueous solution.
Congo red is also used as indicator being red in alkali and blue in acid solution.

❖ SYNTHESIS OF ALIZARIN OR 1, 2 – DIHYDROXY ANTHRAQUINONE:

Alizarin is the type of anthraquinone dyes. It is constituent of madder root.
Alizarin, a red dye originally obtained from the root of the common madder root.
The paraquinoidchromophore is present in this anthracene type dyes of Alizarin.
Alizarinis red crystalline solid.
Alizarin is insoluble in water.
Alizarin is soluble in alcohol and alkali.
Alizarin is used as important mordant dye.
Alizarin is obtained from Phthalic anhydride and benzene by the following steps.



It is used as important mordant dye.
Alizarin is used to dye wool and cotton.

(B) EXPLOSIVES

Preparation of RDX, PETN, nitroglycerine, Tetryl

Introduction:

"Substances which under the influence of mechanical or thermal decomposition undergo extremely rapid and self propagating decomposition with the production of a great amount of heat and large volume of gases are known as explosives."

The explosive is set off in any place, the large volume of these hot gases develop extremely high pressure.

An explosive may consist of single substance or a mixture of two or more substances.

Classification of explosives:

Explosives are classified based on the types of reactions which produce explosions. e.g. mechanical, chemical and nuclear.

However in this unit we are only concerned with the organic chemical explosives which comprise of two types.

A. Low or deflagrating explosives

B. High or detonating explosives.

High or detonating explosives are further classified as primary and secondary detonating explosives.

A. Low or deflagrating explosives:

Low or deflagrating explosives are known as **propellants**.

Low explosive do not undergo explosion suddenly but they only burn. The chemical reactions take place comparatively slowly. The burning proceeds from the surface inwards in layers.

Low explosives are characterized by a reaction rate which increases nearly in direct proportion to the pressure but always remains one or two orders of magnitude lower than in the detonating type.

Low explosives evolve large amount of gases and due to which they help explosion.

The relatively low rates of pressure development and peak pressure of the low explosives in addition to rendering them useful in guns and rockets as propellants, give them a desirable "blasting action" for coal mining and other blasting operations.

The smokeless powder propellants are low explosive and are extensively used as indispensable in the military field. They have commercial importance because of their high cost.

The smokeless powder are the basis of most modern artillery, small arms and rocket ammunition. Three general types are available which are as follows:

a. Single base powders: in this nitrocotton is the basic ingredient
b. Double base powders: in these, nitrocotton and nitroglycerine are the main basic ingredient.
c. Triple base powder: in this nitroguanidine, nitroglycerine and nitrocellulose are the main basic gradient.

B. High or detonating explosives:

These explosives are characterized by very high rates of reactions and pressure.

Detonating or high explosive are divided into the following two types:

a. <u>Primary high explosive:</u>

These explosives are also known as initiating explosives.

These explosives are very sensitive and may be exploded by the application of flame, spark, impact and other primary heat sources of appropriate magnitudes.

These explosive are used in smaller quantities to initiate the explosion of large quantities of less sensitive secondary explosives.

Primary explosives are very dangerous to handle.

Primary explosives are lead azide, mercury fulminde, tetracene, dinol, lead styphnate etc.

b. <u>Secondary high explosive:</u>

Secondary high explosive are quiet insensitive to mechanical shock and flame.

However secondary high explosive explodes with great violence when they are initiated by initiating explosives.

Secondary explosives develop detonation pressure from a minimum of about 2500 to a maximum of about 350000 atmospheres.

The detonation temperatures of secondary explosives may range from as low as about 1500°C to 5500°C or higher depending on the nature of the explosive.

Classification based on their application :

These explosives may also be classified into following two groups on the basis of their applications:

1) **Military explosive:** e.g. RDX, TNT, nitrocellulose, Tetryl, Picric acid, lead azide, EDNA, Dinol etc.
2) **Industrial explosive:** e.g. black powder, nitroglycerin, dynamite etc.

