كيمياء عضوية (IV) (٤٤١ ك)

النواتج الطبيـــعية Natural Products

4th Year Students Faculty of Science
(Chemistry group)
العام الدراسي ٢٠٢٢-٢٠٢٣

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	Structure –elucidation of alkaloids *Classification of alkaloids (Phenyl ethyl amine –Pyrrolidine – pyridine –(pyridine, pyrrolidine group) –quinoline –isoquinoline-* Tropine alkaloids Phenanthrene Group)
Terpenoids	Definition –Extraction -*Structure elucidation -Classification –monoterpenoids* - Cyclic Sesquiterpenoids Monoterpenoids(Limonene-Menthol-Camphor)-Sesquiterpenoids-Diterpenoids-Triterpenoid-tetraterpenoids –Polyterpenoids (rubber)
Steroids	Definition of steroids Classification Determination of ring A in cholesterol and cholic acid Determination of the nucleus - Blanc Rule 1-Sterols (cholesterol **)** 2-Vitamin D(vitamin D2) 3-Bile Acids (cholic acid) 4- Steroidal Hormones or Sex Hormones(progesterone) 5- Adrenocortical hormones (cortisone)

تعريف النواتج الطبيعية –التقسيم
Definition of Natural Product -Classification

As human organs, plants, animal organs, sea organisms and micro-organisms, as a result of the metabolism.
Natural products are organic compounds produced by living organisms, such

According to their physiological influence and according to their structural composition, and they are studied in groups as follows:

1. القلويدات (اشباه القلويات)Alkaloids
2. التربينات Terpenes
3. الاستيرويدات Steroids
4. الفلافونويدات و الانثوسيانينات Flavonoids and anthocyanins
5. الكومارينات Coumarins
6. الفينانثرينات Phenanthrens
7. المضادات الحيوية Antibiotics
8. الفيتامينات Vitamins

And there are some interactions, for example, vitamin A, which is classified as diterpenes . As for the modern classification, it is as follows It is classified into a smaller number of sects, namely :

1. القلويدات Alkaloids
2. التربينات Terpenes
3. الاستيرويدات Steroids
4. المركبات الفينوليه Phenolic compounds

ALKALOIDS --- القلويـدات

Definition of alkaloids

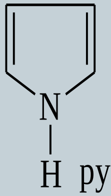
-All organic bases isolated from plants, and it covers wide variety of compounds.

-(Konigs)suggested that alkaloids should be defined as [naturally occurring organic bases which contain a pyridine ring] ,this definition include a limited number of compounds.

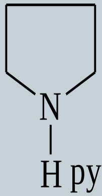
-(Ladenburg definition): natural plant compounds having a basic character and containing at least one nitrogen atom in heterocyclic ring .

Alkaloids have clear physiological effects, and are chemically related to pyrrole, pyridine, quinoline and isoquinoline, which are different heterocyclic rings, some of which are highly toxic, and some are used as medical drugs such as quinine used to treat malaria, morphine to remove pain or cocaine as a local anesthetic and atropine in surgery and ophthalmology.

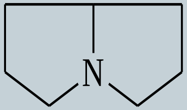
Different heterocyclic rings related to alkaloids



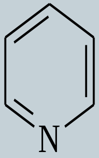
pyrrole



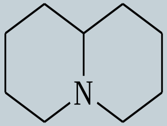
pyrrolidine



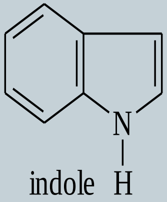
pyrrolizidine



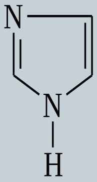
pyridine



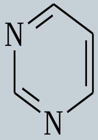
nor-hipinane



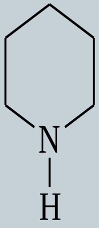
indole
(benzopyrrole)



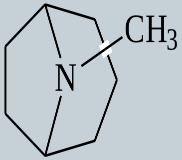
imidazole



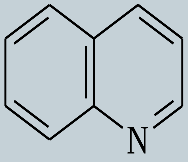
pyrimidine



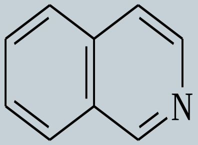
piperidine



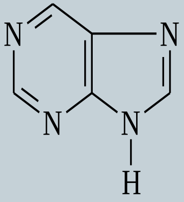
tropane
(piperidine-pyrrolidine)



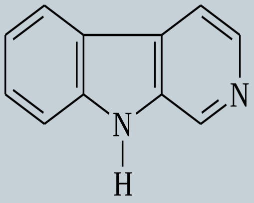
quinoline



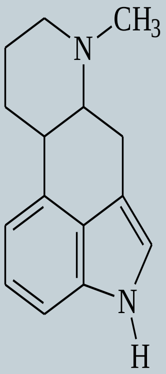
isoquinoline



purine



carboline



indole + hydroquinoline

Extraction of alkaloids استخلاص القلويدات

- Alkaloids are generally found in plants in the form of salts combined with some organic acids such as malic or citric acid .
- .Alkaloids are found mainly in fruits and seeds, as well as in tree bark.
- We extract the alkaloids from the plants by carefully cutting the plants, then adding a solution of hydrochloric or sulfuric acid to form their corresponding mineral salts.
- In this process, the alkaloids (bases) are liberated from the organic acids, and then the alkaloids are dissolved in the form of solutions of salts of hydrochloric or sulfuric acid with sugars and some other compounds found in the tissues of plants.
- As the alkaloids do not dissolve in water, they can be precipitated from chloride or sulfuric salts by adding bases such as sodium or potassium hydroxide.
- In the case of volatile alkaloids such as nicotine, the salt solution or the raw material is treated with the addition of alkali (sodium hydroxide) and treated by steam distillation, then the alkaloids are extracted by organic solvents such as, chloroform or other organic solvents.
- The mixture of alkaloids is separated by various methods into pure substances .

General Properties الخواص العامـــة

. Alkaloids are colorless, in crystalline form, and do not dissolve in water, but dissolve in organic solvents, such as, chloroform, ethyl alcohol … etc.

But there are liquid alkaloids that can be mixed with water, such as coniin and nicotine, and some have a yellow color like piperine.

Most alkaloids have a bitter taste and optically active .

It generally contains one or two nitrogen atoms in a tertiary state in a ring.

Most alkaloids also contain an oxygen.

Structure –elucidation of alkaloids

1-The first step in determining the structure of a pure alkaloid consists in ascertaining its molecular formula and optical rotatory power.

2- Functional nature of oxygen

The oxygen atom may be present in the form of alcoholic or phenolic hydroxyl (-OH), methoxy ($-OCH_3$), acetoxyl ($OCOCH_3$), benzoyl (- COC_6H_5), carboxyl (-COOH) or carbonyl (C=O) group, various oxygen functional groups can be characterized according to the following characteristics

Functional nature of oxygen طبيعة ذرة الأكسجين

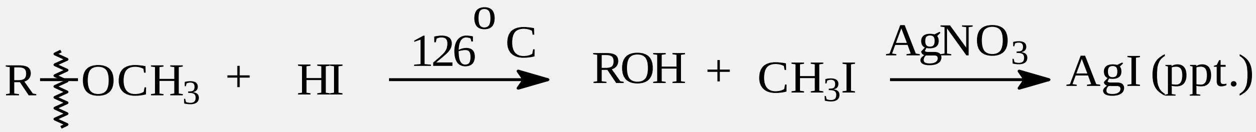
(A) Phenolic hydroxyl group (=C-OH) : The phenolic hydroxyl group is characterized by alkali solubility followed by reprecipitation by carbon dioxide, a colour reaction with ferric chloride, acylation to an ester and alkylation to an ether. The number of phenolic hydroxyl groups is estimated by acetylation.

(B) Alcoholic hydroxyl group (-C-OH) : The alcoholic hydroxyl group is generally indicated by its acylation reaction along with the negative tests for phenolic group. It is further confirmed by characteristics like dehydration, oxidation, and absorption spectrum in the infrared. The three possible alcoholic groups are usually differentiated by their oxidation reactions.

(C) Carboxyl group (-COOH) : The carboxyl group is indicated by its solubility in weak bases, like $NaHCO_3$, NH_3, *etc.*, esterification with alcohols, and specific absorption in the infrared. The groups are generally estimated quantitatively either by acid-alkali titration or by silver salt method.

Functional nature of oxygen

(D) Alkoxyl group (-OR) : The alkoxyl groups, generally methoxy ($-OCH_3$) and sometimes ethoxy ($-OC_2H_5$) occur frequently in the alkaloids. It is detected as well as estimated by Zeisel method which involves boiling of the alkaloid with concentrated hydroiodic acid at its boiling point (126°C) when the alkoxy groups are converted into alkyl halides which can be easily estimated as silver iodide by treatment with ethanolic silver nitrate.



$$R-OCH_3 + HI \xrightarrow{126\,^{o}C} ROH + CH_3I \xrightarrow{AgNO_3} AgI\ (ppt.)$$

The number of moles of silver iodide is equivalent to the number of alkoxyl groups in the alkaloid.

(E) The related group, methylene dioxy ($-O-CH_2-O-$) is estimated on the basis that it librates formaldehyde when treated with hydrochloric or sulphuric acid; thus the quantitative estimation of formaldehyde will give the number of methylene dioxy groups.

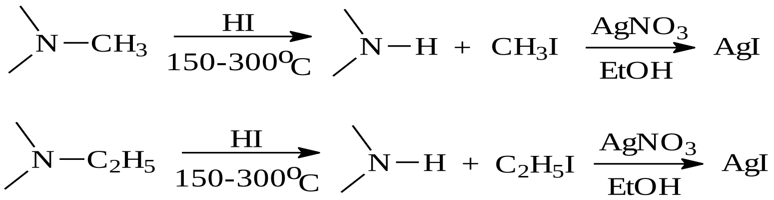
Alkaloids

Determination of the structure The Nature of Nitrogen

a)The general reaction of alkaloid with acetic anhydride,methyl iodide and nitrous acid show the nature of the nitrogen

b)Distillation with aqu.pot.hydroxide gives information about the nature and number of alkyl groups attached to nitrogen

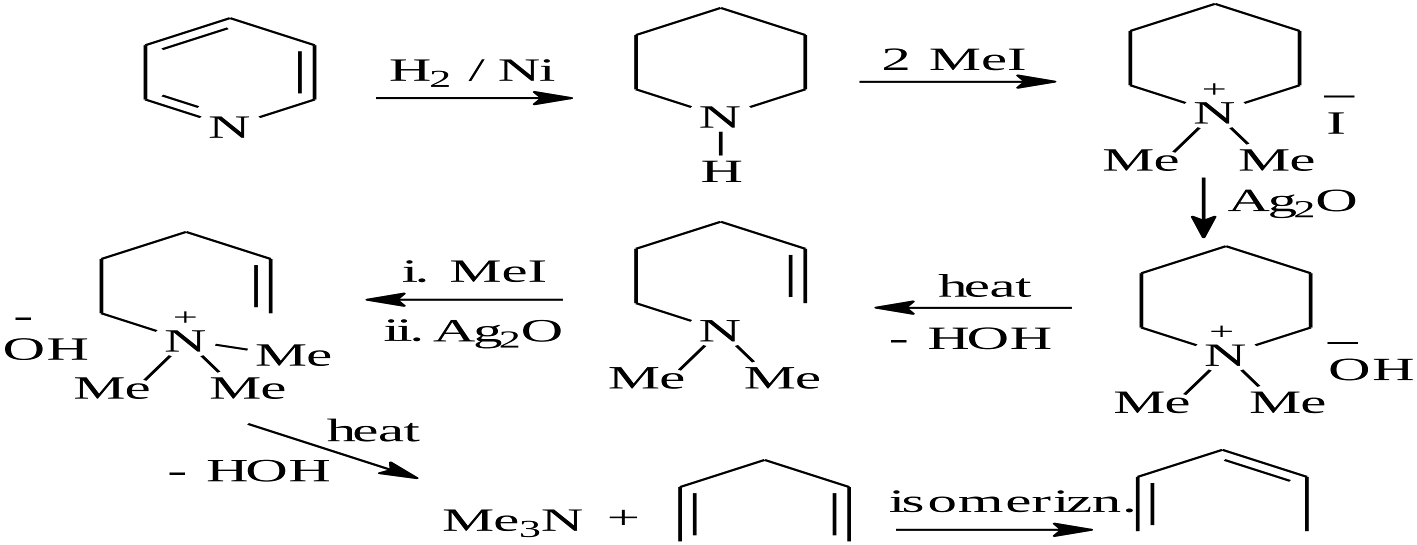
c) The N-alkyl groups are frequently estimated by Herzig Meyer method



d)Hydrolysis show the presence of an amide ,lactam ---in the alkaloid structure .

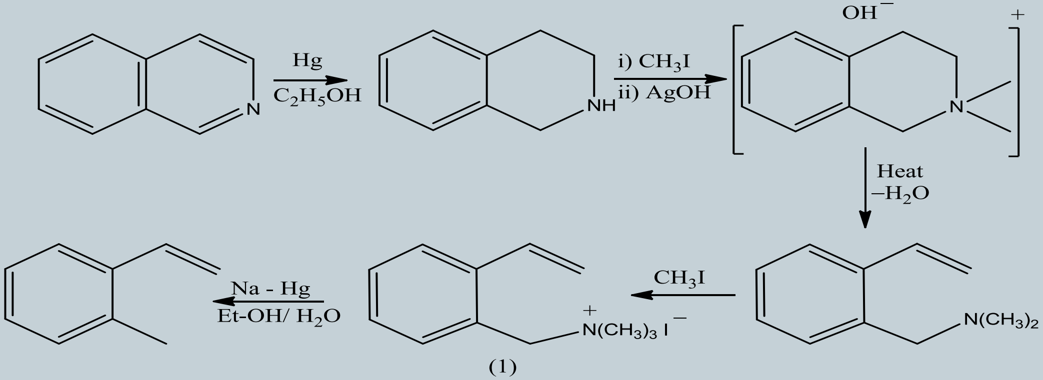
Determination of the structure
Functional nature of nitrogen

e)Hofmann exhaustive methylation :



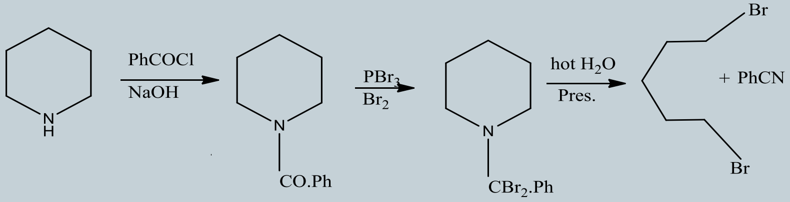
Functional nature of nitrogen

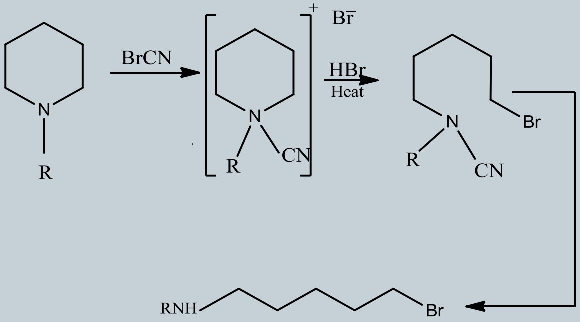
Emid modification



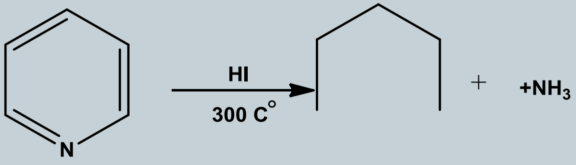
Von Braun methods for tertiary cyclic amines

Von Braun methods for secondary cyclic amines





By using hydro iodic acid



Determination of the structure

4-Detection of the unsaturation : by addition of bromine and halogen acids or by reduction by means of sodium amalgam ,sodium and ethanol and hydrochloric acid etc----- .

5- Oxidation:
a)Mild oxidation (hydrogen peroxide-ozone- iodine in ethanolic solution ---)
b)Moderate oxidation (acid or alkaline pot.permenganate-chromium trioxide in acetic acid--) c)Vigorous oxidation (pot.dichromate in sulphuric acid –conc. nitric acid -chromium trioxide in sulphuric acid ---)
6- Alkali fusion: fusion with solid potassium hydroxide and investigation of the products .
7-Distillation with Zinc dust and investigation of the products .
8-Physical methods : (IR –NMR-MS-UV- X ray)
9- Synthesis :
Finally, the structure proposed by degradative methods is confirmed by the synthesis.

Classification of alkaloids

Phenylethyl amine alkaloids

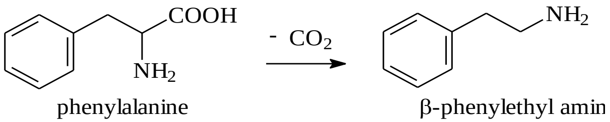
Classification of alkaloids

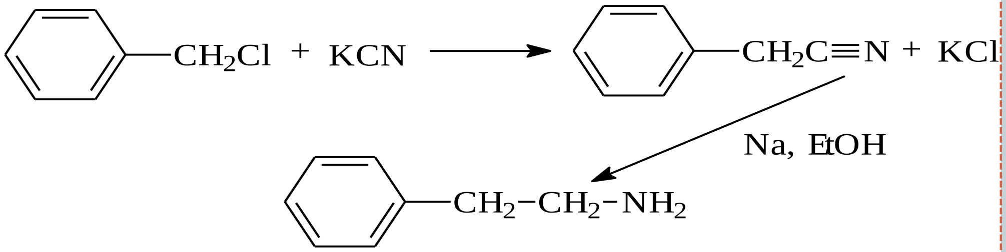
(1) Phenylethyl amine alkaloids
(2) Pyrrolidine alkaloids
(3) Pyridine or piperidine alkaloids
(4) Pyridine-pyrrolidine alkaloids
(5) Tropane alkaloids
(6) Quinoline alkaloids
(7) Isoquinoline alkaloids
(8) Phenanthrene alkaloids
(9) Indole alkaloids

Phenyl ethyl amine group

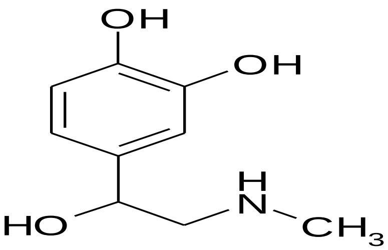
Many compounds of this group are known some natural and other synthetic .The physiological action is to increase the blood pressure .They are referred to as the blood - pressure drugs.

Synthesis of Beta phenyl ethyl amine

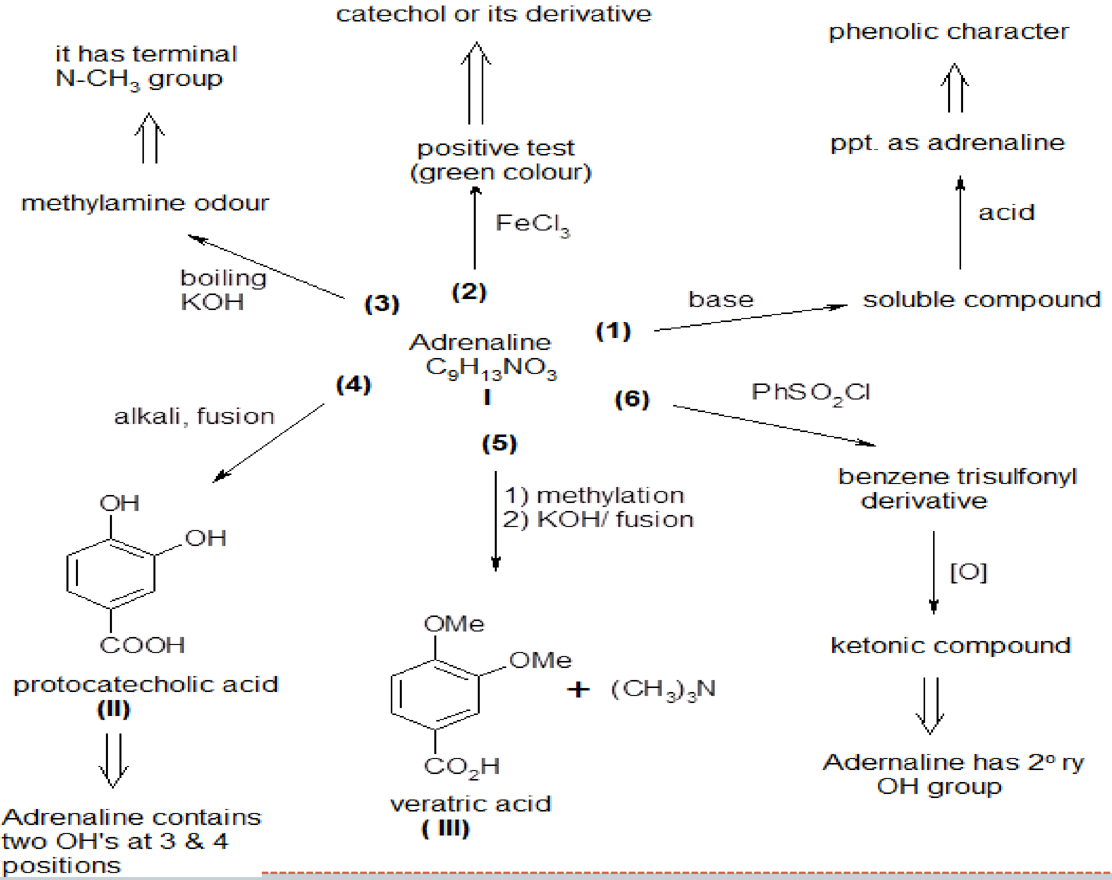




($C_9H_{13}NO_3$) Adrenaline الأدرينالين



adrenaline
I



(1) base → soluble compound; acid → ppt. as adrenaline ⇒ phenolic character

(2) $FeCl_3$ → positive test (green colour) ⇒ catechol or its derivative

(3) boiling KOH → methylamine odour ⇒ it has terminal $N\text{-}CH_3$ group

(4) alkali, fusion → protocatecholic acid (II) ⇒ Adrenaline contains two OH's at 3 & 4 positions

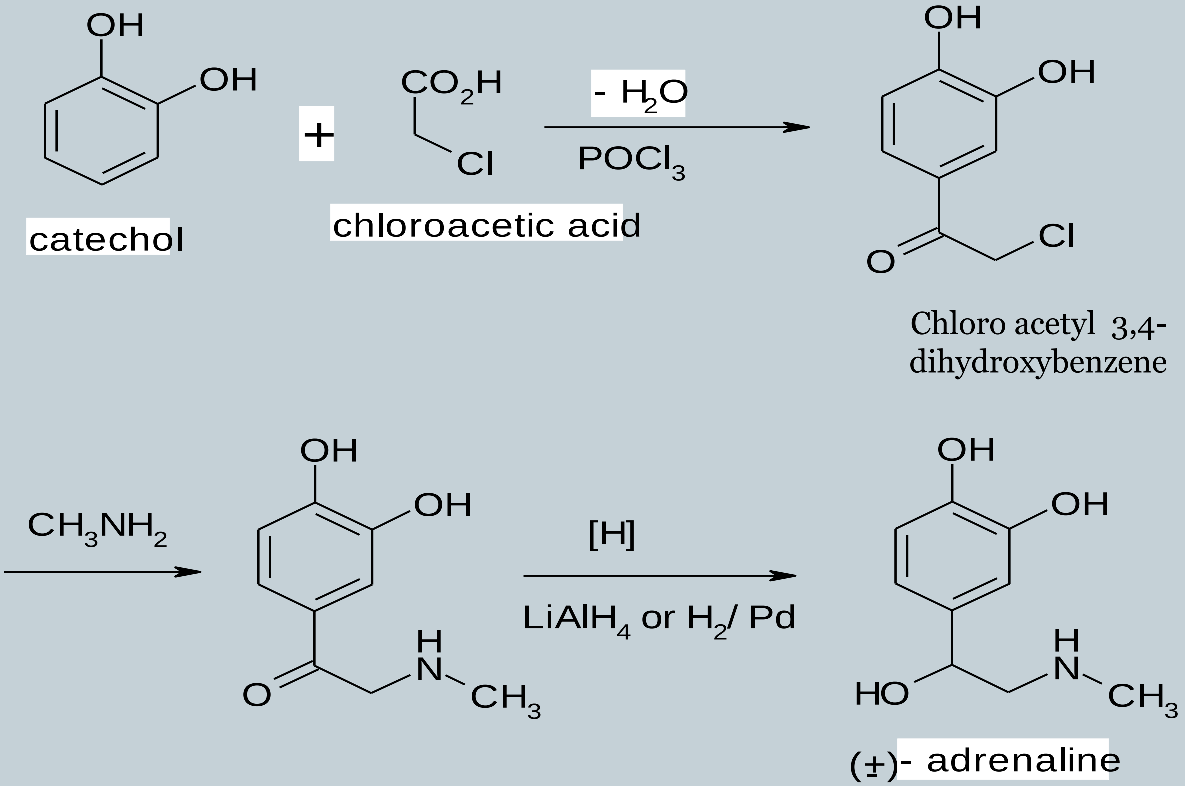
(5) 1) methylation 2) KOH/ fusion → veratric acid (III) + $(CH_3)_3N$

(6) $PhSO_2Cl$ → benzene trisulfonyl derivative; [O] → ketonic compound ⇒ Adernaline has 2º ry OH group

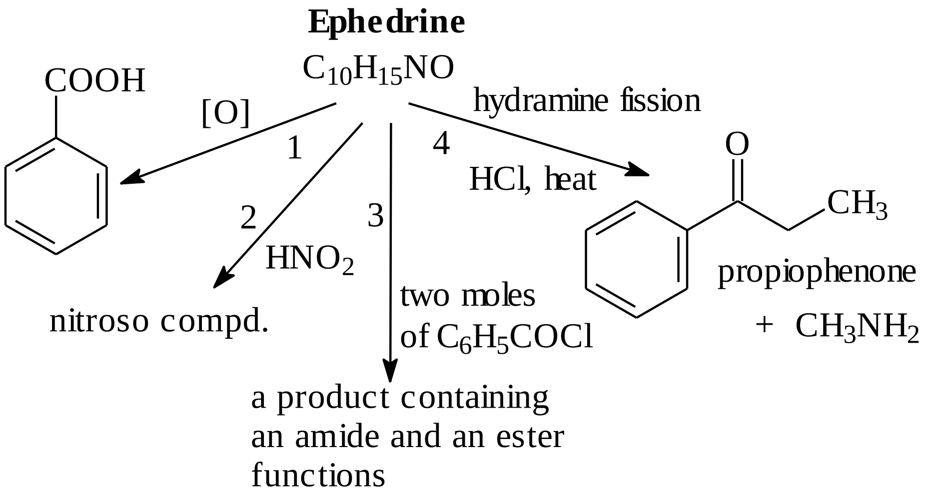
Adrenaline $C_9H_{13}NO_3$ I

($C_9H_{13}NO_3$) الأدرينالين

Synthesis of adrenaline



Ephedrine



Ephedrine

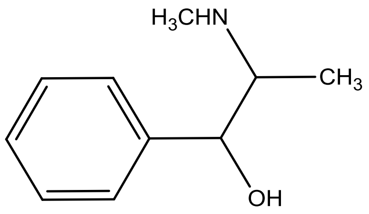
$C_{10}H_{15}NO$

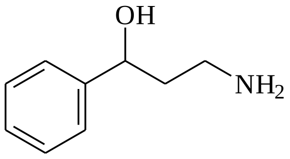
1 [O]

2 HNO_2 → nitroso compd.

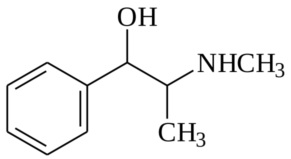
3 two moles of C_6H_5COCl → a product containing an amide and an ester functions

4 hydramine fission, HCl, heat → propiophenone + CH_3NH_2





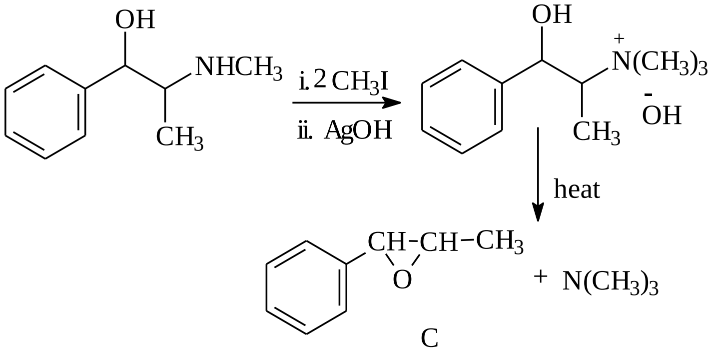
A



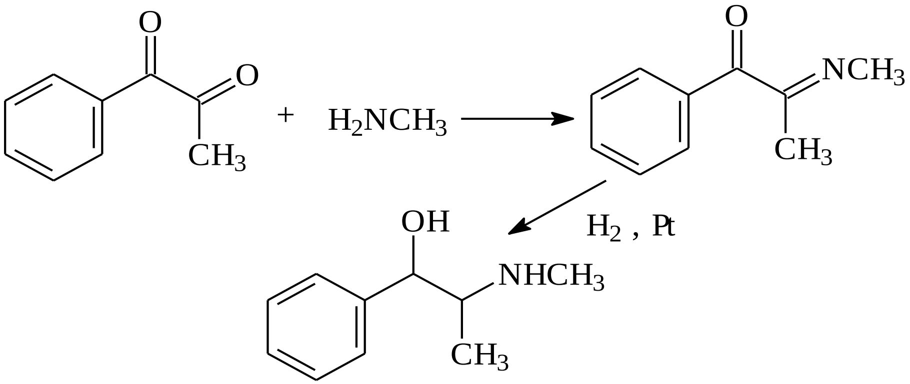
B

Ephedrine

Hofmann exhaustive methylation **:**



Synthesis of ephedrine

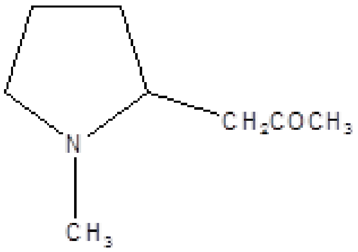


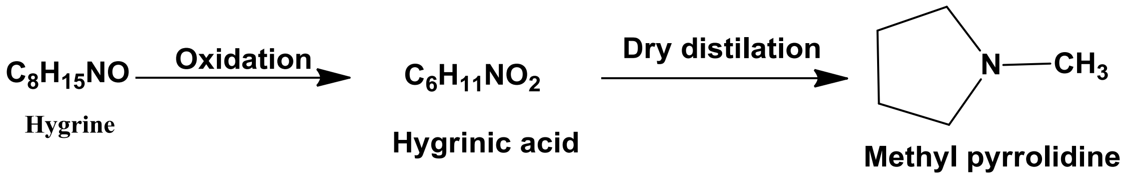
(Pyrrolidine group) قلويدات مجموعة البيروليدين

(Hygrine) الهيجرين $C_8H_{15}NO$

Confirmation of the structure

اثبات الشكل التركيبي للهيجرين :





On oxidation of Hygrine ,Hygrinic acid is formed . Hygrinic acid was first believed to be a one from piperidine carboxylic acids but comparison with the three acids showed this was incorrect.

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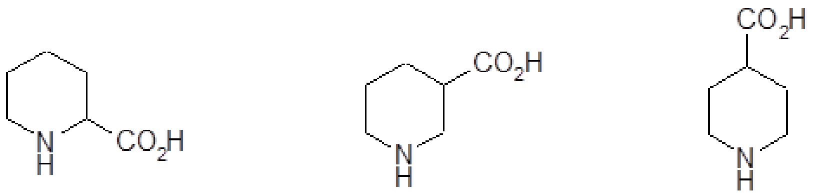
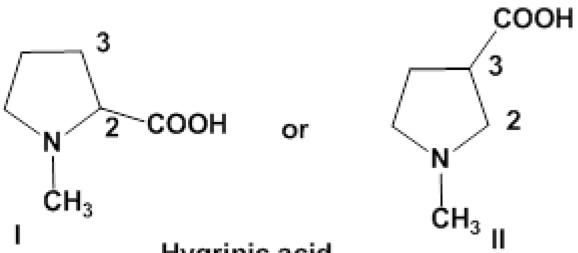


piperidine carboxylic acids

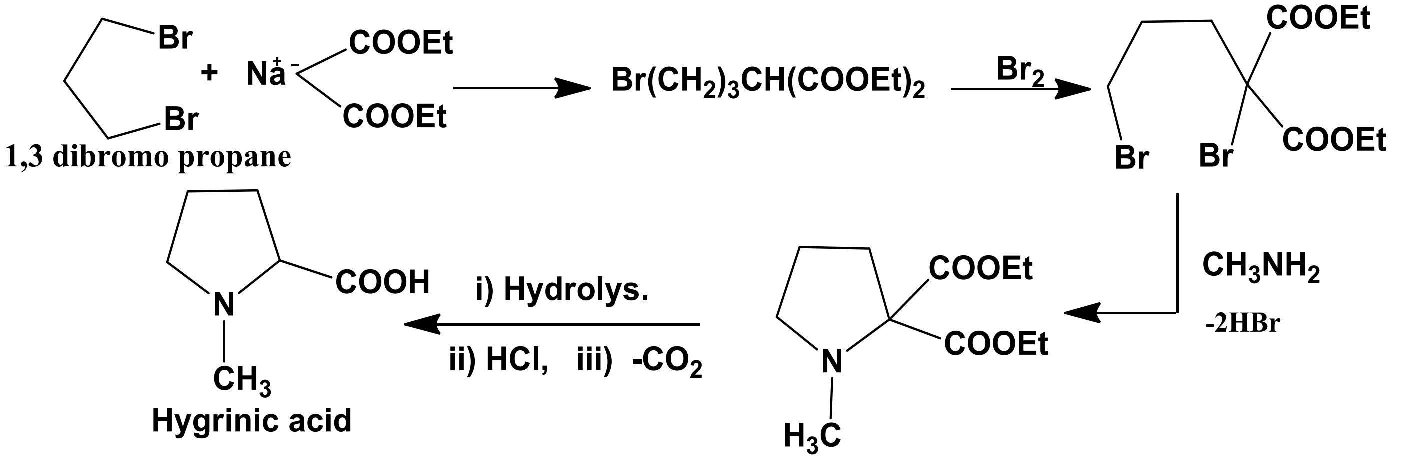


Hygrinic acid

(Hygrine) الهيجرين

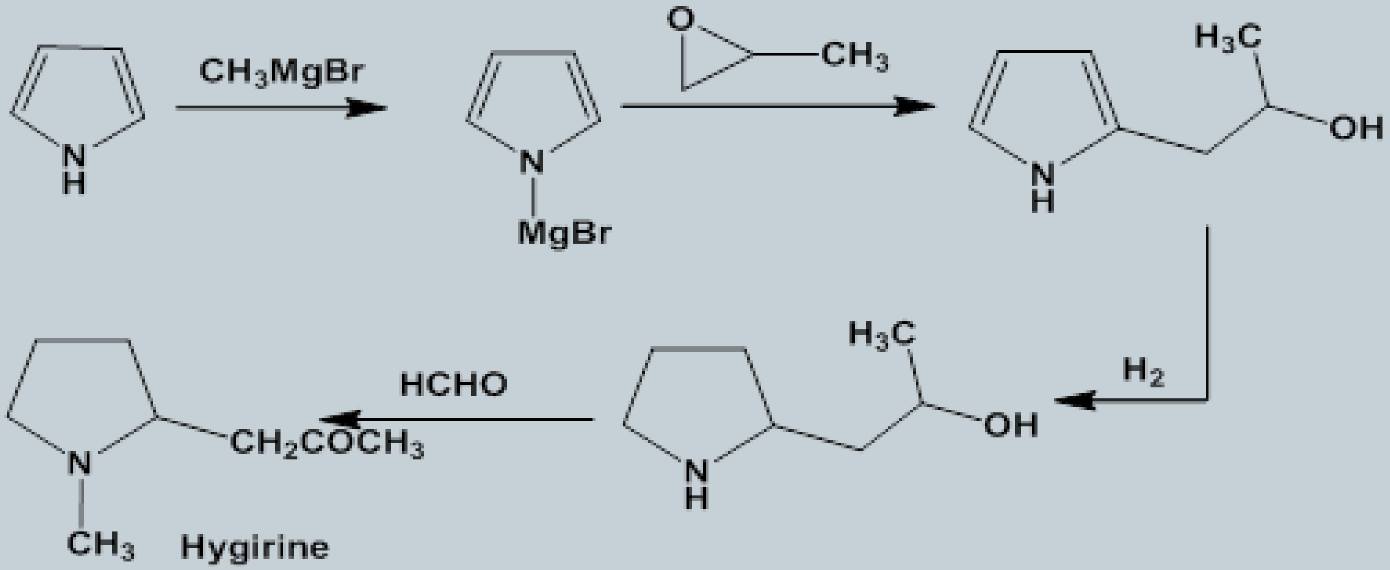
تحضير حمض الهيجرينيك

Synthesis of Hygrinic acid(N-methylpyrrolidine carboxylic acid)



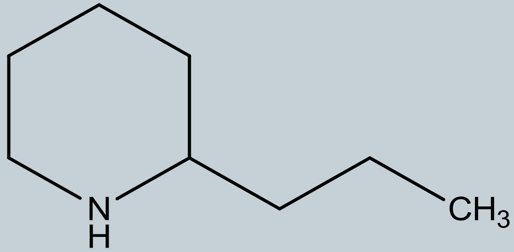
Synthesis of Hygrine تحضير الهيجرين

Synthesis of Hygrine
تحضير الهيجرين



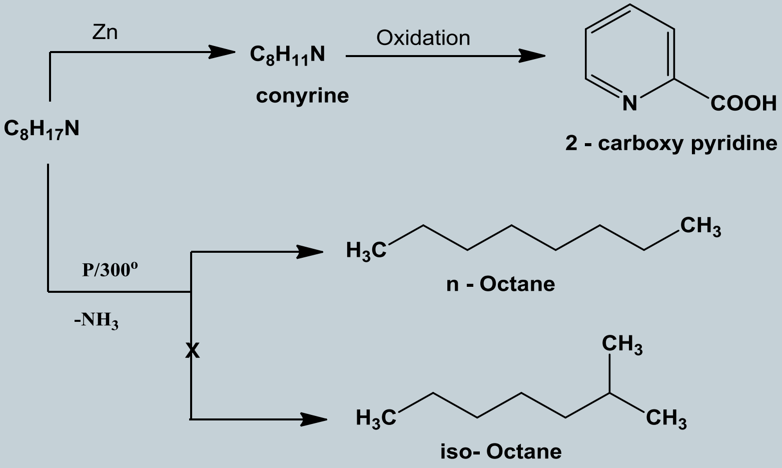
قلويدات مجموعة البيريدين

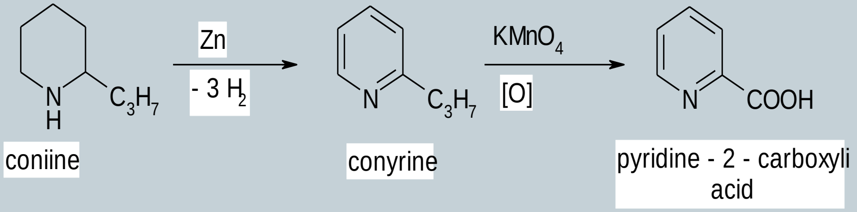
Pyridine alkaloids *Coniine* $C_8H_{17}N$ الكونيين

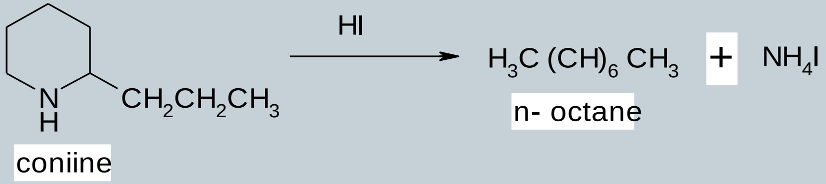


Confirmation of the structure اثبات الشكل التركيبي للكونيين

1-M.F $C_8H_{17}N$
2-Dry dist. with zinc dust coniine is converted into conyrine
3- Pyridine 2-carboxylic acid (α-picolinic acid)was obtained via oxidation of conyrine
4- Coniine is may be piperidine with side chain with three carbon atom
5- the side chain either n-propyl or iso propyl ,it may be n-produces n- propyl (heating coniine with hydroiodic acid octane not iso –octane,so Coniine is 2-n-propylpiperidine which confirmed by synthesis .

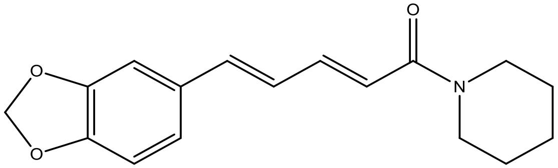






قلويدات مجموعة البيريدين - البيبـــرين $C_{17}H_{19}NO_3$

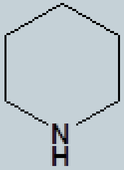
Pyridine alkaloids - Piperine



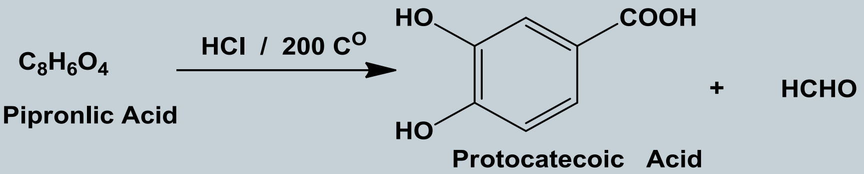
Confirmation of the structure

اثبات الشكل التركيبي للبيبرين

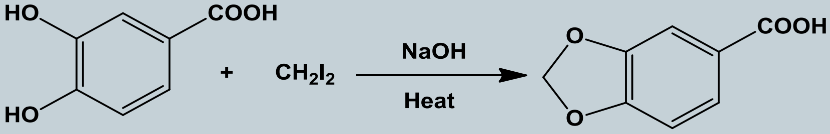
$$\underset{\text{Piprene}}{C_{17}H_{19}NO_3} \xrightarrow{KOH\ /\ H_2O} \underset{\text{Pipric acid}}{C_{12}H_{10}O_4} +$$



$$\underset{\text{Piperic acid}}{C_{12}H_{10}O_4} \xrightarrow{KMnO_4} \underset{\text{Pipronal}}{C_8H_6O_3} \longrightarrow \underset{\text{Pipronlic Acid}}{C_8H_6O_4}$$

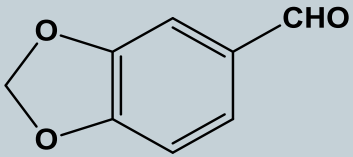


Protocatecoic Acid



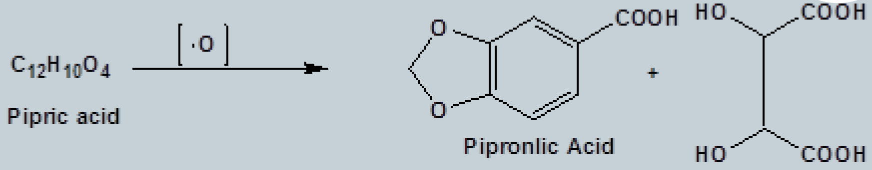
Protocatecoic Acid

Pipronlic Acid

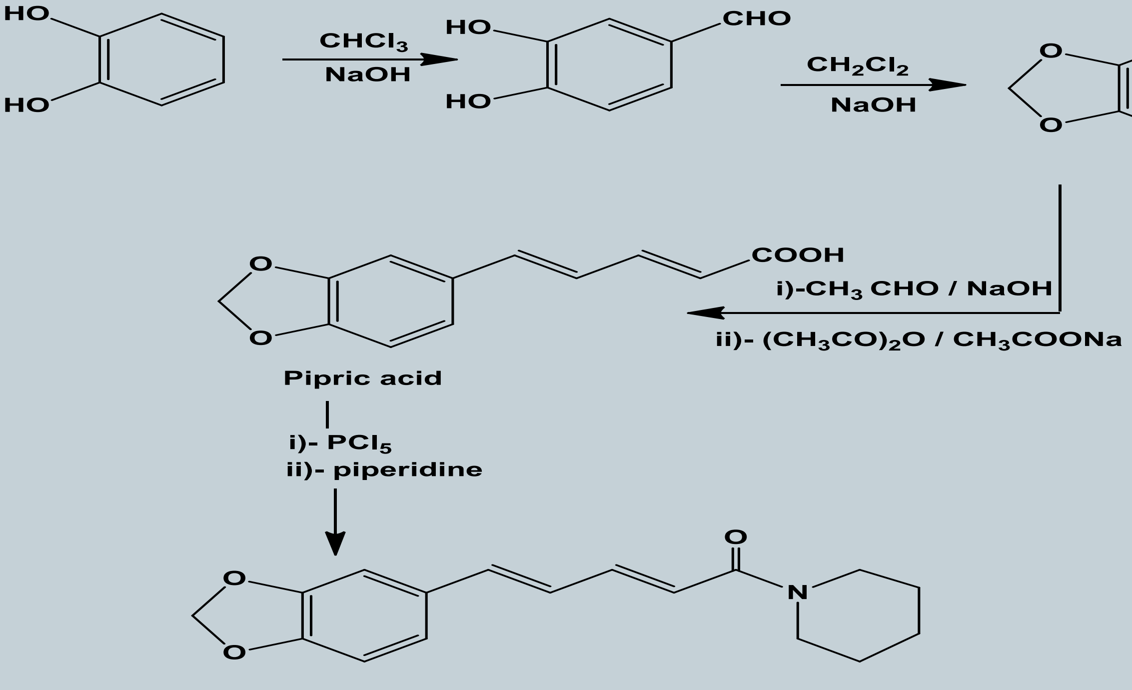


Pipronal

Piperine البيبرين

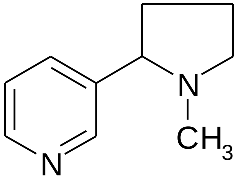


Synthesis of piperine



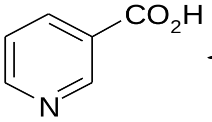
(Pyrrolidine-pyridine group) قلويدات مجموعة البيروليدين بيريدين
Nicotine($C_{10}H_{14}N_2$) النيكوتيـن

Confirmation of the structure
اثبات الشكل التركيبي للنيكوتين :



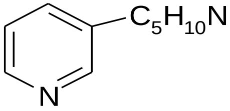
nicotine

(A) nicotine $\xrightarrow[H_2SO_4]{Na_2Cr_2O_7}$ nicotinic acid



nicotinic acid

nicotine has structural formula



(B) nicotine $\xrightarrow{CH_3COCl}$ No reaction

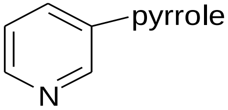
i.e. nicotine is tertiary amine

(C) nicotine $\xrightarrow{CH_3I}$ quaternary salt

quaternary salt $\xrightarrow[\text{mild conditions}]{K_2Fe(CN)_6}$ N - methyl nicotine

N - methyl nicotine $\xrightarrow[H_2SO_4]{Na_2Cr_2O_7}$ N - methyl pyrrole -2- carboxylic acid