1) RDX or Cyclonite:

Or sym-trimethylenetrinitramine

Or cyclo-trimethylenetrinitramine

Or hexogen

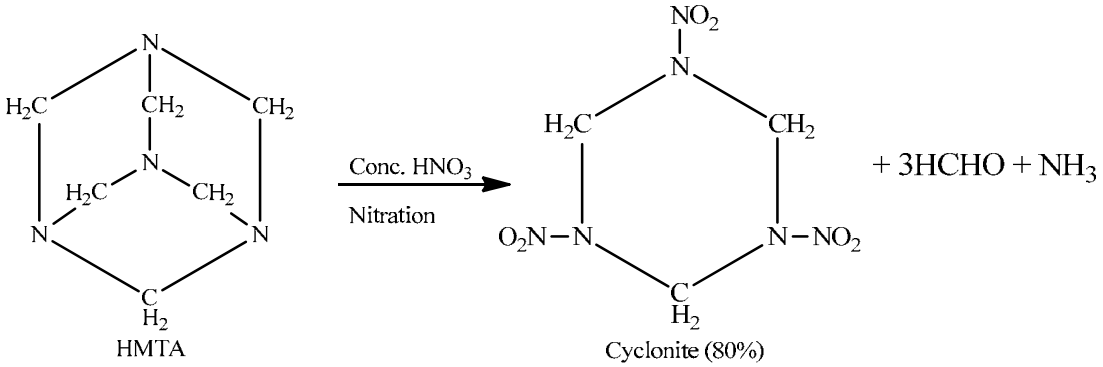
It is one the most powerful explosives. It was widely used in World War II.

Preparation by Hale Method (1925)

When formaldehyde treated with NH_3, a hexamethylenetetramine (HMTA) is obtained.

$$6HCHO + 4NH_3 \rightarrow (CH_2)_6N_4 + 6H_2O$$

When HMTA treated with conc. HNO_3 cyclonite is obtained.



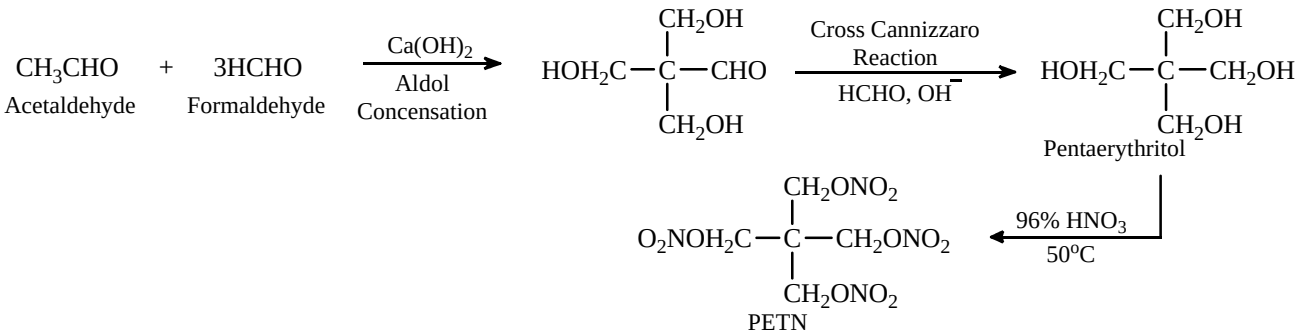
Uses: It is used with TNT. Torpex, a mixture of RDX with TNT and aluminium is used for mines, depth charges and torpedo warheads. It is also used in shells and bombs.

2) PETN (PentaErythritol Tetra Nitrate)

Or Penthrit:

It is one of the most powerful and sensitive high explosives.

Preparation:



Uses: it is used in rifle bullet. It is desensitized by admixture with TNT for its use as booster or high explosive.