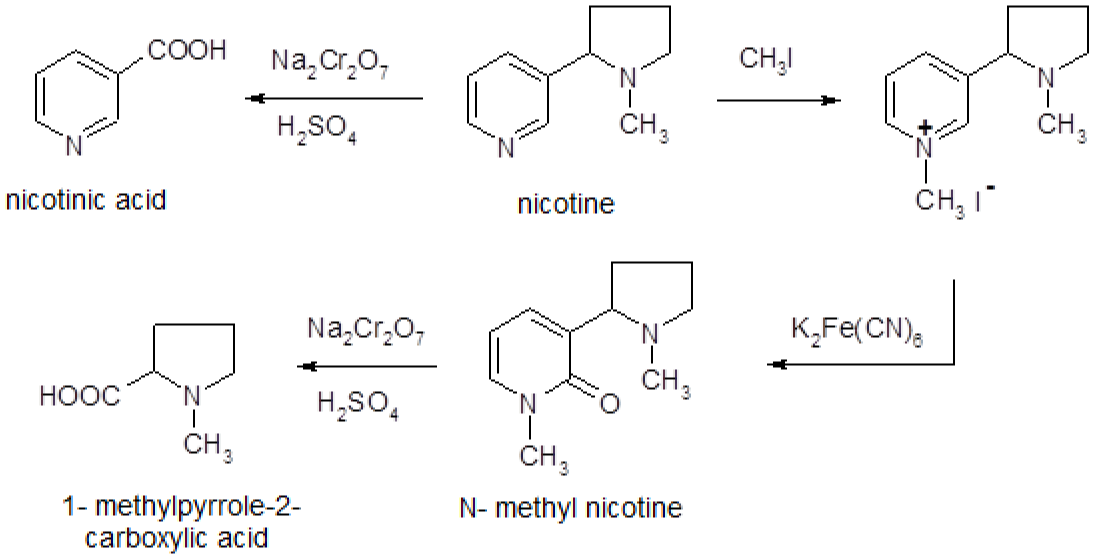
nicotine can be written as ⟸ N - methyl pyrrole -2- carboxylic acid



Nicotine ($C_{10}H_{14}N_2$) النيكوتيــن

Confirmation of the structure

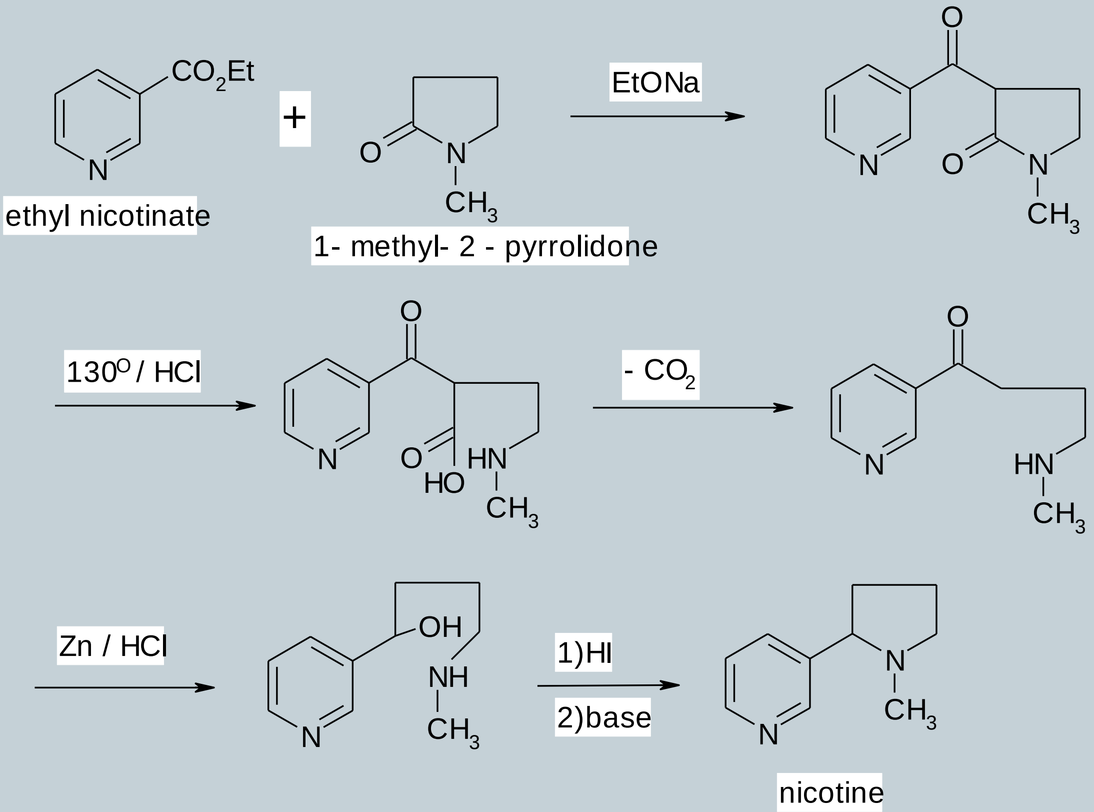
اثبات الشكل التركيبي للنيكوتين



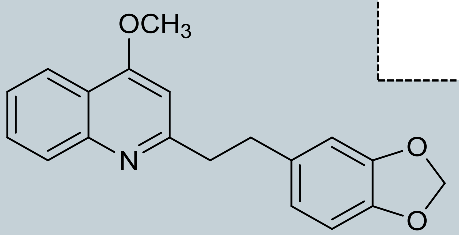
Synthesis of Nicotine تحضير النيكوتين

Synthesis of Nicotine *Spath and Bretsvchneider*

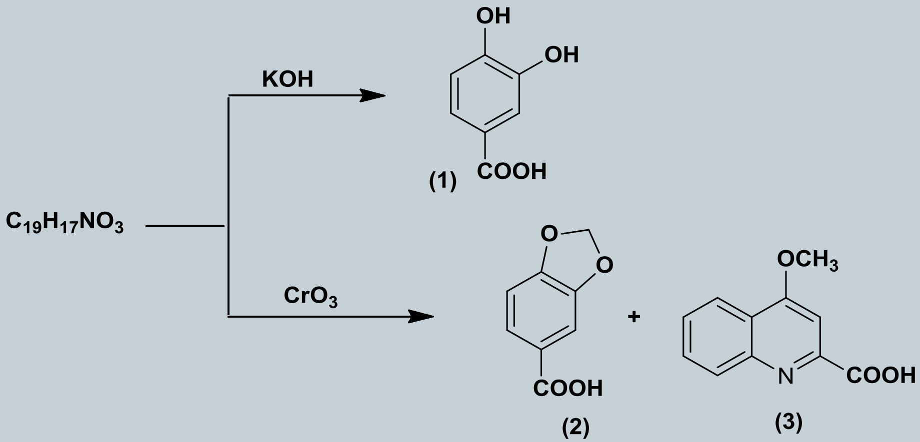
تحضير االنيكوتين طريقة سباث و برتشنيدر



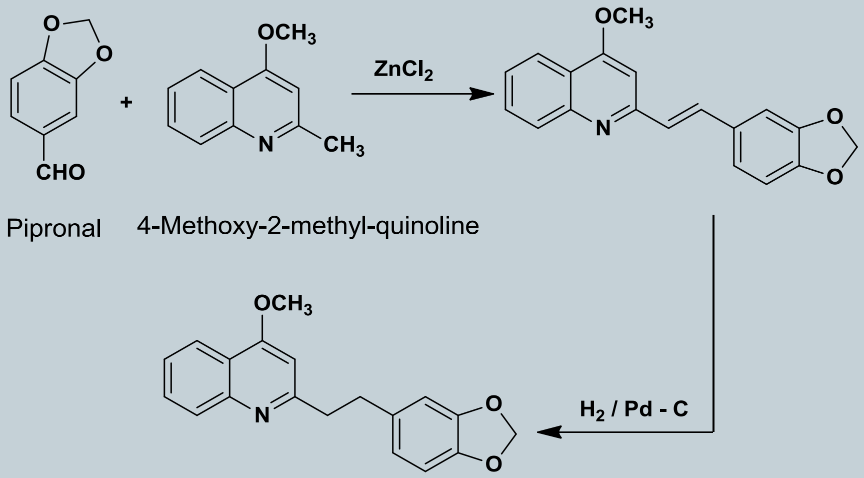
قلويدات مجموعةالكينولين الكسبارين $C_{19}H_{17}O_3N$
Quinoline alkaloids *Cusparine*



Confirmation of the structure اثبات الشكل التركيبي للكسبارين



Synthesis of cusparine
تحضير كسبارين



FACULTY OF SCIENCE, QENA
كلية العلوم بقنا

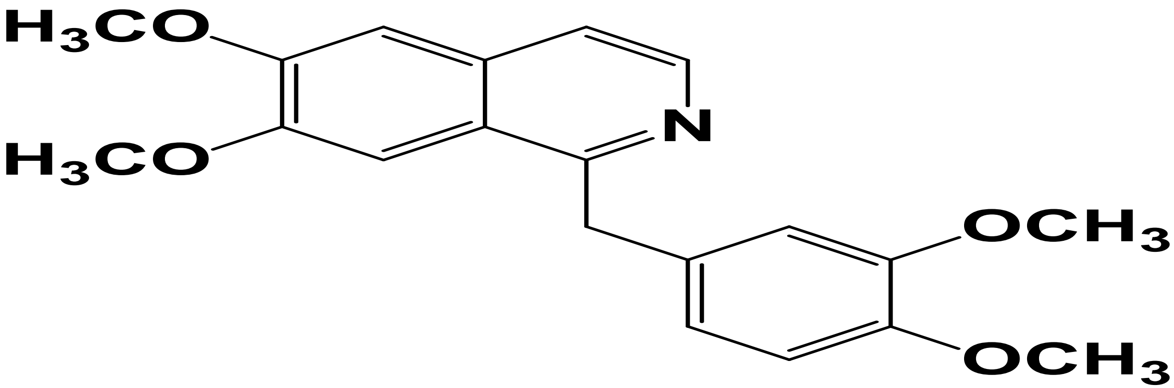
SOUTH VALLEY UNIVERSITY
جامعة جنوب الوادي

NATURAL PRODUCTS
ISOQUINOLINE ALKALOIDS

Dr. Awatef M. Elmaghraby

ISOQUINOLINE ALKALOIDS
($C_{20}H_{21}NO_4$) Papaverine البابافيريـــن

The alkaloids of this group contain in their main composition an isoquinoline nucleus. Most of the members of this group have a physiological toxic effect and cause many diseases for many tissues of the body, especially cancer, and they also have a strong destructive effect on the nervous system of the person.



Papaverine is a solid with a melting point of 147 ° C).

Gold Schmiedt et al established the structure as follow:

Papaverine
Determination of the structure

1-It has been proven that M.F $C_{20}H_{21}NO_4$

2-Papaverine is optically inactive , since it does not contain any chiral center (asymmetric carbon atom).

3- Since papaverine adds one molecule of methyl iodide to form a quaternary iodide salt, this indicates the presence of nitrogen in the tertiary state.

4- Papaverine contains four methoxy groups (Zeisel method).

$$C_{20}H_{21}NO_4 + 4\ HI \longrightarrow C_{16}H_{13}NO_4 + 4CH_3I$$

بابافيرينPapaverine

papaveroline بابافيرولين

Determination of the structure

5-Oxidation by cold dilute permanganate papaverinol is obtained ,thus more vigorous oxidation with hot dilute permanganate a ketone papaveraldine is obtained so papaverinol is a sec. alcohol and papaverine must be contain a methylene group(-CH_2-). The prolonged action of permanganate oxidize the ketone to papaverinic acid .

$$(C_{19}H_{19}NO_4)CH_2 \xrightarrow{|O|} (C_{19}H_{19}NO_4)CH\text{-}OH \xrightarrow{|O|} (C_{19}H_{19}NO_4)C{=}O$$

Papaverine	papaverinol	papaveraldine
بابافيرين	بابافيرينول	بابافيرالدين

6-When oxidized with hot permanganate ,papaverine (or the oxidized product)is broken down into small fragments:

1-Veratric acid

2- Meta hemipinic acid

3-Pyridine 2,3,4-tricarboxylic acid

4- 6,7-dimethoxyisoquinoline -1- carboxylic acid

Determination of the structure

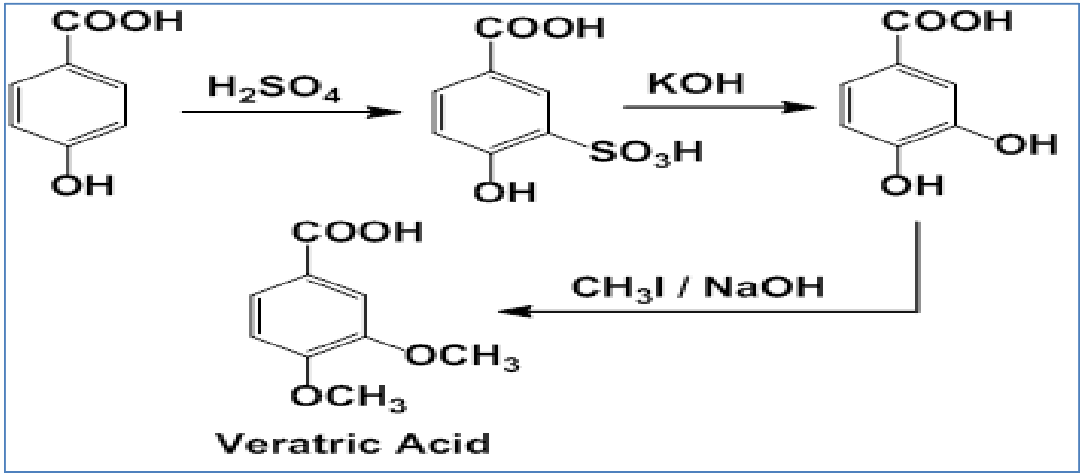
Now, let us consider the evidence for the structure of these compounds :

1- Veratic acid

a) Veratric acid contains one carboxyl group and two methoxy group

b) Decarboxylation of veratric acid veratrol is obtained. Since this is dimethoxy benzene ,so veratric acid is dimethoxy benzoic acid .

c) The position of the carboxyl with respect to methoxy groups established by the following synthesis :



So veratric acid is 3,4 dimethoxy benzoic acid.

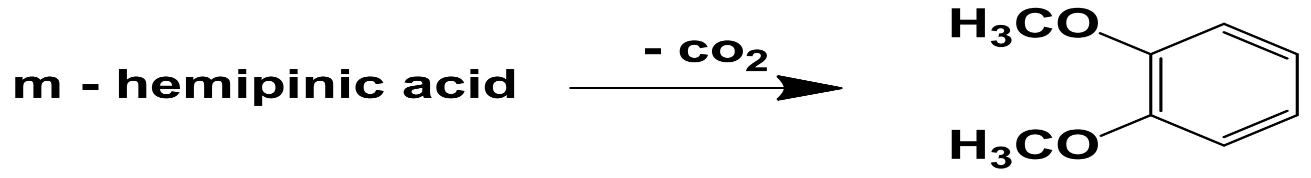
Determination of the structure

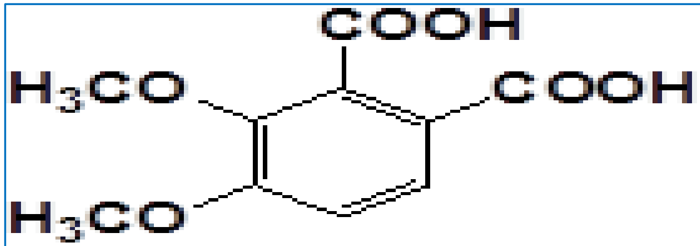
2-Metahemipinic acid:

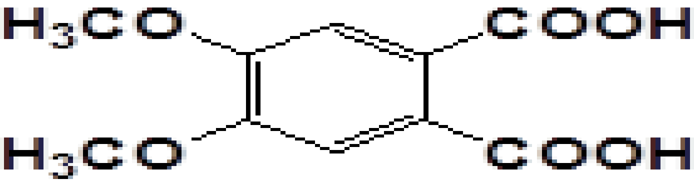
a) This is dicarboxylic acid and decarboxylation with calcium oxide, veratrol is formed .

b) Meta hemipinic acid contains two methoxy group .

c) The meta hemipinic acid is either (1) or (2)



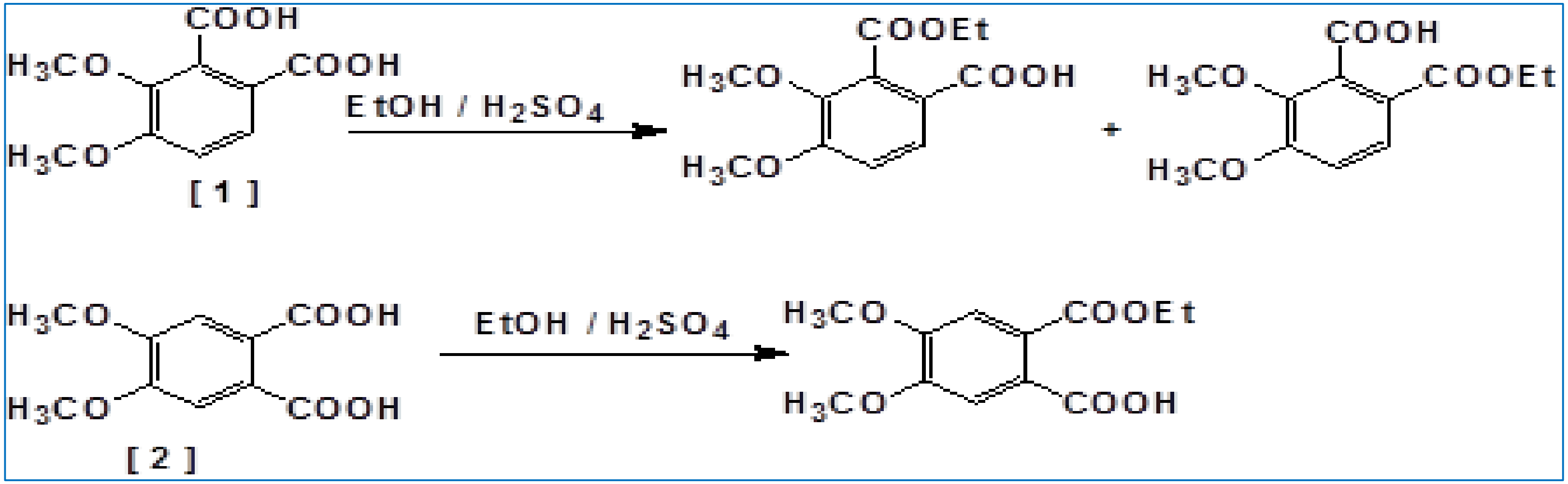

[1]


[2]

Determination of the structure

d)Heating the acid with acetic anhydride an anhydride is formed, so the two carboxyl group must be in the ortho position .

e)Meta hemipinic acid forms only mono ester (2) permits the formation of mono ester so the structure (2) is meta hemipinic acid.



Determination of the structure

3-pyridine 2,3,4-tricarboxylic acid

a) It contains three carboxylic groups .

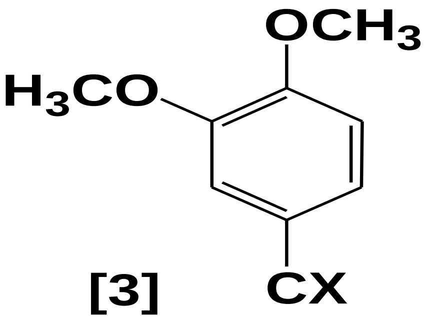
b) Decarboxylation gives pyridine .

The position of three carboxyl group is established by the following synthesis starting with lipidine(4-methyl quinoline).

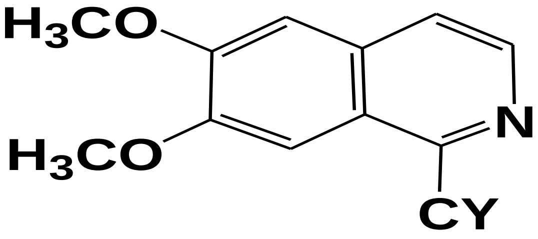
Elucidation of the structure

1-Separation of veratric acid indicates the presence of group [3] in papaverine.

2- The separation of the 6,7 dimethoxyi soquinoline - 1 - carboxylic acid indicates the presence of group [4] in the molecule..



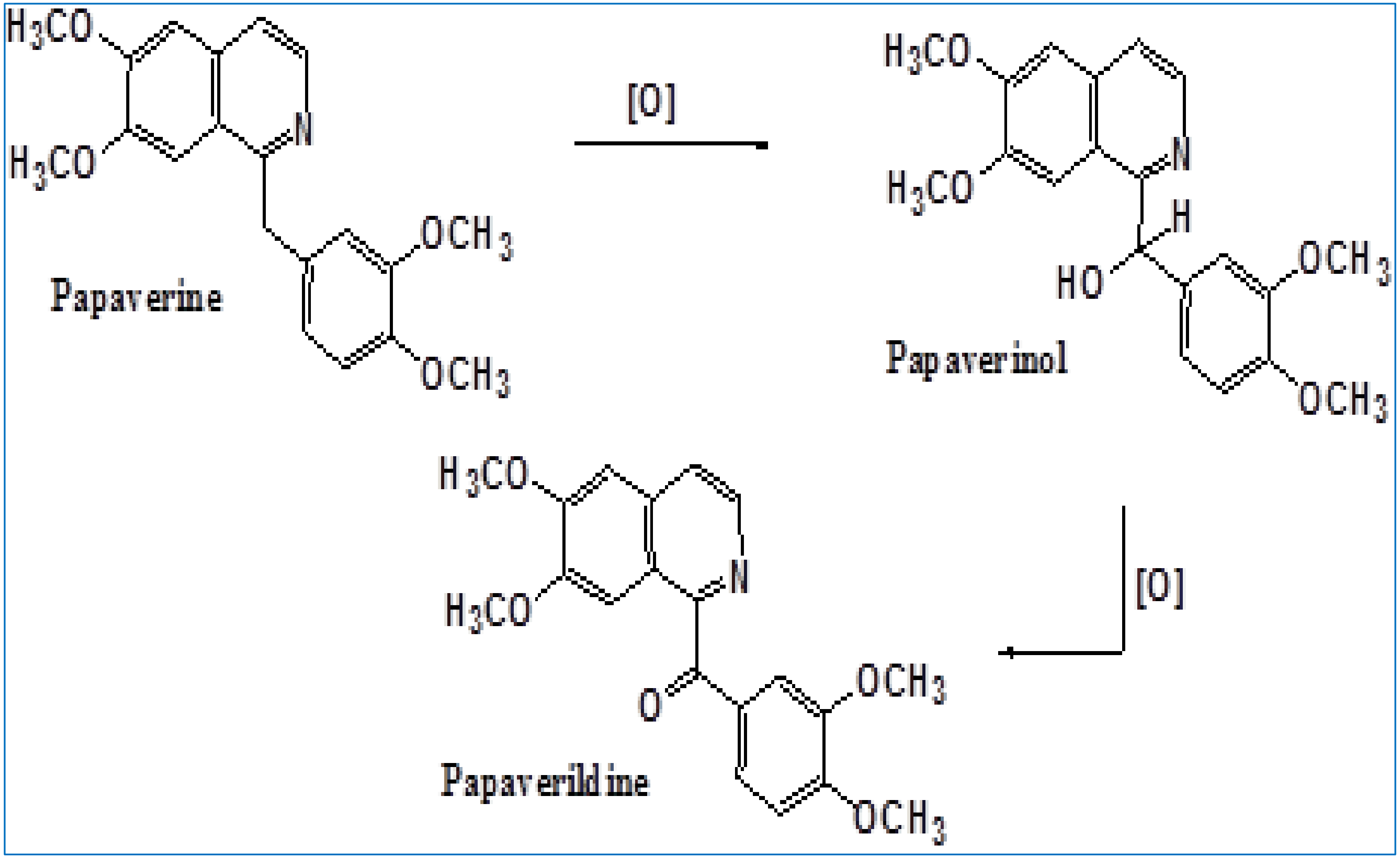
[3]



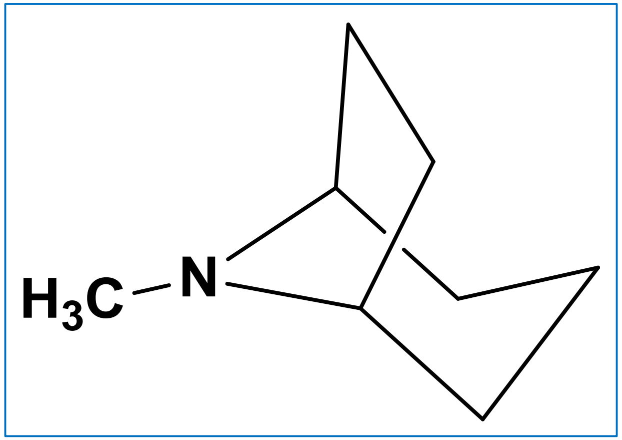
[4]

3- Given that the total number of carbon atoms in groups [3] and [4] is 21 carbon atoms, and papaverine contains only 20 carbon atoms. So, there must be a repeat carbon atom in each of the CX and CY groups. Given that the compound contains a group of CH2 (methylene), then it is likely that it is the same as the duplicated carbon atom.

If we assume that C-x and C-y are one and the same carbon atom of the (X-CH_2 –Y) group, then the following structure of papaverine accounts for all the facts.



Fused pyrrolidine-pyridine group
Tropine alkaloids
قلويدات البيروليدين- بيريدين المتكاثفة
[قلويدات التروبين]



نواة التروبين

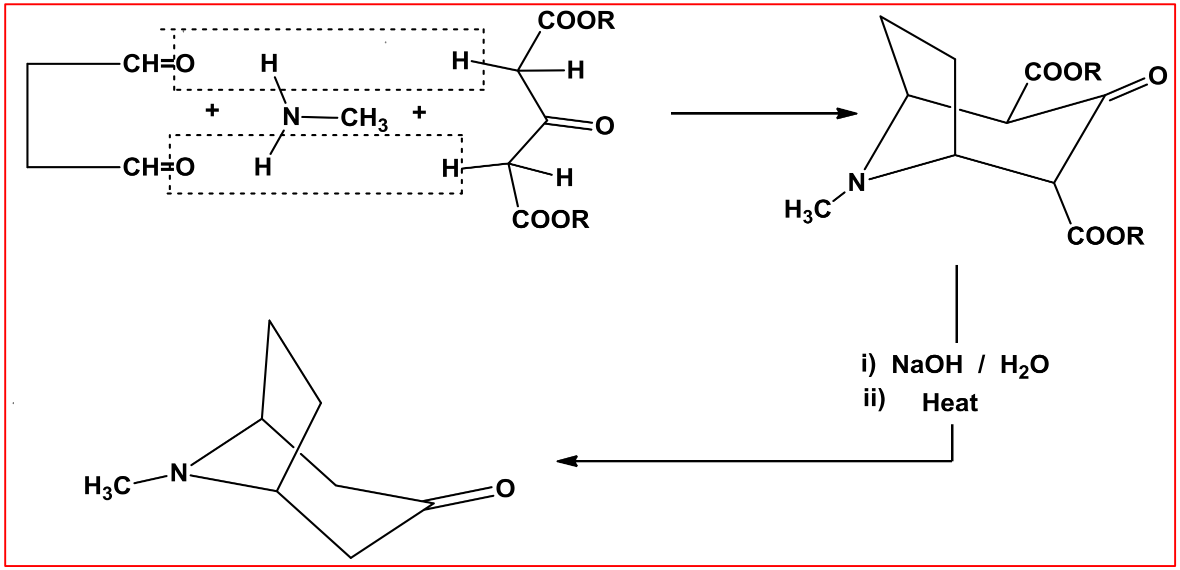
Tropine nucleus

8-methyl-8-azabicyclo[3.2.1]octane

Tropine alkaloids [8-methyl-8-azabicyclo[3.2.1]octane occur in (atropa belladonna). The most important alkaloids that can be obtained from these sources are atropine drugs, high amino acid, scopolamine, etc.

The heterocyclic tropic alkaloids as they consist of the fusion of the pyridine nucleus with the pyrrole nucleus. It is also possible to attribute all of these alkaloids. To the compound tropan.

Tropinone can be synthesized via heating succinaldehyde,methyl amine and alkyl acetondicarboxylate in the presence of hydrochloric acid as follow (Robinson method)



طريقة روبنسون Robinson's method

نبات ست الحسن
(atropa belladonna الاتروبابلادونا)

(hyoscyamus السكران
nizer)

الداتورا الصفراوية
Datura stramonium

Tropinone can be reduced to give tropanol (sec.alcohol) also it can be add hydrogen cyanide to give the cyanohydrine derivative which hydrolyzed into the corresponding hydroxy acid,.In this way it has been possible to create many of these compounds, which have such a structural structure for the purpose of studying their physiological effect.

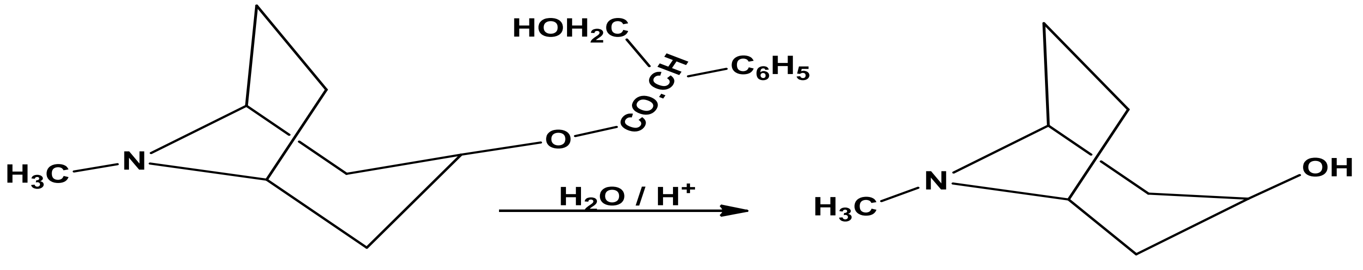
سير روبرت روبنسون جائزه نوبل ١٩٤٧ لتحقيقاته فى المنتجات النباتية ذات الأهمية البيولوجية، وخصوصا القلويدات"

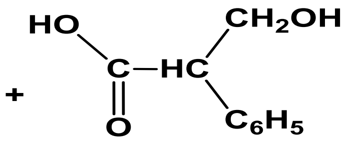
Atropine الأتروبيـــن:

Atropine is occurs in (atropa belladonna) together with hyoscyamine, atropine solid m.p118 °C

-It has been proven that molecular formula $C_{17}H_{23}NO_3$

-Atropine is hydrolyzed to tropic acid and tropine(tropanol),thus atropine is the tropanoyl ester of tropic acid ,atropine can be synthesized by heating of tropic acid with tropanol in the presence of hydrogen chloride. It is known that it is used in ophthalmology, since its solution with a concentration of ½ - 1% in oil causes an expansion in the eye (diffusive effect).





Atropine

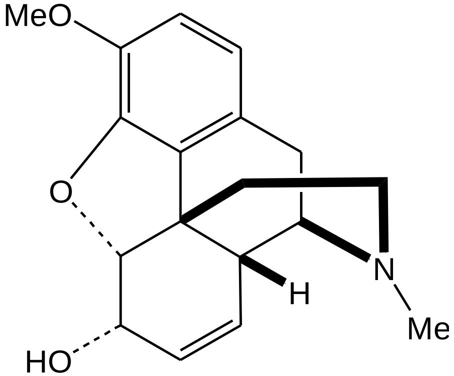
tropanol
(tropin)

tropic acid

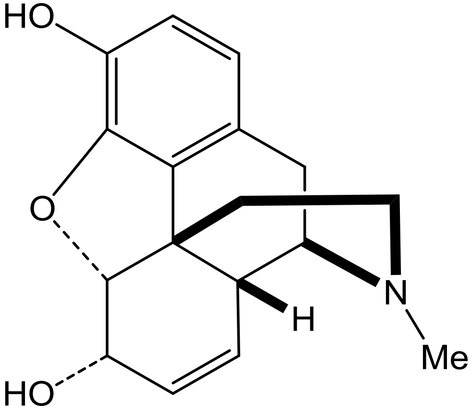
Phenanthrene Group

قلويدات الفينانثرين

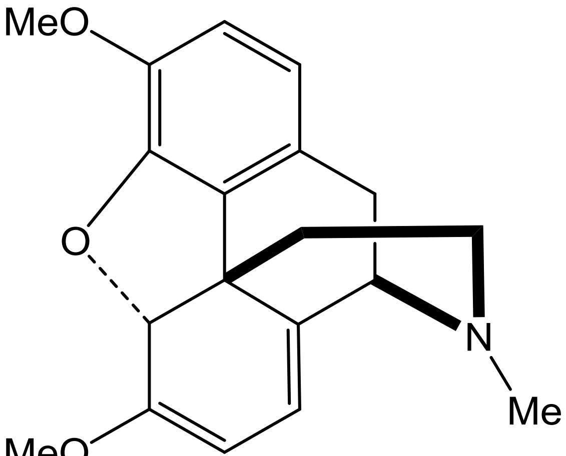
Morphine, Codeine and Thebaine those are the three important opium alkaloids containing the Phenanthrene nucleus.



Codeine



Morphine

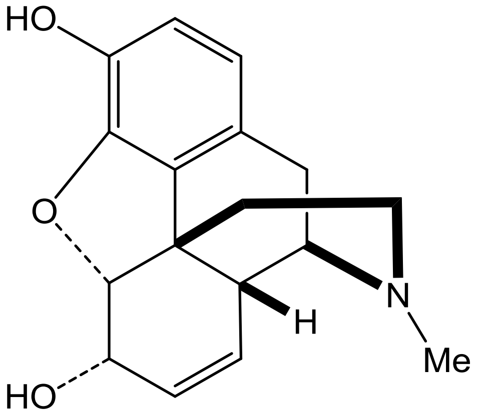


Thebaine

قلويد الكودين

قلويد ا لمورفين

قلويد الثيبايين



Morphine

Morphine المورفين

Morphine is the chief alkaloid in opium and was the first alkaloid to be isolated ,the chemical structure was supported by:

1- It has been proven that molecular formula C_{17} $H_{19}NO_3$ (after purification, Qualitative and quantitative analysis, determination of empirical formula)

2- Routine tests confirmed that nitrogen in the tertiary state .

3- Acetylation of morphine gives morphine diacetate (Heroin),two hydroxyl groups are present in the molecule.

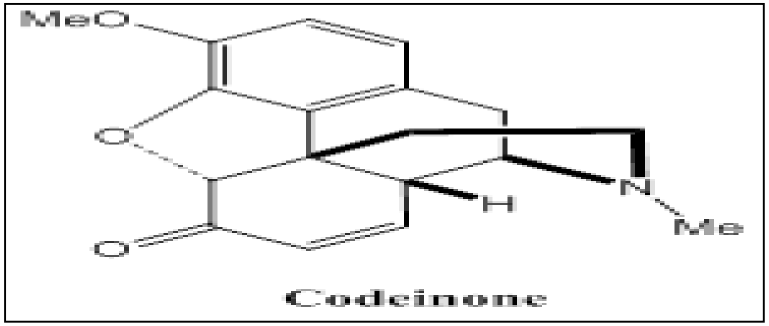
4-Morphine gives the ferric chloride test for phenols and dissolves in aqueous sodium hydroxide to form mono sodium salt ,and this is reconverted into morphine by the action of carbon dioxide,thus one of the hydroxyl groups is phenolic.

5--**Morphine with halogen acids converted morphine into mono halogeno derivative, one hydroxyl group being replaced by halogen atom thus the second hydroxyl is secondary alcoholic hydroxyl group.**

6-Morphine is methylated by heating with methyl iodide and aqueous potassium hydroxide to give Codeine, therefore follow that it is only the phenolic hydroxyl group in morphine has been methylated.

7- Oxidation of codeine by using chromic acid to give Codeinone ,(a ketone).Thus the hydroxyl group in codeine(and this one in morphine) is secondary alcoholic, and so codeine is the monomethyl (phenolic)ether of morphine .

8-When morphine is distilled with zinc dust phenanthrene and other bases are produced .This suggests that phenanthrene nucleus is present.



Codeinone

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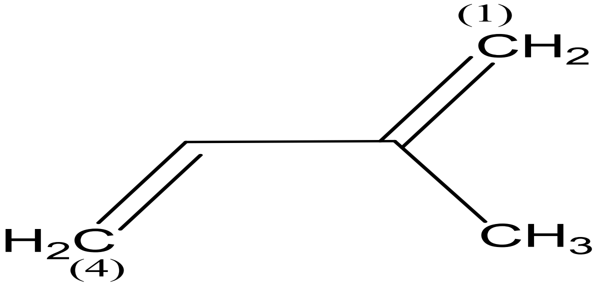
Natural Product Terpenoids

The terpenoids form a group of compounds most of them occur in the plant kingdom. The distinctive aroma of many flowers and roses, as well as the colors of the fruits of some plants, such as carrots, tomatoes, etc., are attributed to terpenoids (terpenes). Terpenoids comprise most of the Kingdom's vegetable products and are involved in the synthesis of many volatile oils. They are also used to make perfumes, medicines and food flavors. This family also belongs to the natural rubber that we obtain as a white liquid from the rubber tree.

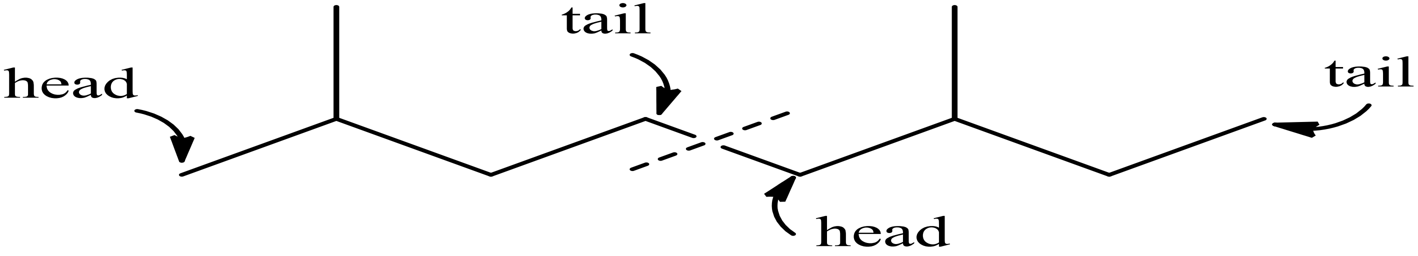


isoprene (2-methyl 1,3 butadiene

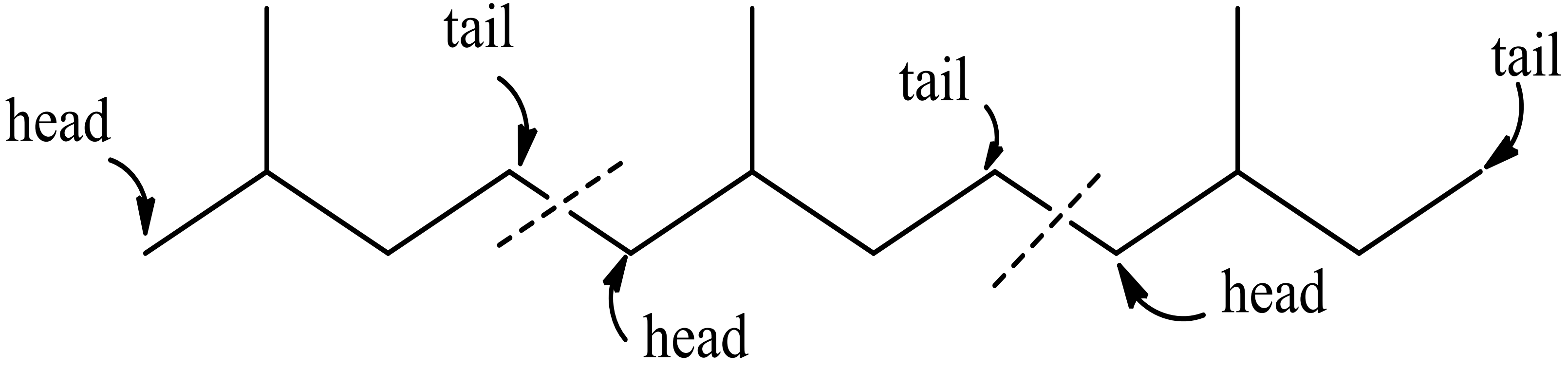
Classification of Terpenoids M.F$(C_5H_8)_n$

The thermal decomposition of almost all terpenoids gives isoprene as one of the products ,this led to suggestion that:
The skeleton structures of all naturally occuring terpenoids can built up of isoprene units this is known as the isoprene rule
Ingold pointed out that isoprene units in natural terpenoids were joined head to tail .
Several exceptions occur ,e.g.the carotenoids joined tail to tail .

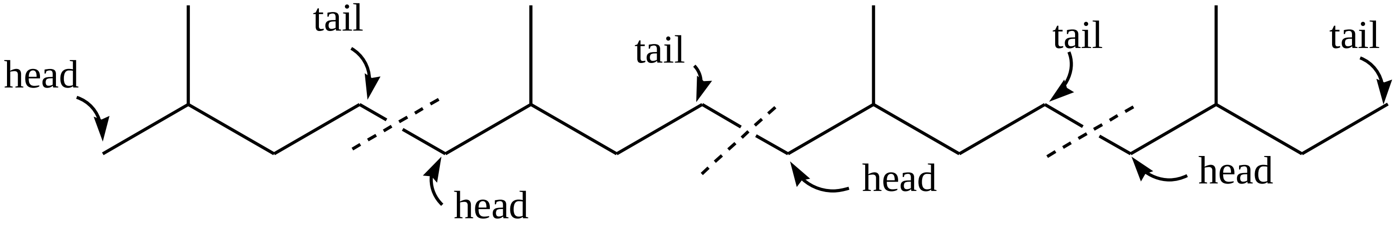
n	Number of carbon	Class	Formula	examples
٢	١٠	Monoterpenes	$C_{10}H_{16}$	Volatile oils
٣	١٥	Sesquiterpenes	$C_{15}H_{24}$	Volatile oils
٤	٢٠	Diterpenens	$C_{20}H_{32}$	Gums and resins
٥	٢٥	Sesterterpenes	$C_{25}H_{40}$	Gums and resins
٦	٣٠	Triterpenes	$C_{30}H_{48}$	Gums and resins
٨	٤٠	Tetraterpens	$C_{40}H_{64}$	Carotenoids
>٨	>٤٠	Polyterpenes	$(C_5H_8)_n$	Natural rubber



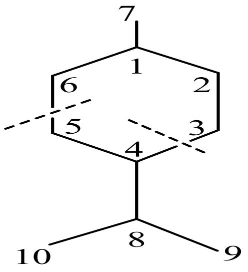
open chain monoterpenoid



open chain sesquiterpenoids

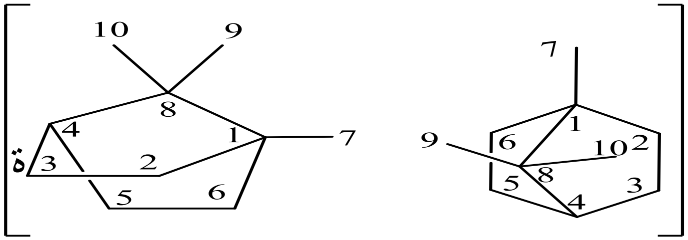


Open chain diterpenoid تربين ثنائي مفتوح السلسلة



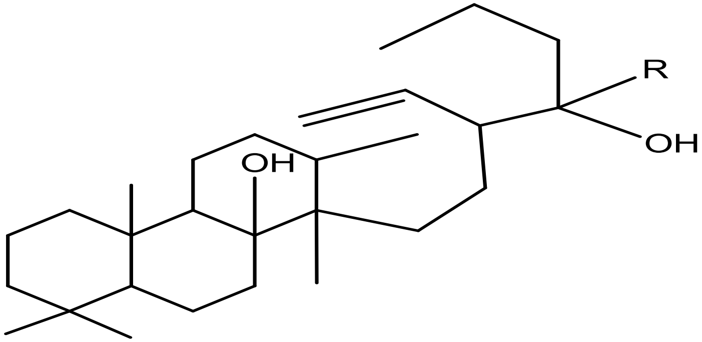
monocyclic monoterpenoid

تربين احادي أحادى الحلقة

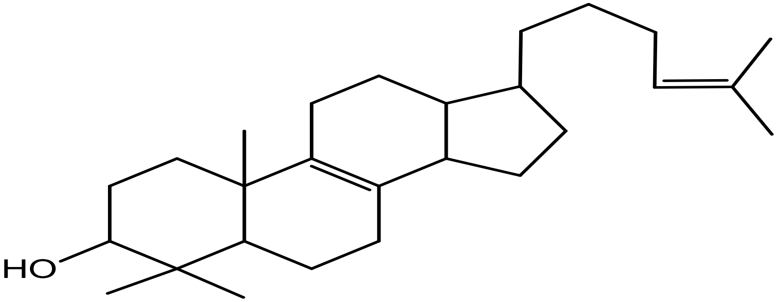


bicyclic monoterpenoid

تربين أحادى ثنائي الحلقة ملتحم



fused tricyclic triterpenoid



fused tetracyclic triterpenoid

تربين ثلاثى رباعي الحلقة ملتحم   تربين ثلاثي ثلاثى الحلقة ملتحم

Separation and Extraction of Monoterpenoids and Sesquiterpenoids

1-Expression
2- Steam distillation
3- Extraction by means of volatile organic solvents
4- Adsorption on fats.

Steam distillation or extraction with volatile organic solvents is one of the most important multiple methods used to extract terpenes from plants, and the method of steam distillation is the most commonly used method, especially when extracting monoterpenes , sesquiterpenes and some diterpenes.

The method of extracting is summarized in grinding the vegetable parts well and then distilling them with steam. Volatile oils by fractional distillation. One of the methods widely used to separate terpenoids is the thin layer (TLC) or column method (CC) or HPLC, and the column method (on silica gel) is one of the most suitable methods of color separation for high terpenes such as di ,tri,and tetraterpenoids.

Methods for Separation of mixtures

- Fractional distillation
- thin layer chromatography
  TLC
- column chromatography
  CC
- high pressure liquid chromatograp
  HPLC
- Other methods

If the compound is decomposes due to the high temperature, it may be extract by means of several organic solvents, where the petroleum ether is used for extraction at a low temperature (50 ° C) and for a period sufficient to extract all types of terpenes, or at least most of them, The ether is then distilled at reduced pressure to maintain the terpenes without decomposition . Then the volatile oil mixture is separated by fractional distillation under reduced pressure or by column .chromatography

General methods of determining structure of terpenoids

1-After extraction and separation then purification of sample ,the molecular formula is ascertained by usual methods (qualitative and quantitative analysis – empirical formula-determination of M.Wt).

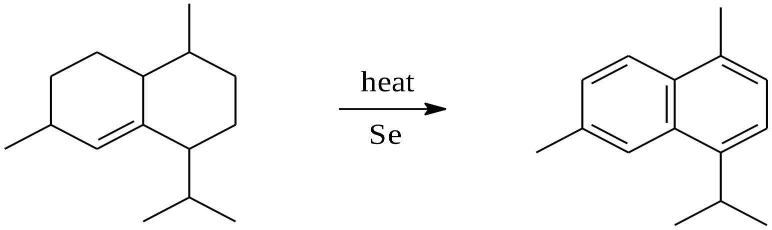
2-If the terpenoid is optically active ,its specific rotation is measured.