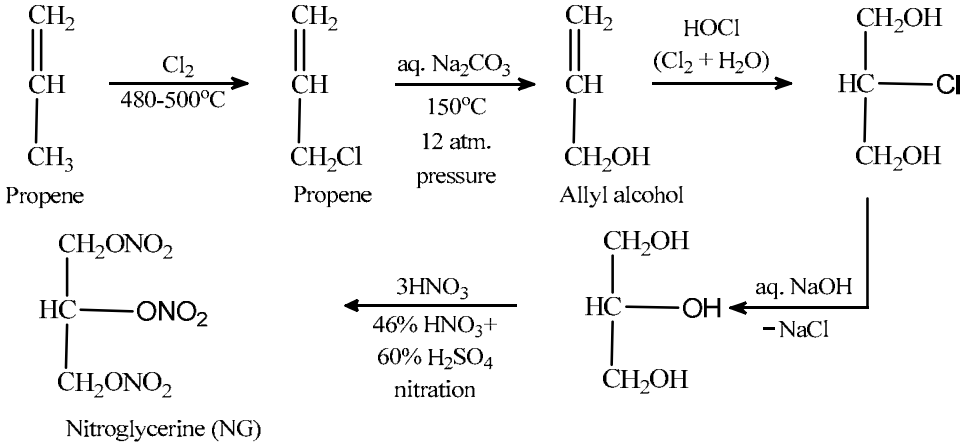
3) Nitroglycerin (NG) orGlyceryltrinitrate or Glyercoltrinitrate:

Preparation:

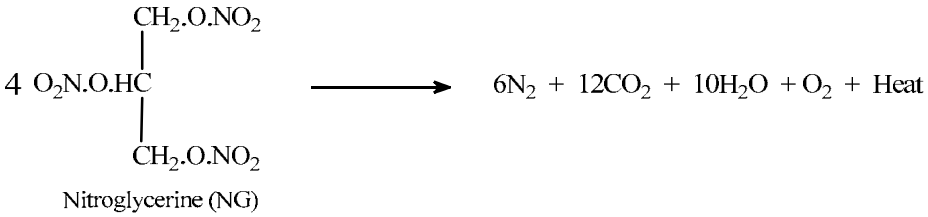
Nitroglycerine is prepared by nitration of glycerine of glycerol.

During the manufacture of soap, glycerol is obtained as by-product.

Glycerol can also be prepared by following method.

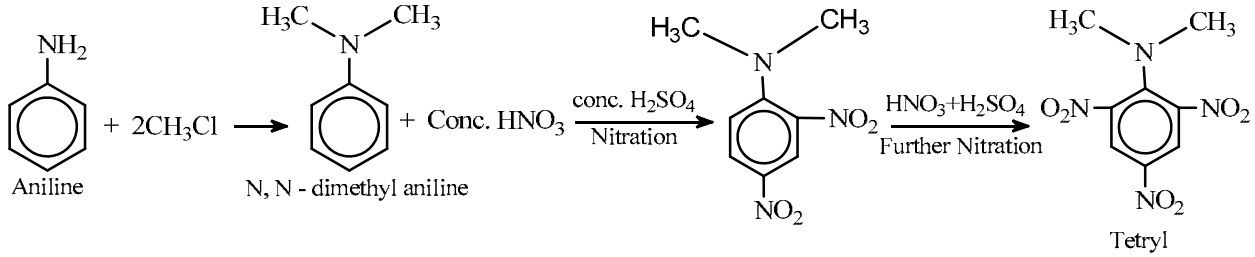


Uses: it is a powerful and sensitive explosive. The decomposition of nitroglycerine may be as below:



It is used in the manufacture of dynamite and smokeless powders.

4) Tetryl or (2, 4, 6 trinitrophenyl) methylnitramine:



It is intermediate between the detonators and the high explosives and is used as a booster explosive.

(C) PESTICIDES

Preparation of Aldrine, Malathion, Parathion, Methoxychlor.

General:

Pesticide (insecticide) are chemicals which are to control damage caused by insects by poisoning them through oral ingestion of stomach poisons, by contact with cuticle or by fumigant action through the air.

OR

“A substance or a mixture of substances used for killing the Pest (insects) is known as pesticides(insecticides).”

Pest (Insect) may also be controlled by chemicals such as attractants and repellents which adversely influence their behavior by chemosterilants which prevent their reproduction.

The term insecticides has been replaced by pesticides which include toxic chemicals, weather used against insects, fungi, weeds or rodents etc.

Agricultural disinfectants and animal health products are in many instances also included under the term **pesticides**.

The use of pesticides(insecticides) has permitted the control of diseases transmitted by pest (insects) and also has lead to increased food production and better health.