3-The nature of functional oxygen atom if it is present (hydroxyl-carbonyl -carboxyl --------- etc).

4-The presence of unsaturation olefinic bonds is ascertained by means of bromine and catalytic hydrogenation.

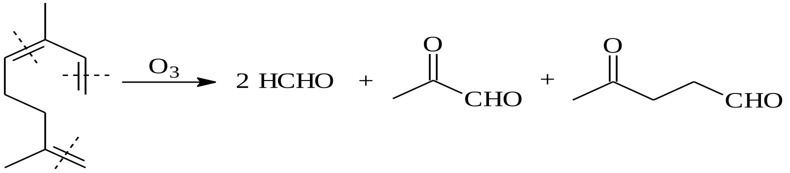
5-Conjugated and isolated double bonds are differentiated by Diel's Alder reaction also by using UV spectroscopy.

6-Dehydrogenation by heating the terpene with S or Se converts the terpene into aromatic derivative which is easily identified.

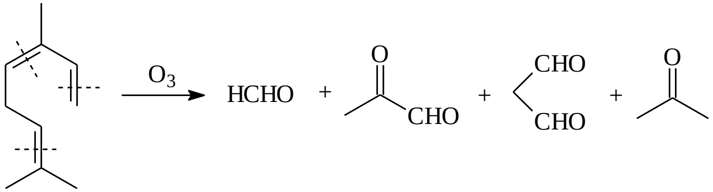


7- Ozonolysis is an example of oxidative degradation methods (O_3, $KMnO_4$, CrO_3 & OsO_4),this method produced two type of products, acetone arising from the terminal isopropylidene group($Me_2C=$) and formaldehyde arising from isopropenyl group($CH_2=CMe$) or terminal methylene group($CH_2=$).

(i)



(ii)



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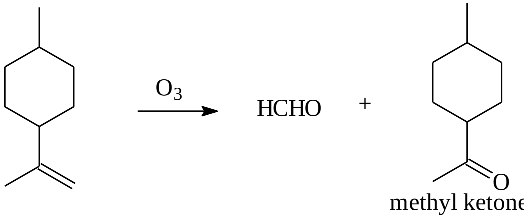
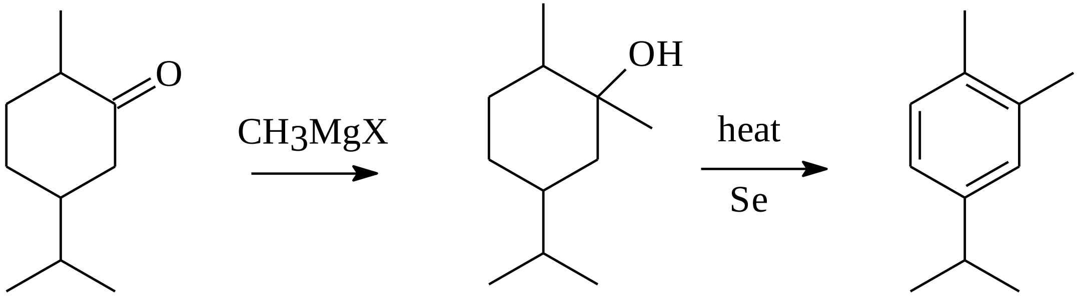


8-Grignard reagent useful for detecting the position of carbonyl group in terpenoids.



9-Infrared spectroscopy (IR) is useful by detecting the presence of hydroxyl group ,carbonyl group -------- etc , NMR (^{1}H-NMR & ^{13}C-NMR give information about the nature and the number of hydrogen and carbon, Ultraviolet spectroscopy (UV),mass spectrometry and X-Ray analysis are very useful for elucidating structure and stereochemistry of terpenoids.

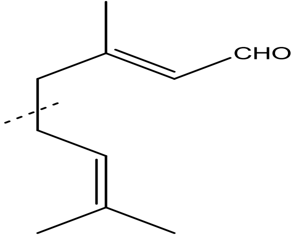
10- A final confirmation of the proposed structure is usually achieved by synthesizing the compound and comparing the spectral data with those of an authentic sample.

Monoterpenoids التربينـــات الأحادية

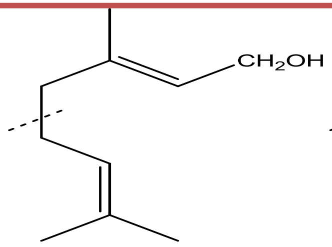
Monoterpenoids are classified into three groups (acyclic,monocyclic,bicyclic)

Acyclic Monoterpenoids

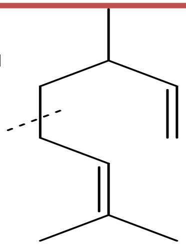
The carbon skeleton being formed by the head to tail of two isoprene units.



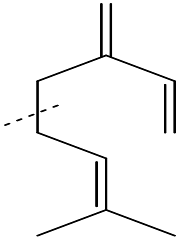
Citral



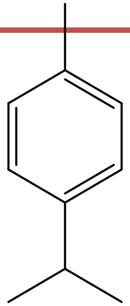
Geraniol



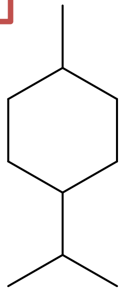
Ocimene



Myrcene



P-cymene

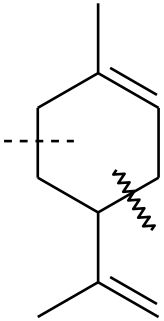


P-menthane

Monocyclic monoterpenoids contain a six membered ring and most natural monocyclic monoterpenoids are derivatives of p-cymene and the parent substance is named P-menthane.

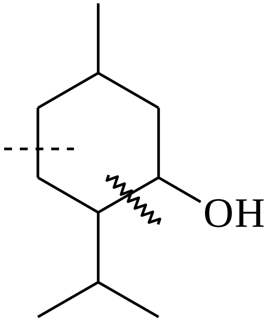
Bicyclic monoterpenoids contain a six membered ring and a three,four or five membered ring .

Monocyclic monoterpenoids

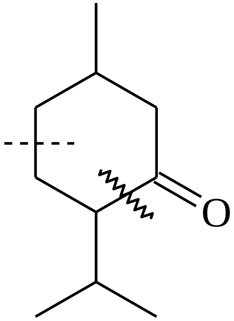


Limonene

occurs in lemon
and orange oils



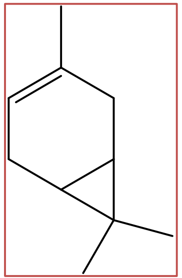
Menthol



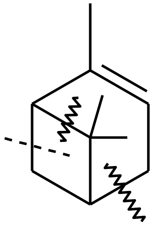
Menthone

both occur in pepermint oil

Bicyclic monoterpenoids

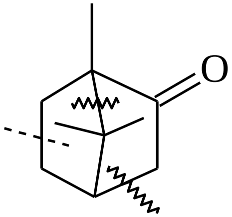


carene



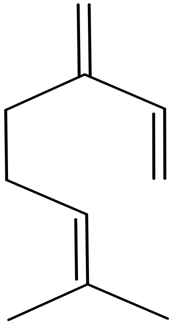
α-Pinene

occurs in turpentine oil



Camphor

occurs in camphor tr



($C_{10}H_{16}$)Myrcene المـايرسيـــــن

Myrcene occurs in verbena and bay oils ,myrcene is optically inactive and highly unsaturated.

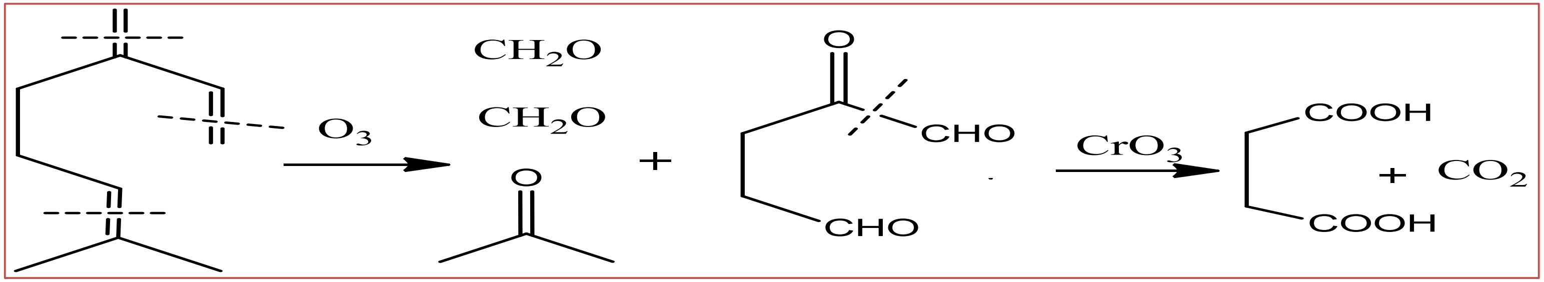
<u>Structure of myrcene is supported by</u> :

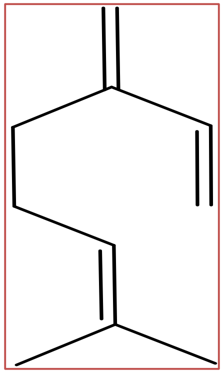
1-Molecular formula is $C_{10}H_{16}$.

2-Catalytic hydrogenation of myrcene gave saturated alkane$C_{10}H_{22}$ (isodecane) thus myrcene is an open chain and contains three double bond .

3-Since myrcene forms adduct with maleic anhydride, thus two of the double bond are conjugated .

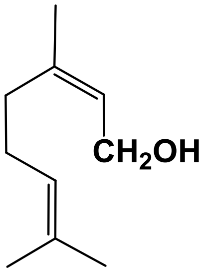
4-Ozonolysis of myrcene produces acetone ,two molecule of formaldehyde and ketodialdehyde which oxidized with chromic acid to give succinic acid and carbon dioxide.



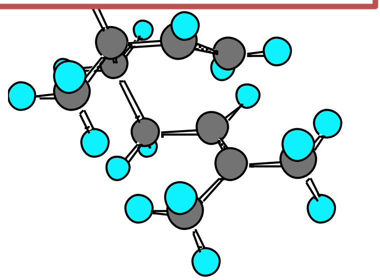


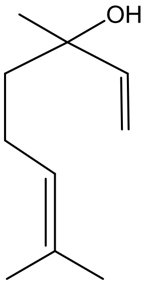
7-methyl-3-methylene-octa-1,6-diene

($C_{10}H_{18}O$) Linalool اللينالول



Geraniol





3,7-Dimethyl -octa-1,6-diene 3 -ol

Structure of Linalool : ($C_{10}H_{18}O$) b.p:198-199C

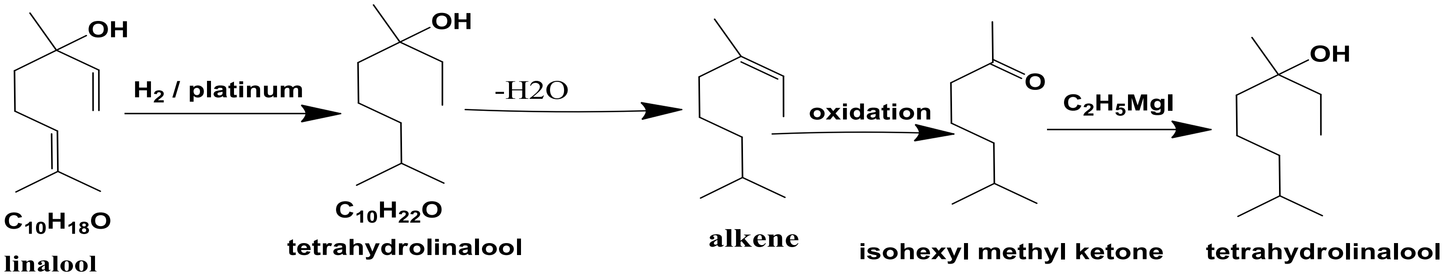
1- It is an optically active the (-)form occurs in rose oil and the (+) form in orange oil.

2- It adds on two molecule of hydrogen in catalytic hydrogenation ,and give negative with maleic anhydride it must be contain two (non conjugated) double bond .

3-It is converted into geranyl acetate by heating with acetic anhydride and converted into linalool by heating with steam at 200C under pressure , also linalool isomerizes in the presence of acid to geraniol .

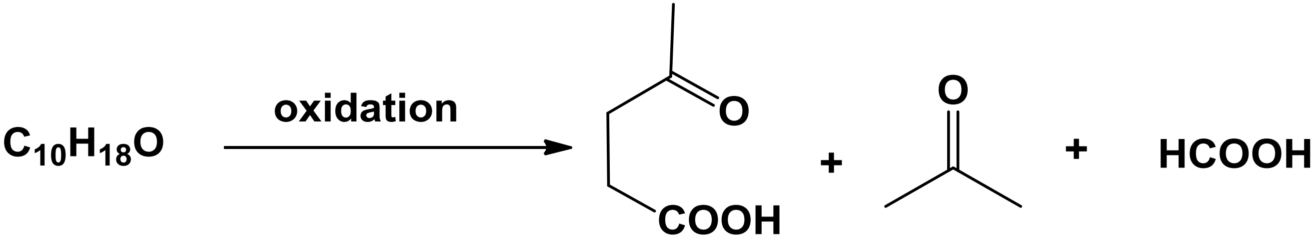
4-It has a tertiary alcoholic group and the position confirmed as follow:

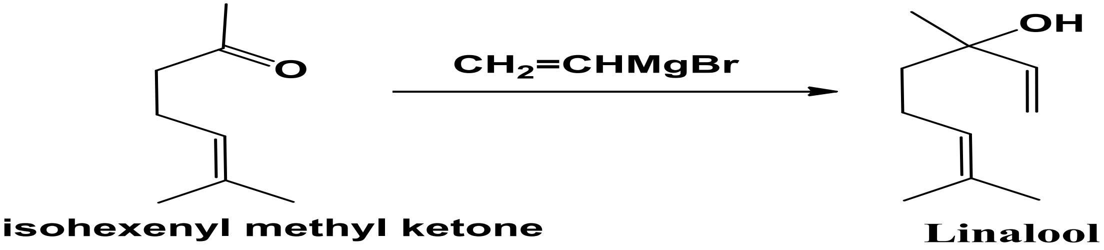
. .



5-Oxidation of linalool by pot. Permenganate converted it into levulinic acid ,acetone and formic acid .

6-Normant has synthesized linalool in one step by the action of vinyl magnesium bromide with 6-methyl -5-heptene-2-one(isohexenyl methyl keton).



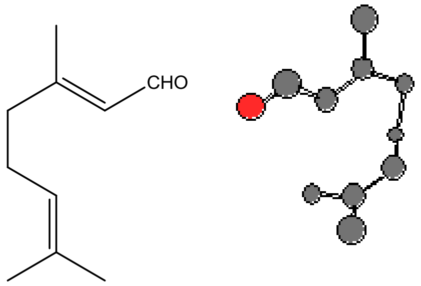


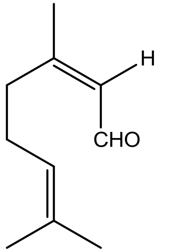
Citral ($C_{10}H_{16}O$)

3,7 dimethyl 2,6 -octadienal

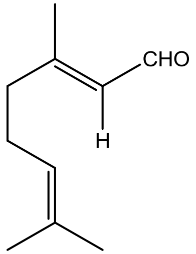
Citral occurs to an extent 60-80 per cent in lemon grass oil

Structure of citral was supported by:

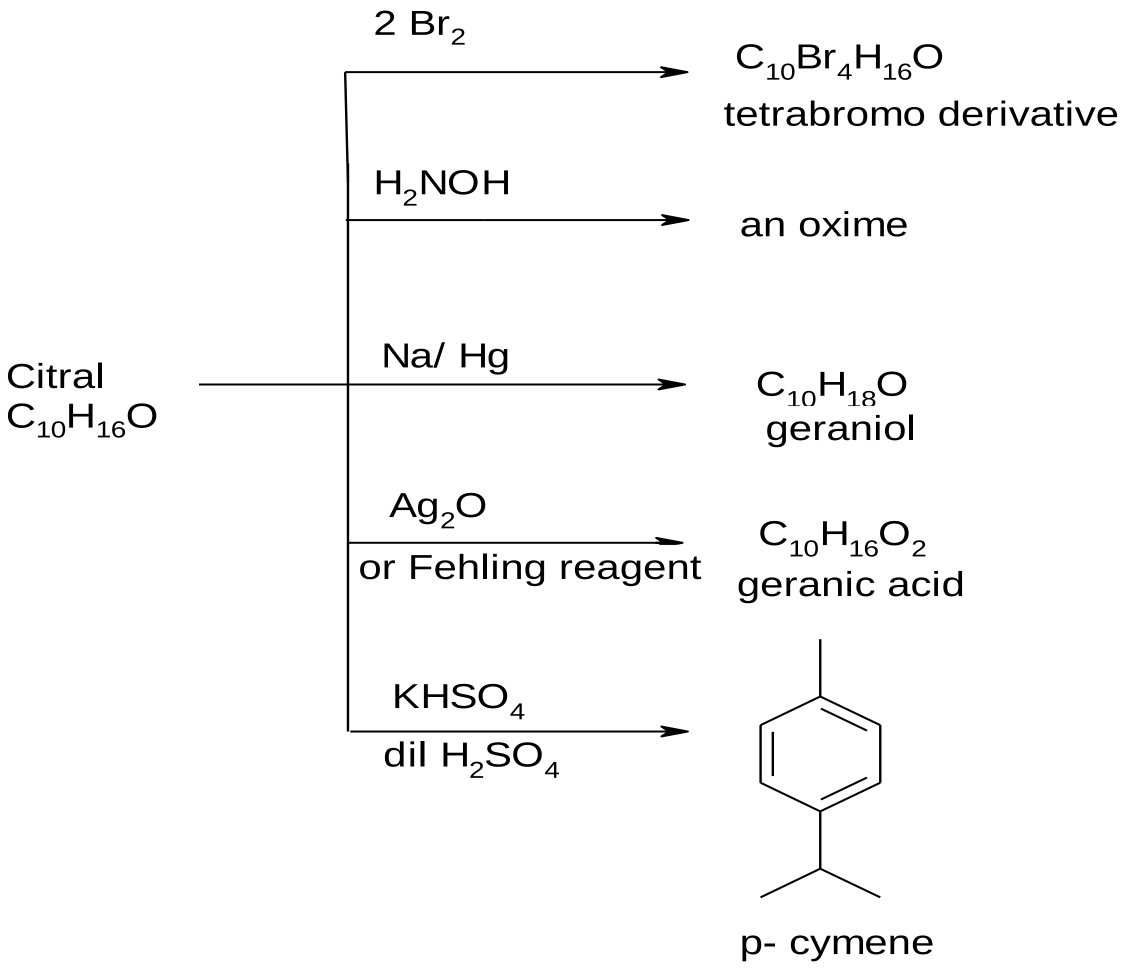




cis form
citral b or neral



trans form
citral a or geranial



Citral
$C_{10}H_{16}O$

$2\ Br_2$ → $C_{10}Br_4H_{16}O$
tetrabromo derivative

H_2NOH → an oxime

Na/ Hg → $C_{10}H_{18}O$
geraniol

Ag_2O
or Fehling reagent → $C_{10}H_{16}O_2$
geranic acid

$KHSO_4$
dil H_2SO_4 → p- cymene

1-It has been proven by analysis that Molecular formula is **$C_{10}H_{16}O$** .

2-It added two molecule of bromine thus citral contains two double bond .

3-It forms oxime derivative with hydroxyl amine citral contains oxo group.

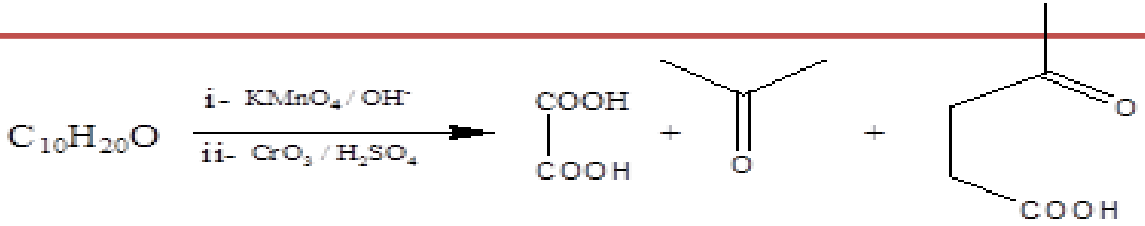
4-Citral can be reduced by sodium amalgam to an alcohol geraniol.

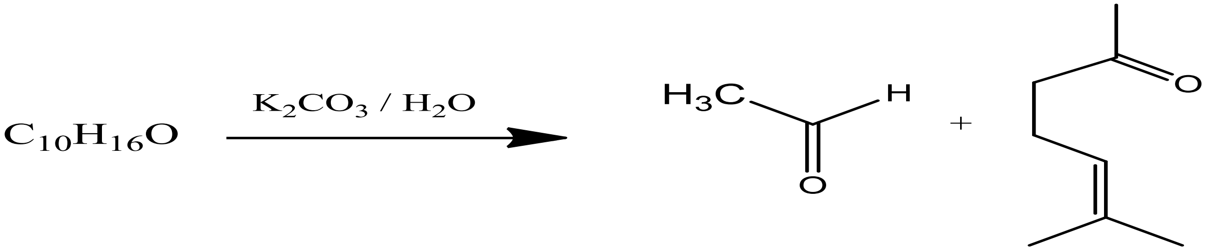
5-Citral oxidized with silver oxide to geranic acid since there is no loss of carbon oxidation to acid ,the oxo group in citral is t here an aldehyde group .

6-On heating with potassium hydrogen sulphate citral forms p-cymene ,this reaction was used to determine the position of methyl and isopropyl groups .

7-Oxidation of citral with alkaline permanganate,f ollowed by chromic acid ,gives acetone, oxalic acid and levulinic acid.

8-Citral with aqueous potassium carbonate gives acetaldehyde and 6-methylhept-5-en-2one .





Natural Products
Terpenoids
Cyclic Monoterpenoids
Limonene-Menthol-Camphor

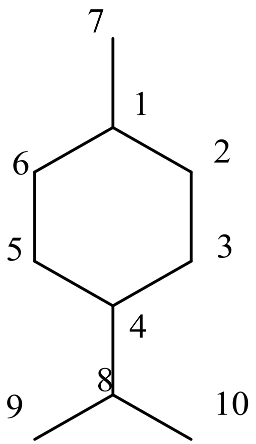
كلية العلوم

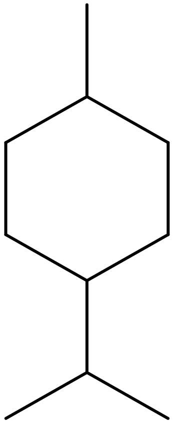
الفرقة الرابعة (شعبة كيمياء)

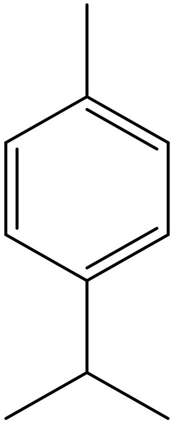
د /عواطف محمد أحمد المغربي
استاذ الكيمياء العضوية المساعد
قسم الكيمياء – كلية العلوم

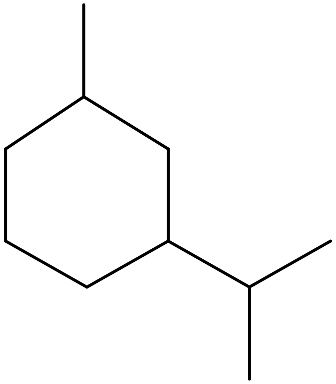
Monocyclic Monoterpenoids

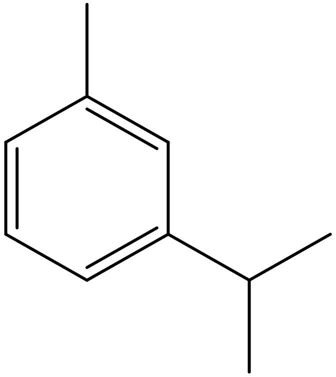
Monocyclic Monoterpenes is subdivided into two groups the larger group with carbon skeleton which are related to P-cymene(4-isopropyl toluene), the smaller group with carbon skeleton are related to m-cymene.