Classification of insecticides:

Insecticides are classified into the following two types:

A. Mode of action

B. Chemical nature

A. Mode of Action:

Insecticides have been classified into the following classes according to their mode of action.

a. Stomach or Internal pesticides (insecticides):

pesticides(insecticides) which are eaten by insects are known as stomach or internal pesticides(insecticides).

These pesticides(insecticides) are generally applied against pest (insects) with chewing mouthparts but under certain conditions

pesticides(insecticides) are also effective against insects with sponging, siphoning, lapping or sucking mouthparts.

Stomach or internal pesticides(insecticides) are applied in the following manner.

I. The food of the insect is covered with a thick layer of insecticides so that the insect cannot feed without ingesting it.

II. The insecticide is mixed with an attractant substances from which insects are eaten.

III. Finely divided powder of insecticides is sprayed over the runways of the insects.

IV. pesticides(insecticides) may be applied as a systematic poison which is absorbed and distributed throughout the tissues of plant or animal host so that insects feeding thereon are killed.

b. Contact or External pesticides (insecticides):

pesticides(insecticides) which kill the pest (insects) by means of external contact are known as contact or external insecticides.

Contact or external insecticide may be applied directly to the insects.

Contact or external insecticides may also be applied as residues to plant surfaces, animals, habitations or other places visited frequently by insects.

c. Fumigants:

Pesticides(insecticides) which exert their action in the gaseous state are known as fumigants.

Fumigants are effective against all insects since the gas enters the insect body through the spiracles during respiration.

Application of fumigants is limited to plants or products in tight enclosures or those which can be enclosed in gas tight tents or wrappings or to soil.

d. Attractants:pesticides(insecticides) which lure (attract) insects through olfactory stimulation.They may be food lure (attractants) or sex lure (attractants).

e. Repellents: pesticides(insecticides) which are mildly poisonous or only offensive which make food or living conditions unattractive for insects are known as repellents. Repellents are used for termites and other household insects.

f. Natural plant insecticides :Natural pesticides such as lavender, garlic, tea tree oil, and diatomaceous earth are natural forms that help repel pests.

Alternatives to Pesticides (insecticides):

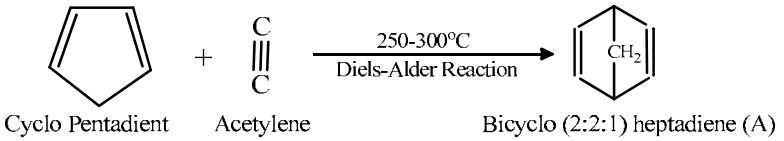
As Pesticides(insecticides)are highly poisonous several alternatives to the massive application of insecticides have recently been explored. Insect attractants including the pheromones have been used. A “confusion technique” where by pheromone is sprayed into the air in such a high concentrations that much insects are no longer able to locate the female has been developed. Recent researches have been focused on the use of an insect’s own biochemical process as a means to control pests. Experiments with juvenile hormone are found promising.

The use of Pesticides(insecticides)has not only permitted the control of diseases transmitted by insects but also led the increased food production and better health.

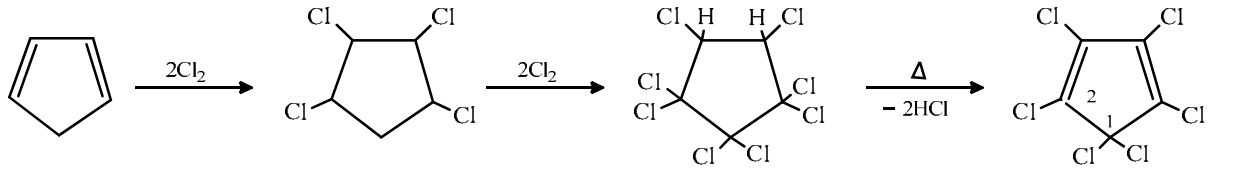
Preparation of Aldrin

(A)