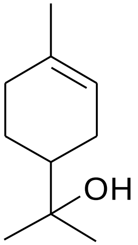



P-menthane

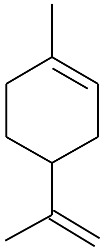

P-cymene

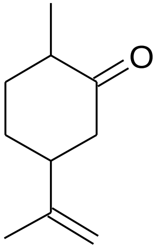

m-menthane


m-cymene

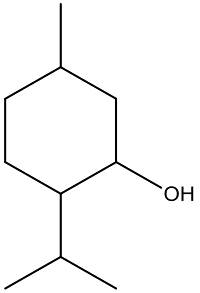


α – terpineol

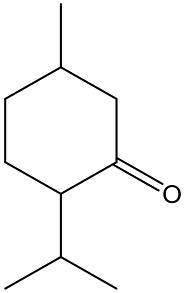

limonene



carvone



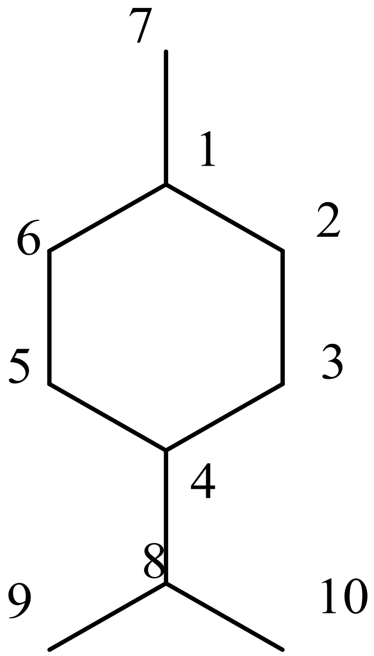
Menthol

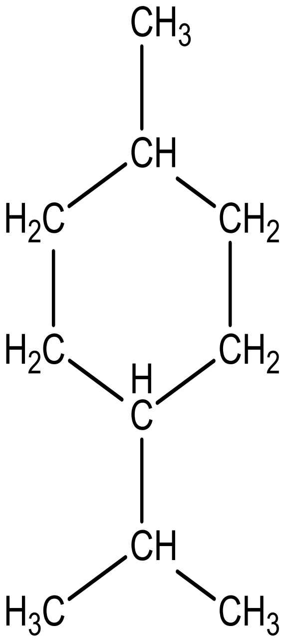


Menthone

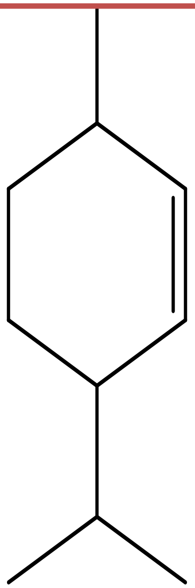
Nomenclature

The fully saturated compound p- methyl isopropylcyclohexane, hexahydro p-cymene or **p- menthane** $C_{10}H_{20}$ is used as parent substance.

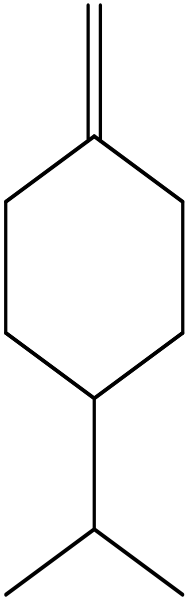




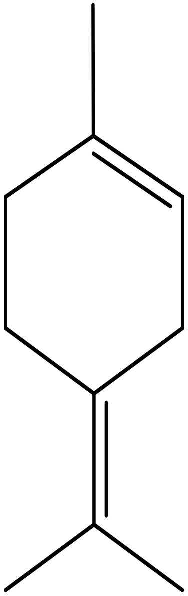
P-menthane



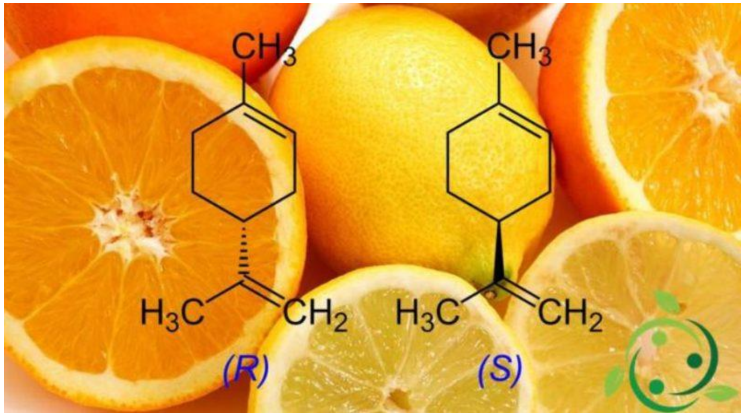
P-menthene-2
2-P-menthene
P-meth-2-ene

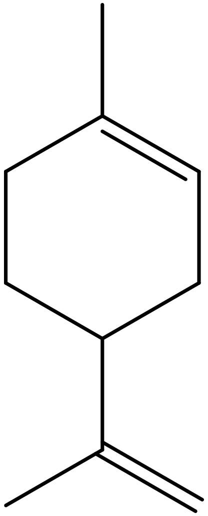


P-mentha-1(7) ene



P-meth-1,4(8)diene





Limonene

$C_{10}H_{16}$ اللـيمونيـن

P-menth1,8(10)diene

Limonene

٨، ١بارامينثادايين

Limonene is optically active, (+) form in lemon,orange oils (-)form in peppermint oil and racemic mixture(dipentene) in turpentine oil b.p 175-176°C

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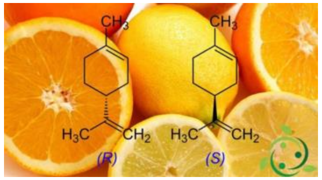
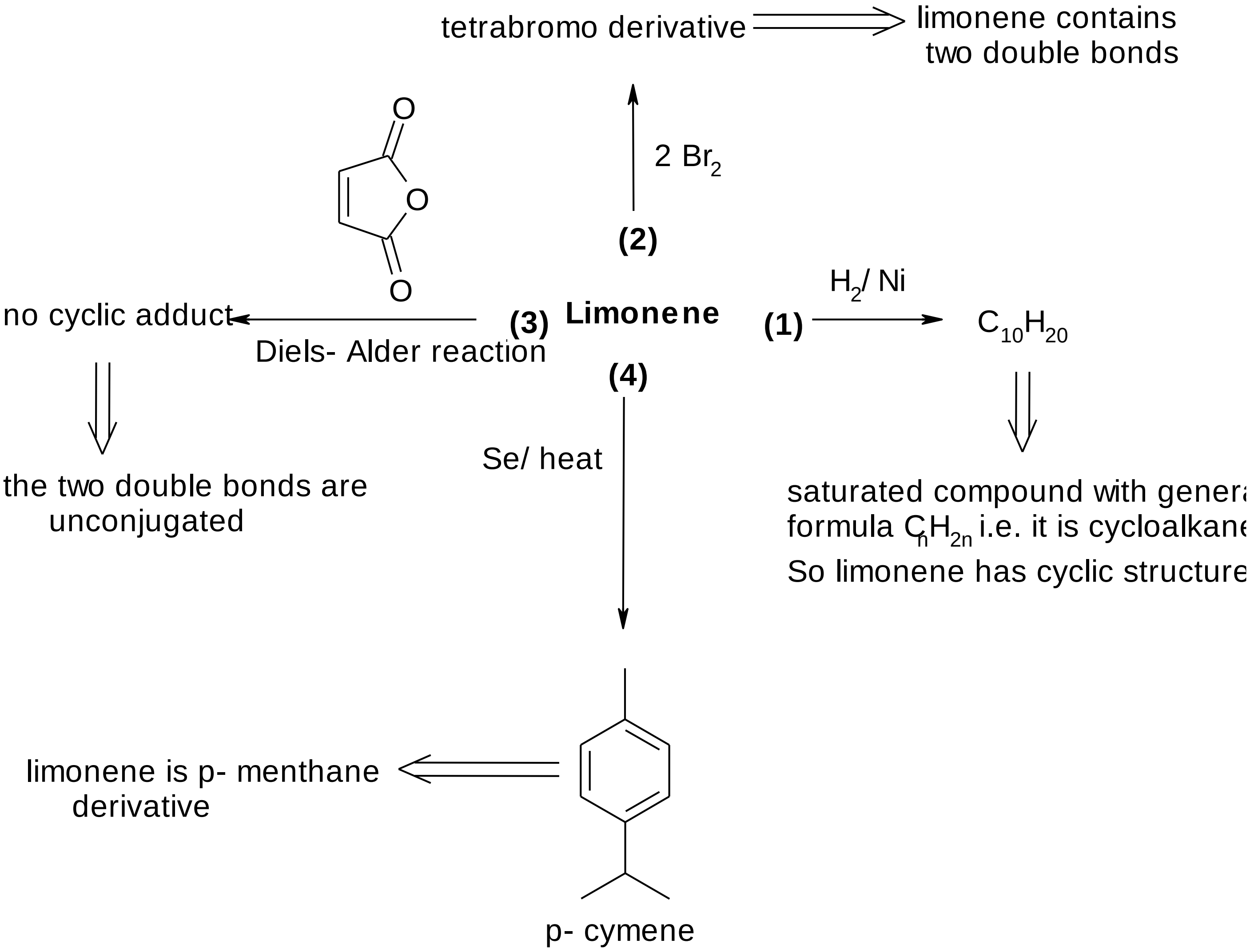


Structure of Limonene was supported by



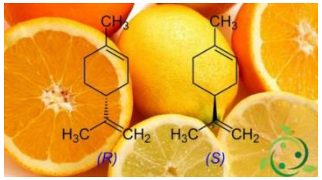
Limonene

(1) $\xrightarrow{H_2/\ Ni}$ $C_{10}H_{20}$ ⟹ saturated compound with genera formula C_nH_{2n} i.e. it is cycloalkan
So limonene has cyclic structur

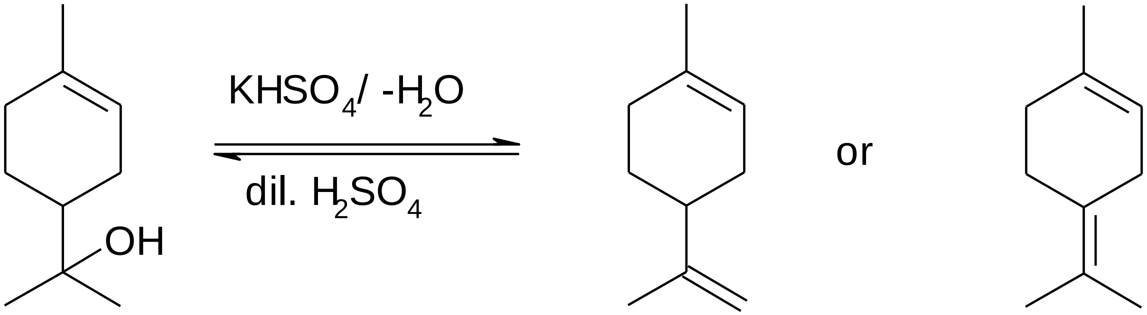
(2) $\xrightarrow{2\ Br_2}$ tetrabromo derivative ⟹ limonene contains two double bonds

(3) Diels- Alder reaction ⟶ no cyclic adduct ⟹ the two double bonds are unconjugated

(4) Se/ heat ⟶ p- cymene ⟹ limonene is p- menthane derivative



Structure of Limonene



α – terpineol

I

التركيب البنائي الصحيح
لليمونين لأنه نشط ضوئيا

II

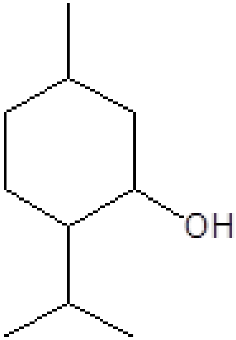
مستبعد لأنه تركيب بنائي
غير نشط ضوئيا

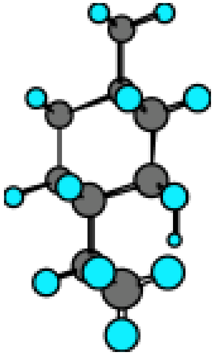
5-limonene may be prepared by dehydrating α- terpineol by using potassium hydrogen sulphate ($KHSO_4$) ,and on shaking with dilute sulphuric limonene may be converted to α- terpineol .

6-The carbon skeleton and the position of double bond in limonene are known ,but the other double bond remains uncertain (may be C8-C10 or C4-C8).

7-Structure (I) contains a chiral center(C4)and hence can exhibit optical activating .

Structure (II) is symmetric and so cannot be optically active. Therefore (I) must be **Limonene**





المنثول
Menthol
$C_{10}H_{20}O$

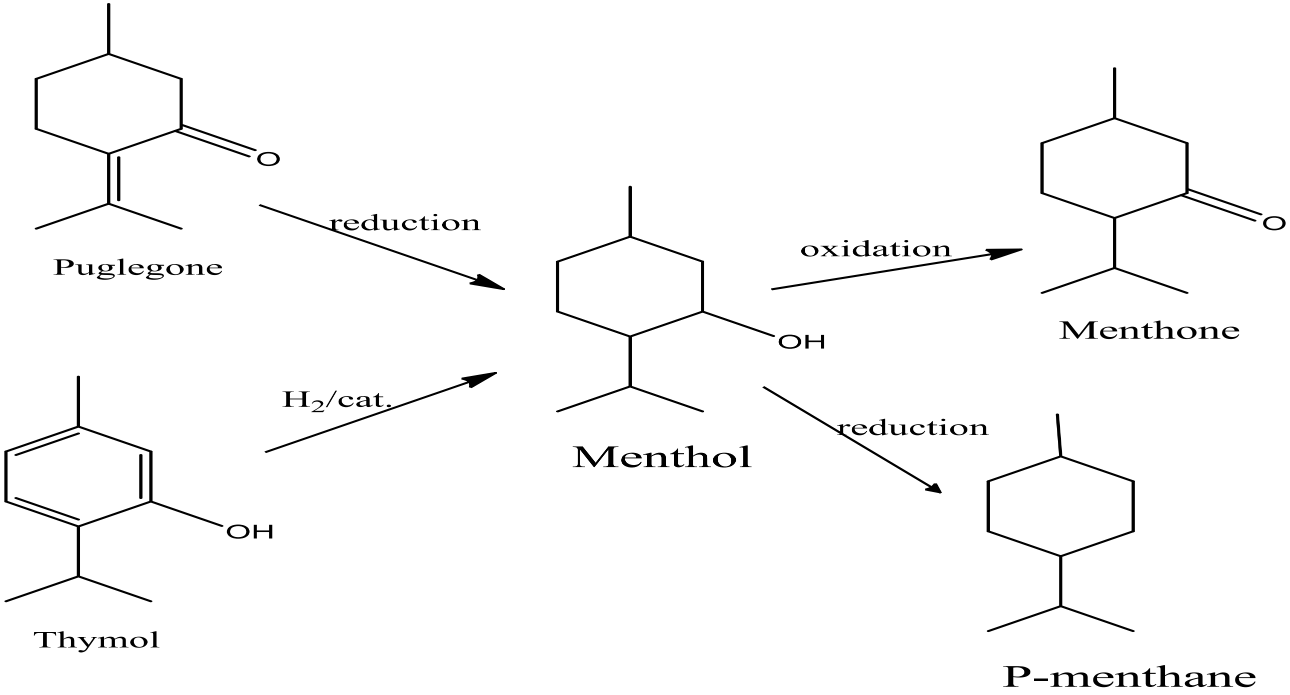
Menthol is optically active compound ,(-)form occurs in peppermint oil.

Menthol has medical uses :as anti-inflammatory ,analgesic, used in dental care as a topical antibacterial agent.

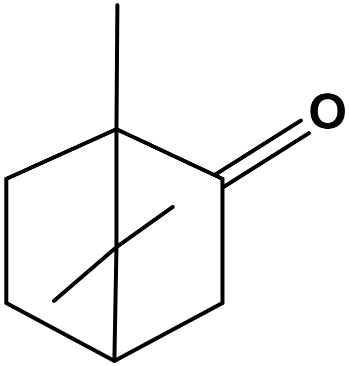
3-Hydroxy-4-Isopropyl-1-methyl cyclohexane , which is one of the most important monocyclic alcohols and contains three chiral carbon atoms (1,3,4), so that it can have eight enantiomers.

Structure of Menthol was supported by

1-It has been proven that molecular formula is $C_{10}H_{20}O$ and menthol is saturated compound .
2-The nature of oxygen atom is alcoholic (menthol forms ester).
3 -Oxidation of menthol gives menthone (a ketone)thus menthol is secondary alcohol.
4-Reduction using hydrogen iodide give p-menthane thus menthol contains this carbon skeleton.
5-Pulegone gives menthol on reduction .
6-Menthol can be synthesized by catalytic hydrogenation of thymol(3-hydroxy p-cymene)

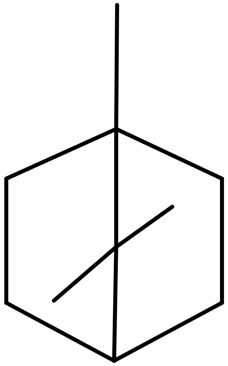


التربينات الأحادية ثنائية الحلقة
Bicyclic monoterpenoids



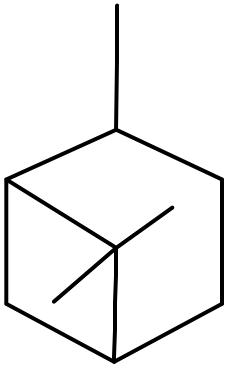
camphor

6+5



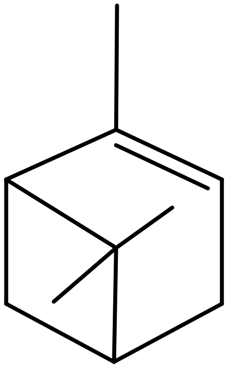
camphane
bornan

6+5



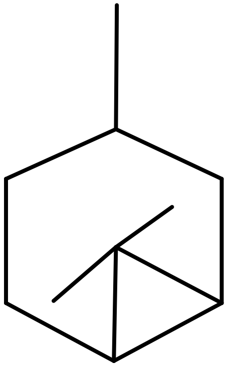
Pinane

6+4



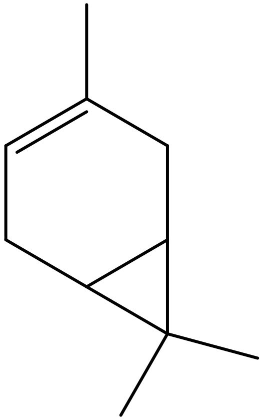
Pinene

6+4

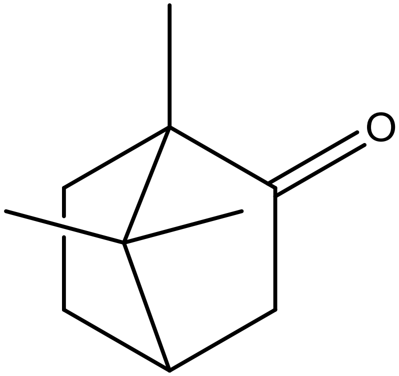


carane

6+3



Carene
6+3



Camphor الكافور

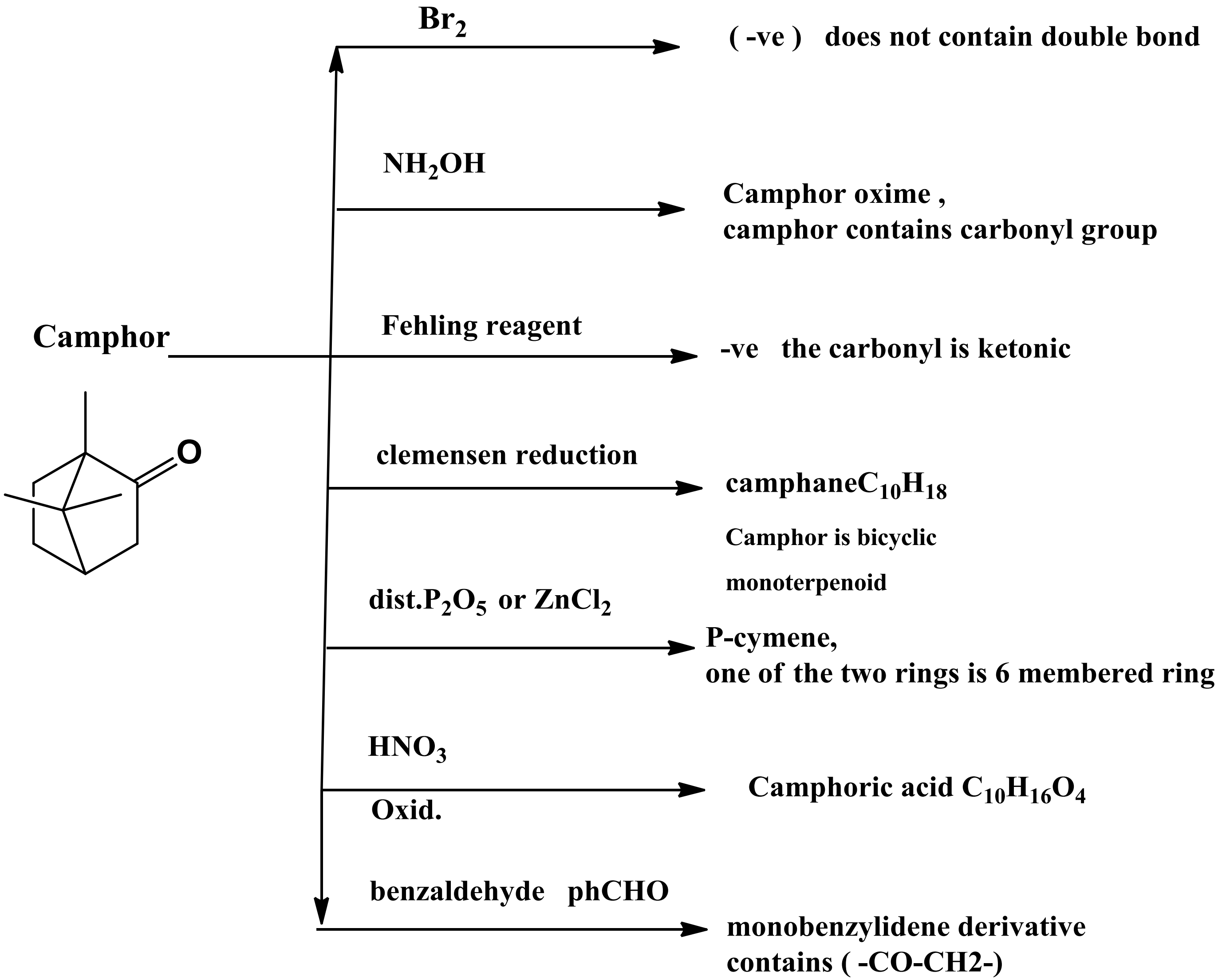
Camphor occurs in the camphor tree of Japan . It is an optically active solid with m.p 180 ° C the(-)and (+)forms occur naturally and racemic camphor is the usual form of synthetic camphor .