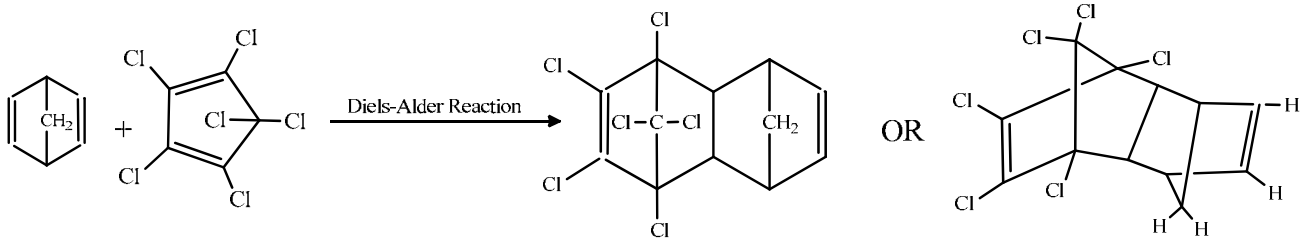
(B)



(B)



(C) Condensation of (A) + (B)



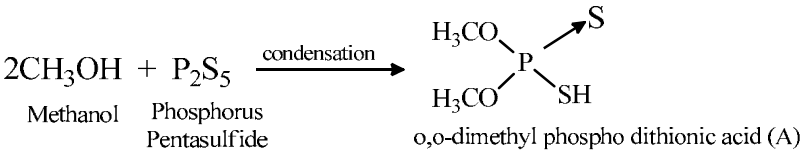
Uses: It is used for the control of grasshoppers, cotton insects and soil insects.

Malathione:

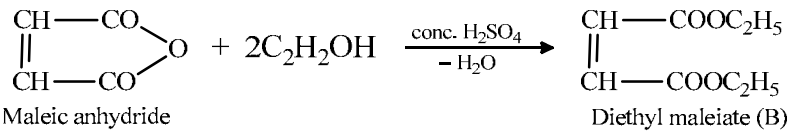
It is also known as o-o-dimethyl dithiophosphate of diethyl mercapto-succinate.

Preparation:

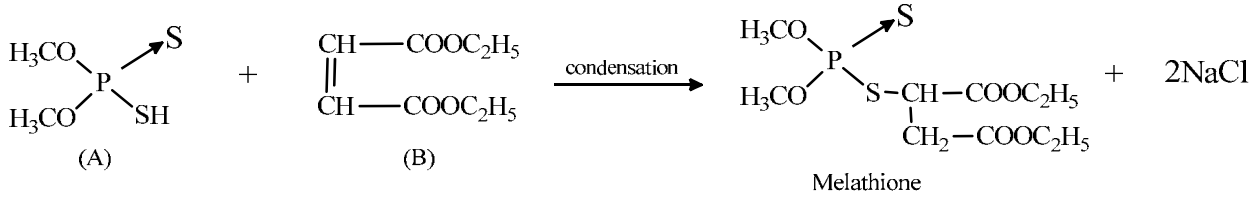
(A)



(B)



(C) Condensation of (A) + (B)

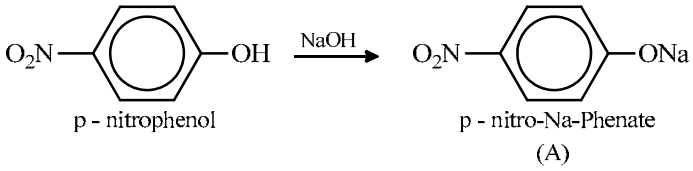


Uses: It is used as insecticide for nearly all fruits, vegetables, and field crops and household insects.

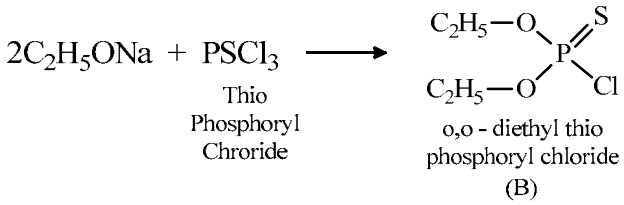
Parathion:

It is also known as o – o – diethyl – o – p – nitrophenylthiophosphate

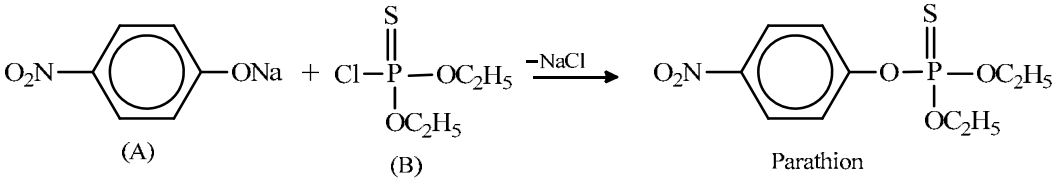
(A)



(B)



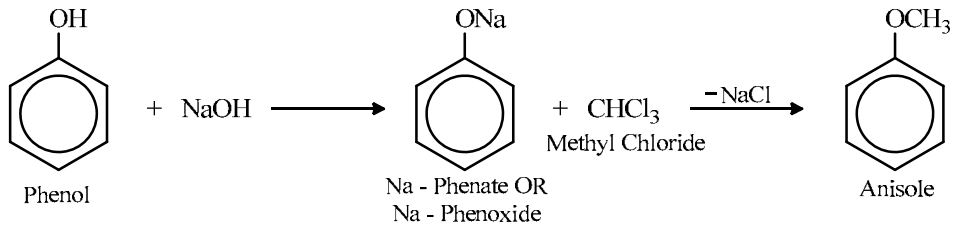
(C) Condensation of (A) + (B)

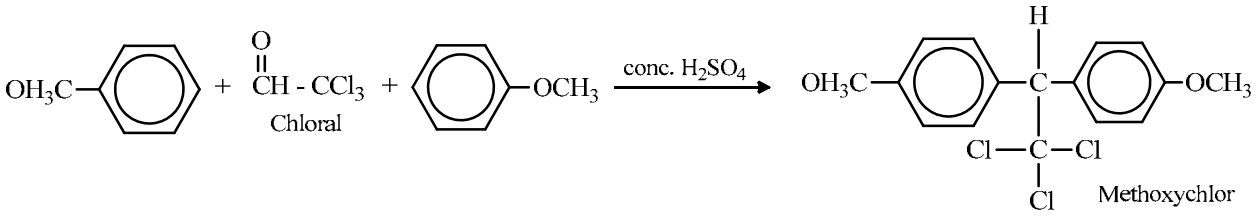


Precaution: it is extremely poisonous, so many precautions taken for its formation and handling.

Uses: It is used as general insecticide.

Methoxychlor:





Uses: it is a strong insecticide with low toxicity to warm-blooded animals and safe to plants.

It is used safely on cattle, vegetable, crops and household pests.

It is also used in dairies.

Exercise: A

1) What is dyes? Give classification of dyes.
2) Write note on anionic and cationic dyes
3) Write note on mordant dyes
4) Write note on
   a) Vat dyes
   b) Dispersed dyes
   c) Reactive dyes
5) Give synthesis and uses of:
   a) Alizarin
   b) Malachite green
   c) Indigo
   d) Congo red
   e) Eosin

Exercise: B

6) Give synthesis and uses of
   a) RDX
   b) PETN
   c) Nitroglycerine
   d) Tetryl

Exercise: C

7) Give preparation and uses of
   a) Aldrin
   b) Malathion
   c) Parathion
   d) Methocychlor

Long Question :

(1) Define the term dyes. Give the classification of dyes.
(2) Define the term dyes.Give synthesis and uses of Alizarin/Malachitegreen/Indigo/Congo red/Eosin.
(3) Define the term explosives. Give the synthesis and uses of RDX/PETN/Nitroglycerine/Tetryl
(4) Define the term pesticides. Give the synthesis and uses of Aldrin/Malathion/Parathion/Methocychlor

ShortQuestion :

(1) Give the classification of dyes based on their application ?
(2) Define the term dyes. What are the uses of Alizarin/Malachite green/Indigo/Congo red/Eosin.
(3) Define the term explosives ?
What are the uses of RDX/PETN/Nitroglycerine/Tetryl.
(4) Define the term pesticides ?
What are the uses of Aldrin/Malathion/Parathion/Methocychlor.
(5) Give the structure and uses of Alizarin/Malachitegreen/Indigo/Congo red/Eosin.

(6) Give the structure and uses of RDX/PETN/Nitroglycerine/Tetryl.
(7) Give the structure and uses of Adrin/Malathion/Parathion/Methocychlor