Camphor used in manufacture of cellulose as well as has many medical uses, including that it is used as a disinfectant and as a local anesthetic, and in the laboratories it is used as a solvent in experiments determining the molecular weight of organic compounds.

Structure of camphor was supported by :

1-The molecular formula of camphor is $C_{10}H_{16}O$,and the general reactions show that it is saturated .

Structure of Camphor



Camphor

Br_2 → (-ve) does not contain double bond

NH_2OH → Camphor oxime , camphor contains carbonyl group

Fehling reagent → -ve the carbonyl is ketonic

clemensen reduction → camphane$C_{10}H_{18}$

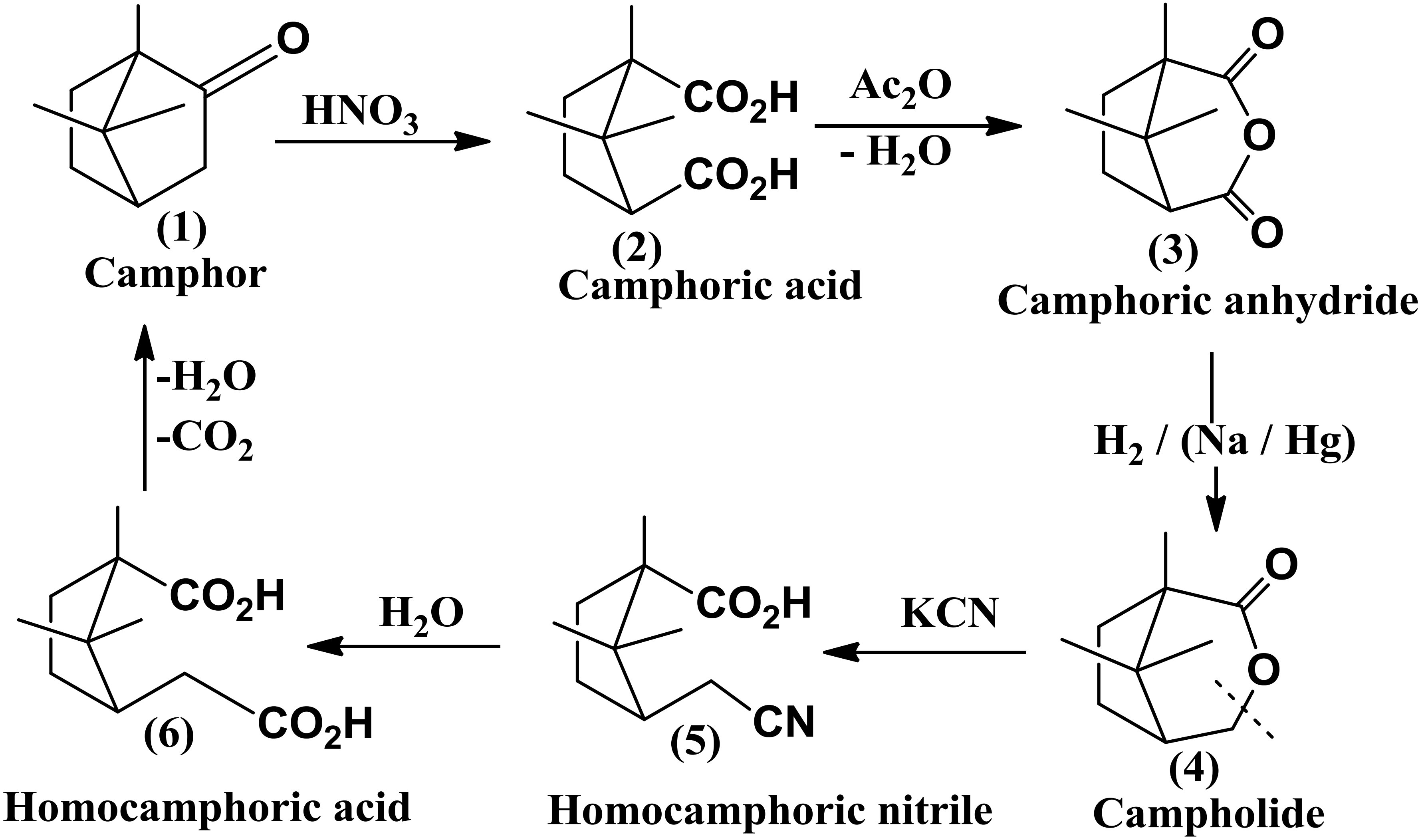
Camphor is bicyclic monoterpenoid

dist.P_2O_5 or $ZnCl_2$ → P-cymene, one of the two rings is 6 membered ring

HNO_3 Oxid. → Camphoric acid $C_{10}H_{16}O_4$

benzaldehyde phCHO → monobenzylidene derivative contains (-CO-CH2-)

Structure of Camphor



(1) Camphor

HNO_3

(2) Camphoric acid

Ac_2O

$- H_2O$

(3) Camphoric anhydride

H_2 / (Na / Hg)

(4) Campholide

KCN

(5) Homocamphoric nitrile

H_2O

(6) Homocamphoric acid

$-H_2O$

$-CO_2$

Natural Product

Sesquiterpenoids- Diterpenoid- Triterpenoids- Tetraterpenoids-Poly terpenes-

كلية العلوم
الفرقة الرابعة (شعبة كيمياء)

د /عواطف محمد أحمد المغربي
قسم الكيمياء – كلية العلوم

التربينات النصف ثلاثيــة (السيسكوتربينات)
Sesquiterpenoids

The sesquiterpenoids are naturally occuring compounds containing fifteen carbon atoms, in general they form the higher boiling point fraction of the essential oils and may be acyclic or cyclic hydrocarbons ,alcohols , ketones or lactones ,the sesquiterpenoids structure is built up from three isoprene units but there are some exceptions.

The sesquiterpenoids are classified into four groups :

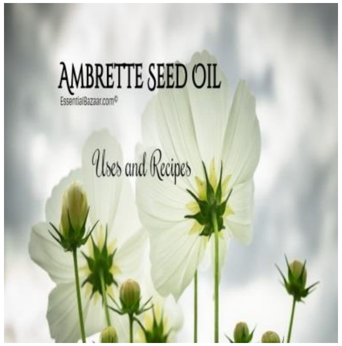
1-Acyclic sesquiterpenoids contain four double bonds (farnesene) .

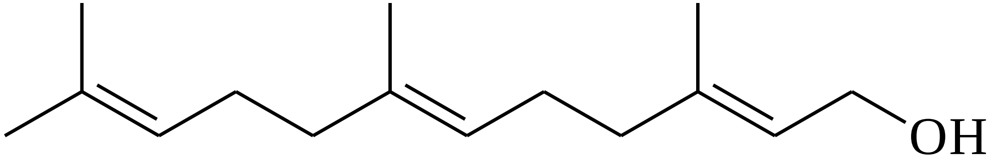
2-Monocyclic sesquiterpenoids contain three double bonds (zingiberene from ginger oil) .

3-Bicyclic sesquiterpenoids contain two double bonds (selinene occurs in celery oil).

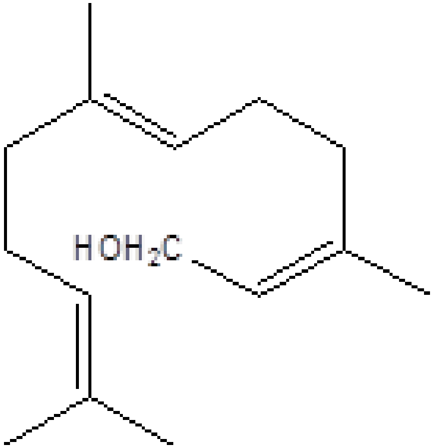
4-Tricyclic sesquiterpenoids contain one double bond (cedrol in sedar wood oil) .

($C_{15}H_{26}O$)Farnesol الفارنيسول





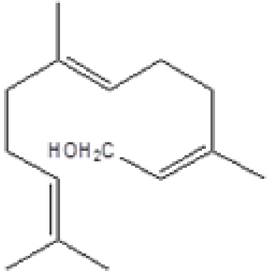
Farnesol
occurs in oil of ambrette seeds



Farnesol considered acyclic sesquiterpenoid contains 15 carbon atom and the carbon skeleton can be formed by the union of three isoprene units.

Farnesol is a primary alcohol ,it is used in perfume manufacture and it occurs in ambrette seeds.

الفارنيسول($C_{15}H_{26}O$)Farnesol
Determination of structure



Farnesol

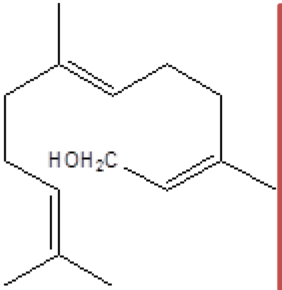
catalytic hydrogenation
$3H_2$ → **(+ve) saturated alcohol Hexahydro - farnesol thus it contains 3 double bond**

maleic anhydride → **(-ve) the double bonds are unconjugated**

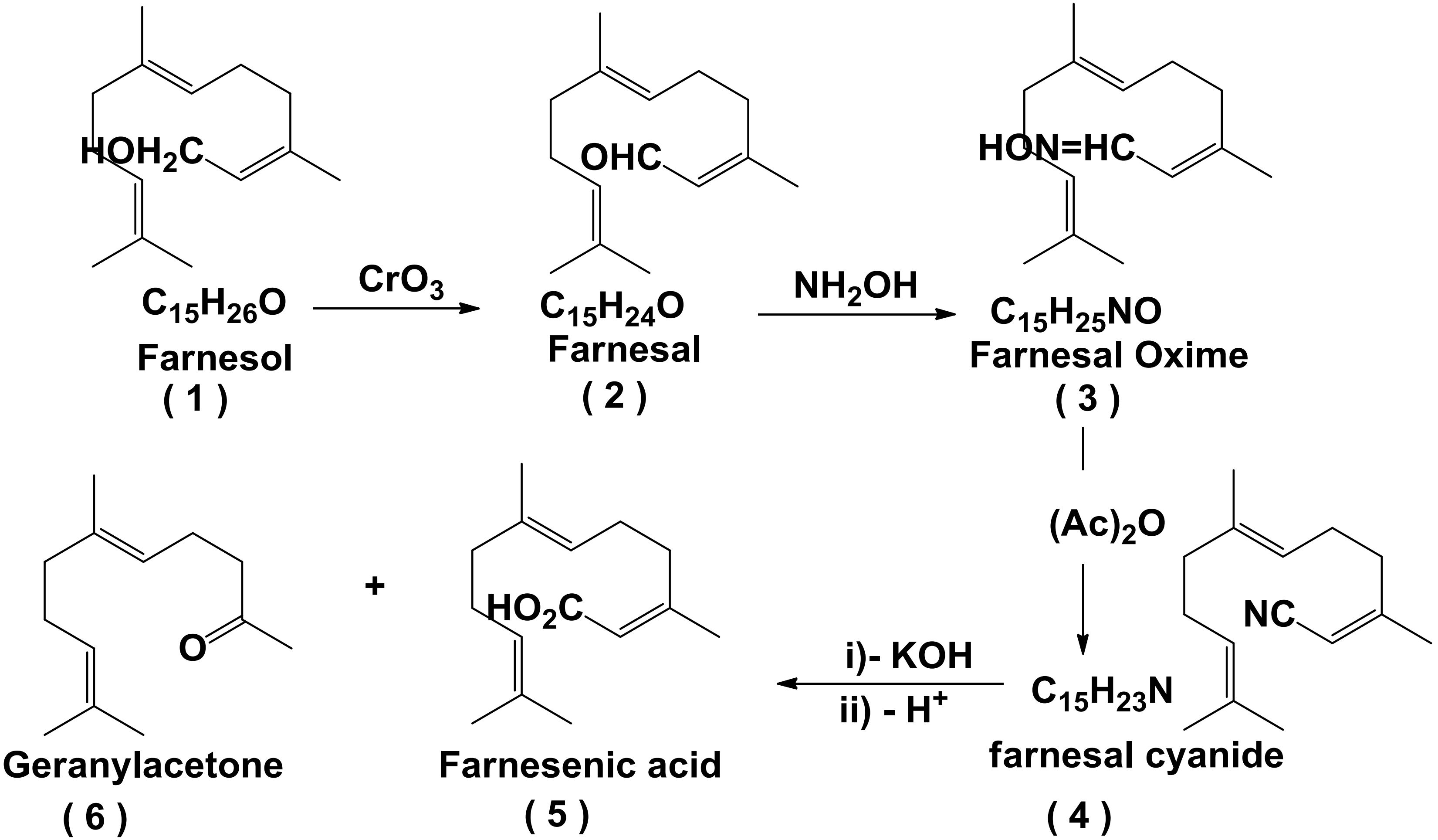
Analysis → **Molecular Formula $C_{15}H_{26}O$**

Oxidation
chromic acid → **Farnesal $C_{15}H_{24}O$, farnesol is primary alcohol**

Ozonolysis → **acetone+2mole of Laevulaldehyde +glycolaldehyde**



($C_{15}H_{26}O$)Farnesol Determination of structure



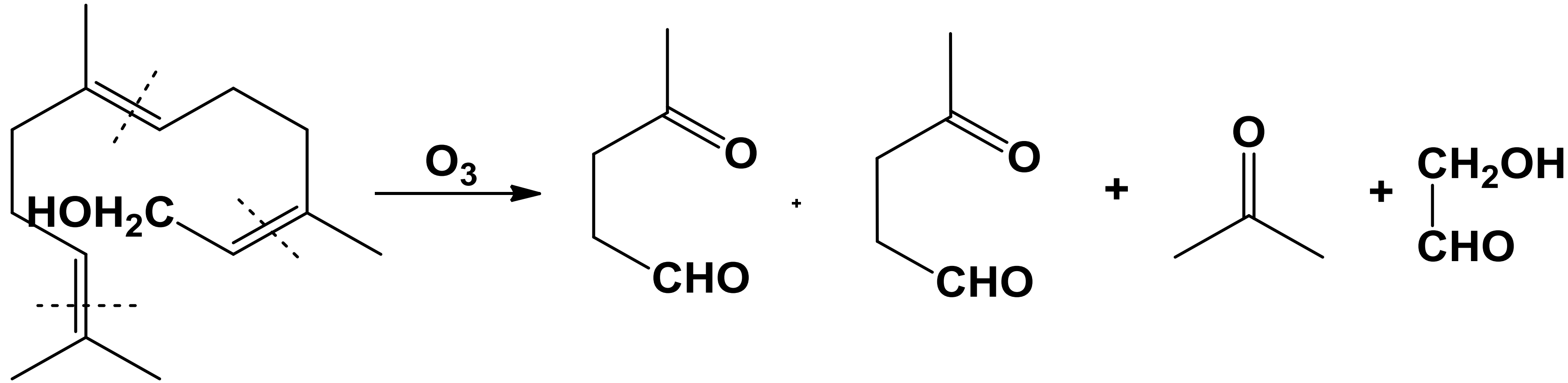
$C_{15}H_{26}O$ Farnesol (1) $\xrightarrow{CrO_3}$ $C_{15}H_{24}O$ Farnesal (2) $\xrightarrow{NH_2OH}$ $C_{15}H_{25}NO$ Farnesal Oxime (3)

(3) $\xrightarrow{(Ac)_2O}$ $C_{15}H_{23}N$ farnesal cyanide (4)

(4) $\xrightarrow[\text{ii) - }H^+]{\text{i)- KOH}}$ Geranylacetone (6) + Farnesenic acid (5)

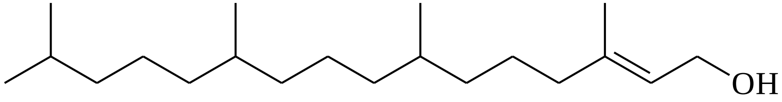
$C_{15}H_{26}O$ Farnesol

Determination of structure

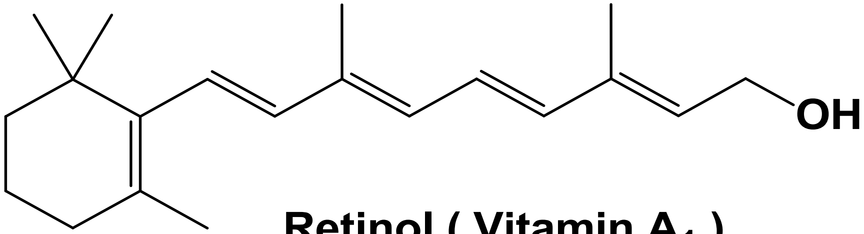


التربينات الثنائية (الداي تربينات)
Diterpenoids

The diterpenoids are naturally occurring compounds containing 20 carbon atoms and four isoprene units ,which distributed in plants kingdom. Diterpenoids are classified on the basis of the number of carbon ring present into acyclic (phytol) monocyclic (vitaminA1and vitaminA2) , dicyclic, tricyclic and tetracyclic diterpenoid .

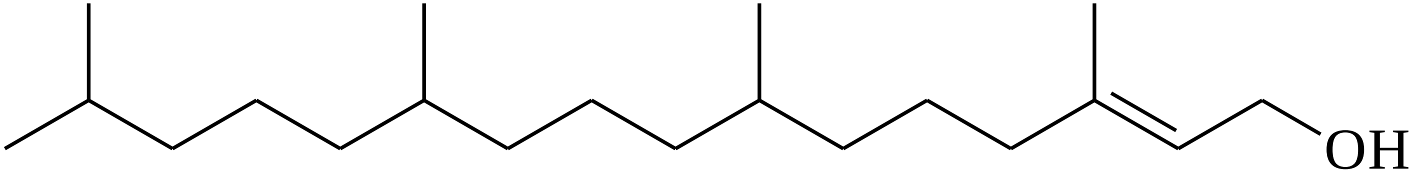


Phytol
is produced from hydrolysis of chlorophyll



Retinol (Vitamin A_1)

Phytol $C_{20}H_{40}O$



Phytol
is produced from hydrolysis of chlorophyll

Phytol is an acyclic diterpenoid ,it is produced from hydrolysis of chlorophyll , and it forms a part of the molecules of vitamins E and K .

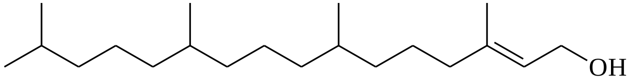
Determination of the structure

1-General reactions and analysis showed that molecular formula is $C_{20}H_{40}O$ and it is a primary alcohol .

2-On catalytic hydrogenation it forms dihydrophytol **$C_{20}H_{42}O$** so phytol is acyclic diterpenoid and contains one double bond.

Phytol $C_{20}H_{40}O$

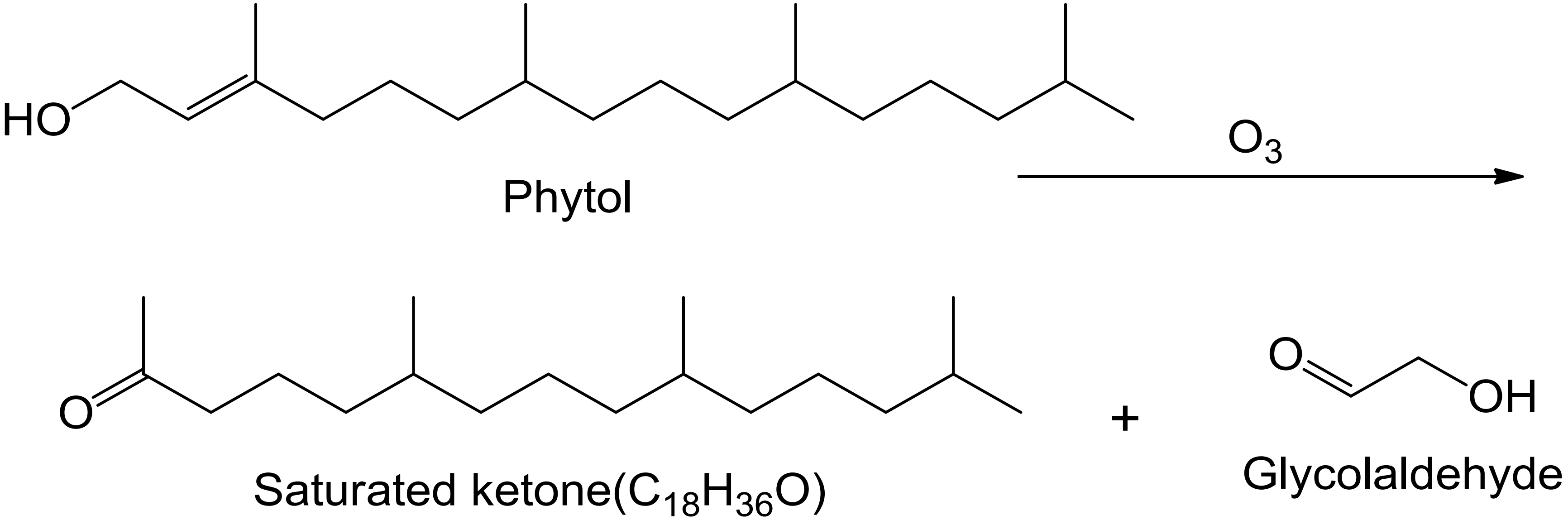
Determination of the structure



Phytol
is produced from hydrolysis of chlorophyll

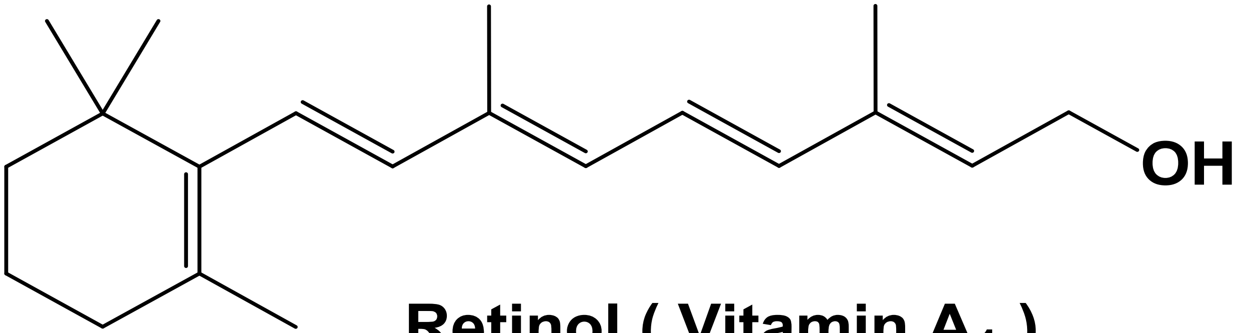
3-Ozonolysis of phytol gives glycol aldehyde and a saturated ketone $C_{18}H_{36}O$.

4-Phytol contains four isoprene units connected (head-tail).



Monocyclic Diterpenoids

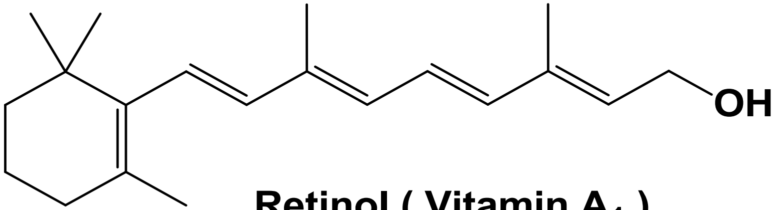
Retinol VitaminA$_1$ ($C_{20}H_{28}O$)



Retinol (Vitamin A_1)

- Retinol or Vitamin **A$_1$** is a monocyclic diterpenoid occurs in many flowers and carrots as a β-carotene which converted into vitamin A_1 by hydrolysis .
- Retinol occurs free and as esters in fats in fish liver and in blood,it was originally isolated as viscous yellow oil ,but later it was obtained as crystalline solid .
- Vitamin **A$_1$** is estimated by the blue color reaction it gives with a solution of antimony trichloride in chloroform .
- Vitamin **A$_1$** influences growth in animals and increased the resistance to disease . ***Night blindness*** is due to Vitamin **A$_1$** deficiency .

($C_{20}H_{28}O$) Retinol VitaminA$_1$



Retinol (Vitamin A$_1$)

Structure of Retinol was supported by

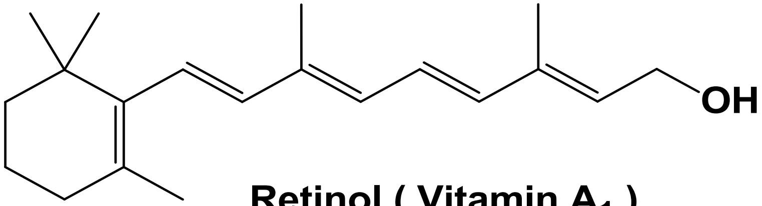
1-Routine tests confirmed that M. F $\mathbf{C_{20}H_{30}O}$ and it is a primary alcohol since mild oxidation it yields the corresponding aldehyde retinal $\mathbf{C_{20}H_{28}O}$ **.**

2-Catalytic hydrogenation converts it into perhydro vitamin A$_1$

$\mathbf{C_{20}H_{40}O}$ thus it contains five double bond and vitamin A$_1$ must be monocyclic.

3-Ultra violet absorption measurments show the presence of conjugation, so it is a conjugated polyene alcohol .

Retinol VitaminA$_1$ ($C_{20}H_{28}O$)

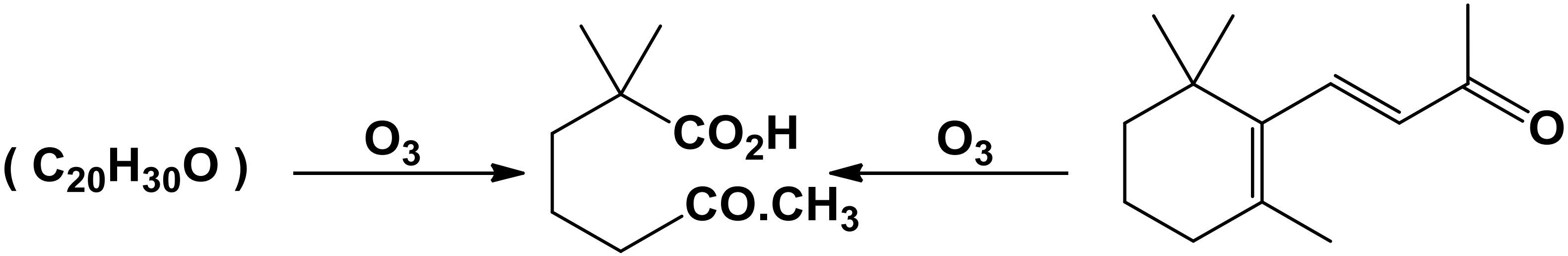


Retinol (Vitamin A$_1$)

4-Ozonolysis of retinol afforded one molecules of geronic acid which was isolated also from oxidative degradation of β-ionone nucleus .

5-Application of isoprene rule led to confirmation of carbon skeleton .

6- The structure of retinol also can be confirmed by using β-ionone as a starting material in synthesis .



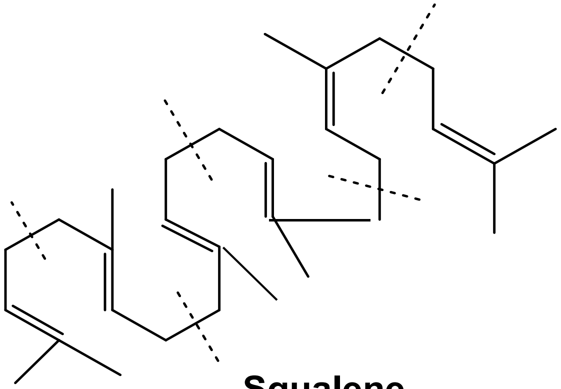
Retinol (Vitamin A$_1$)

Geronic acid

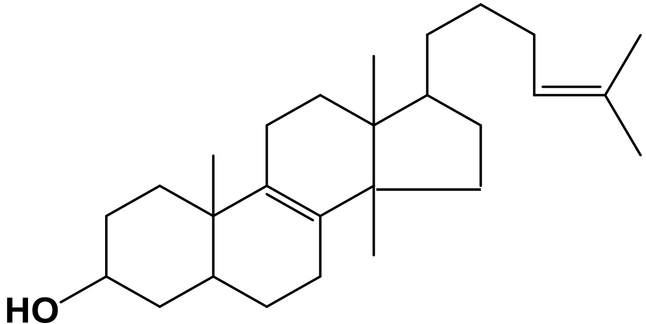
B - Ionone

Triterpenoids
التربينات الثلاثية

- Triterpenoid compounds are widely distributed in nature mainly in plants where they found in resins and plant saps in the free state and as esters . A few have been found in animal sources as in the liver oils of certain fish .
- Triterpenoids contain 30 carbon atom and most of them have carbon skeleton which may be built up by the union of six isoprene units , they may be acyclic or cyclic.
- Squalene is acyclic triterpenoid occurs in the fraction of liver oil and also in various plant sources and it is an intermediate in the biosynthesis of cholesterol from acetic acid .
- Lanosterol is a very important tetracyclic triterpenoid which contains the steroid carbon skeleton.



Squalene



Lanosterol

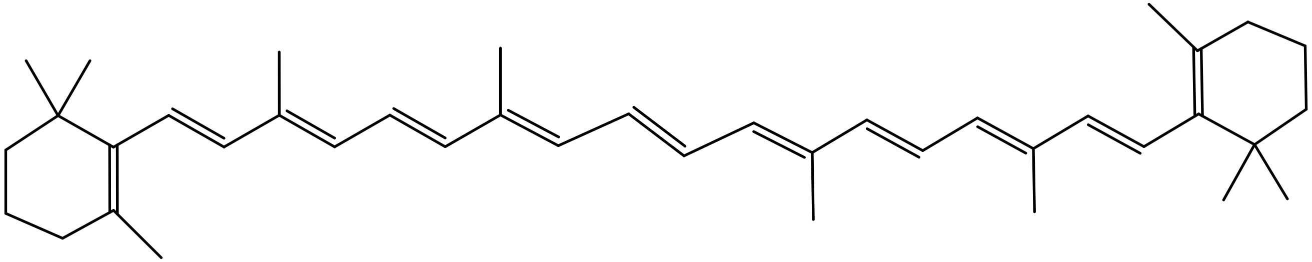
Tetraterpenoids

التربينات الرباعية (التترا تربينات)

1- The tetraterpenoids more commonly referred to as the carotenoids , are compounds containing eight isoprene units and 40 carbon atoms , constitute a group of natural pigments which are widely distributed in plants and animals.

2- A characteristic reaction shown by carotenoids is the formation of deep blue color with antimony trichloride in chloroform solution .

3- β-Carotene was isolated from carrots and M.F $\mathbf{C_{40}H_{56}}$, and isolated by extraction with light petroleum .



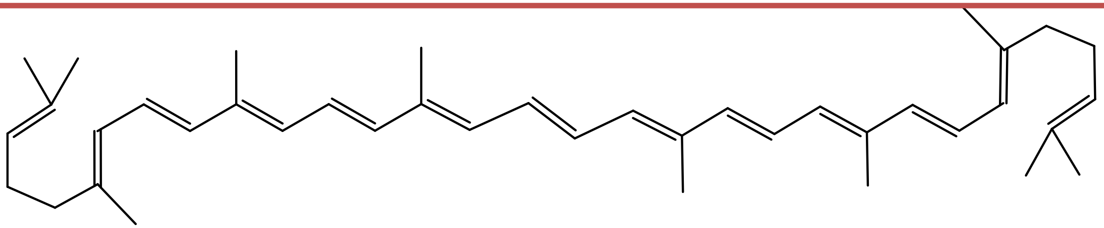
B - Carotene

التربينات الرباعية (التترا تربينات) الكاروتينات
(Carotenoids) Tetraterpenoids

4- Lycopene is a carotenoid that is the red tomato pigment .

5-Lycopene is considered the acyclic isomer of β-Carotene and β-Carotene shows vitamin A activity owing to the fact that it is converted into vitamin A in animal blood .

6—Carotenoids are polyenes , most of them the central portion of the molecules is composed of long conjugated chain comprised of 8 isoprene unites , the center two of which are joined tail to tail .

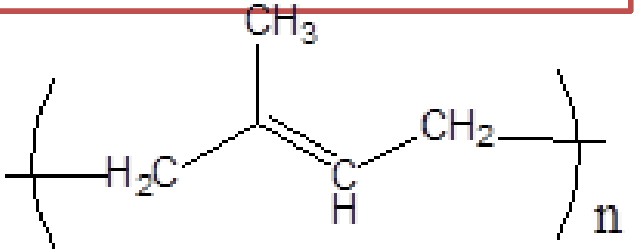


Lycopene $C_{40}H_{56}$

Poly terpenes- التربينات العديدة Rubber

- Poly terpenoids consist of several units of isoprene connected together in large chains .
- Natural rubber is the most important example ,rubber is obtained from latex which is an emulsion of rubber particles with water , it is obtained from the inner bark of many types of trees which grow in the tropic and sub tropics .
- Addition of acetic acid coagulate the rubber which is separate from the liquor either pressed into blocks or rolled into sheets finally dried in a current of warm air
- Crude latex rubber contains in addition to the actual rubber hydrocarbon , proteins, sugar, fatty acids and resins the amount of these substance depends on the source .

Poly terpenes-Rubber



Structure of natural rubber

1-The destructive distillation of rubber gives isoprene as one of the main products thus rubber is a polymer of isoprene and molecular formula **$(C_5H_8)_n$** .

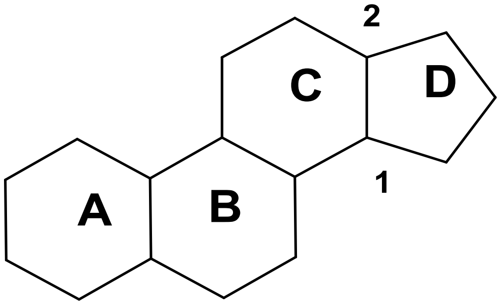
2-Rubber is unsaturated hydrocarbon , on catalytic hydrogenation at high temperature and pressure ,the product is ***hydro rubber which*** is an elastic solid which is fully saturated and resistant to oxidation.

3-Rubber reacts with hydrogen chloride or hydrogen bromide to give rubber hydrochloride or rubber hydrobromide formed by the addition of hydrogen halide to the double bonds ***(Markwnikoff) .***

Natural Products
Steroids

Dr. Awatef Mohamed El-maghraby
Chemistry Department
Faculty of Science
South Valley University

Steroids

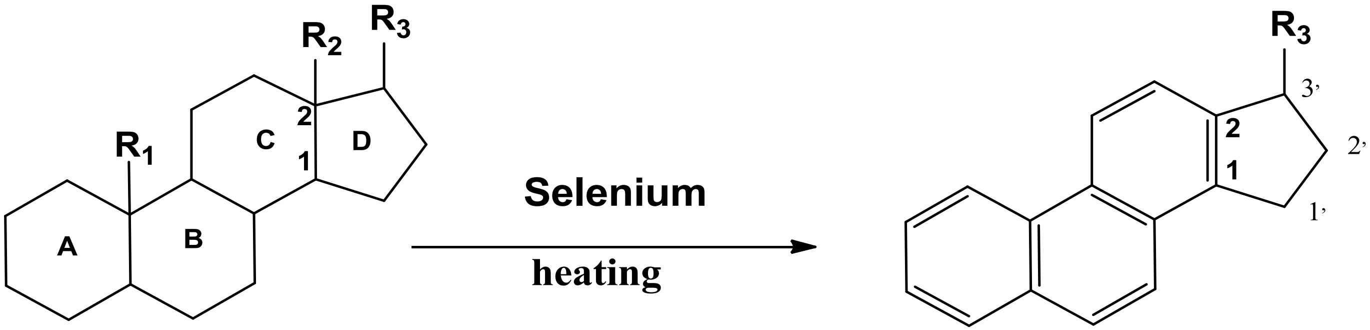


Perhydro-1,2-cyclopentanophenanthrene

Definition of steroids

Saturated natural products possessing the tetracyclic carbon skeleton ,ring **A,B,C** are six membered ring while ring **D** is five membered ring, the side chain R1, R2 and R3. R1 may be absent when ring **A** is aromatic ,R1 and R2 are generally methyl groups . The side chain R3 may be absent

.



Steroid

R_3=Me (Diels hydrocarbon)

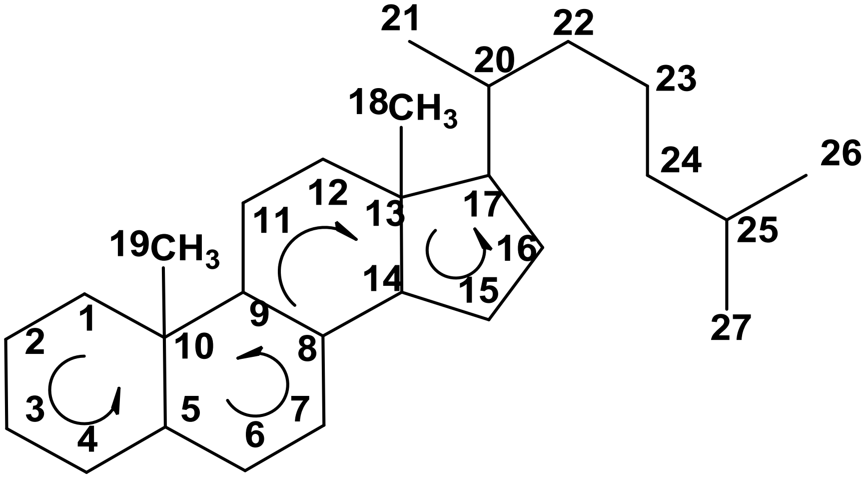
3'-methyl-1:2-cyclopentenophenanthrene

R_3 = H   1: 2-cyclopentenophenanthrene

A steroid could be defined, in another way, as any compound which gives Diel's hydrocarbon(beside other products) when distilled with selenium.

Classification of Steroids

The carbon skeleton of the hydrocarbon cholestane is given which shows the correct numbering of the system .



Cholestane

Classification of Steroids

1- **Sterols (cholesterol)**

2-Vitamin D(vitamin D2)

3-Bile Acids (cholic acid)

4- Steroidal Hormones or Sex Hormones(progesterone)

5- Adrenocortical hormones (cortisone)

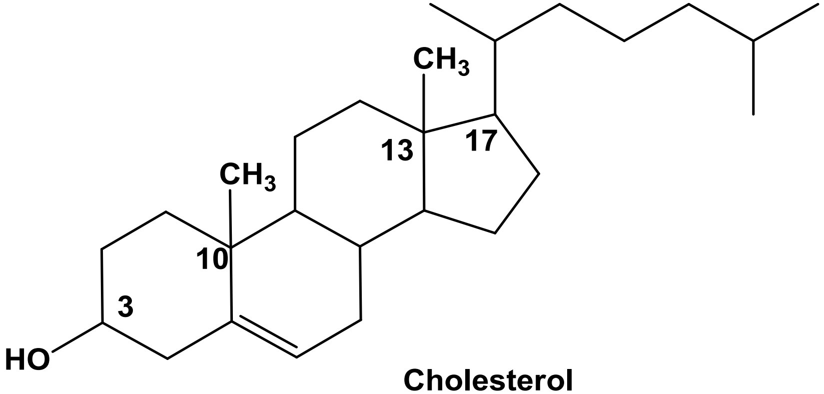
6-Cardiotonic glycosides

7- Saponins and Sapogenins

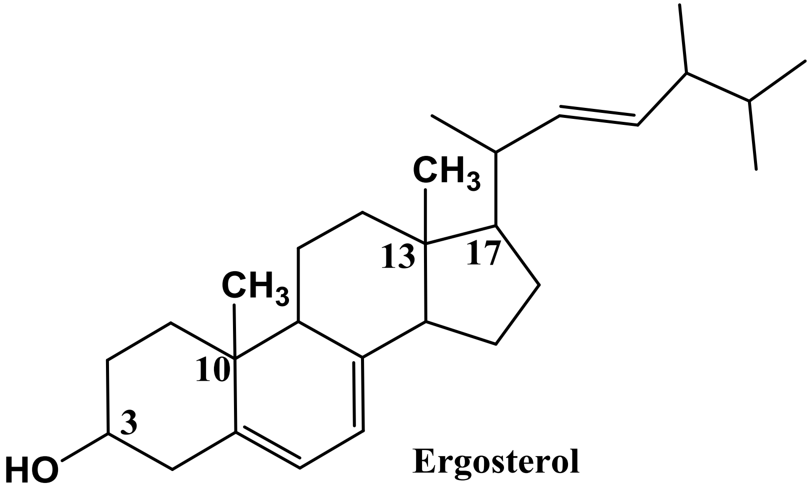
Sterols

Sterols are steroid alcohol containing an aliphatic side chain they are crystalline, widely Distributed in nature .

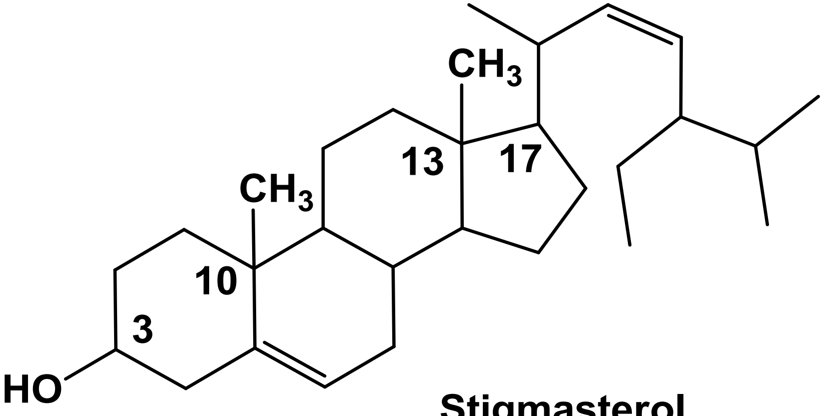
Sterols may be classified on the basis of occurrence as Zoo sterols(animal), Phytosterol (plants), mycosterol (yeast and fungi) and marine sterols(sponges).



Cholesterol
Zoo sterol

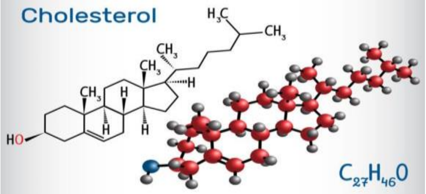


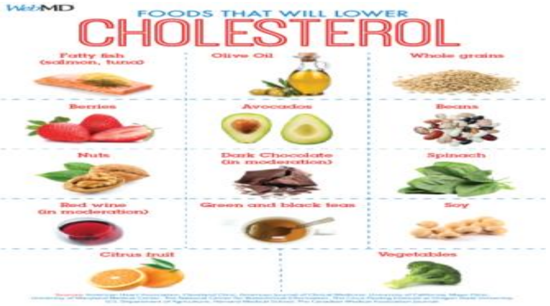
Ergosterol
mycosterol
occurs in yeast

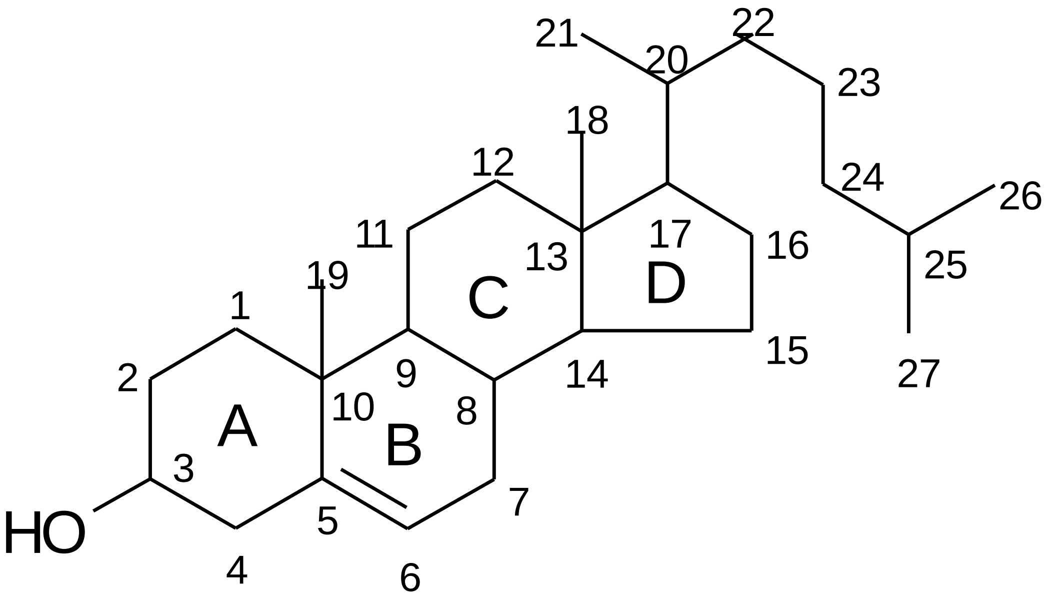


Stigmasterol
Phytosterol
obtained from soya bean oil

كوليسترولCholesterol







characteristic features :-

1- The nucleus of cholesterol is tetracyclic composed of three six-membered rings (A, B and C) and one five-membered (D) ring.

2- There is a secondary OH group at C-3, and a double bond at C-5 (between C-5 and C-6).

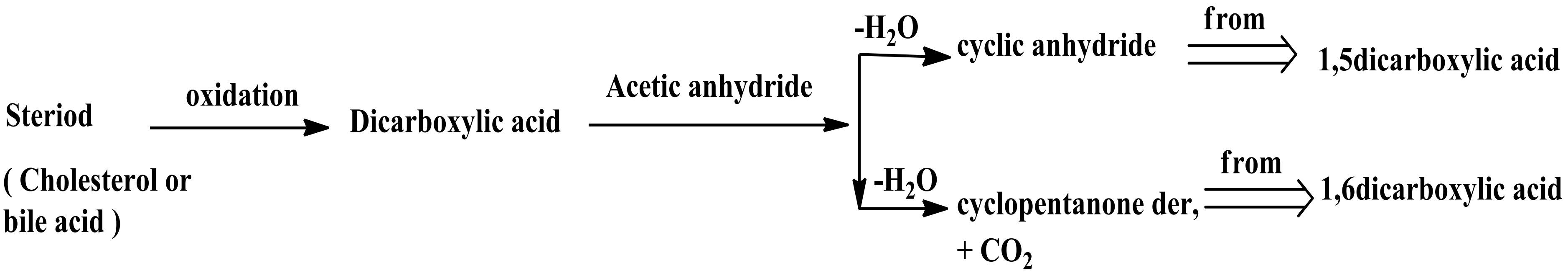
3- There are two angular methyl groups at C-10 and C-13, and a saturated side-chain C_8H_{17} at C-17.

Determination of the nucleus - Blanc Rule

All the steroids possess the same tetracyclic carbon skeleton (cyclopentaneperhydrophenanthrene) ,it has been confirmed by heating steroid with selenium which gives cyclopentenophenanthrene derivative.

The rings of the steroid nucleus were opened by oxidation to give dicarboxylic acid and the relative position of the two carboxyl groups were determined by the application of **Blanc rule:**

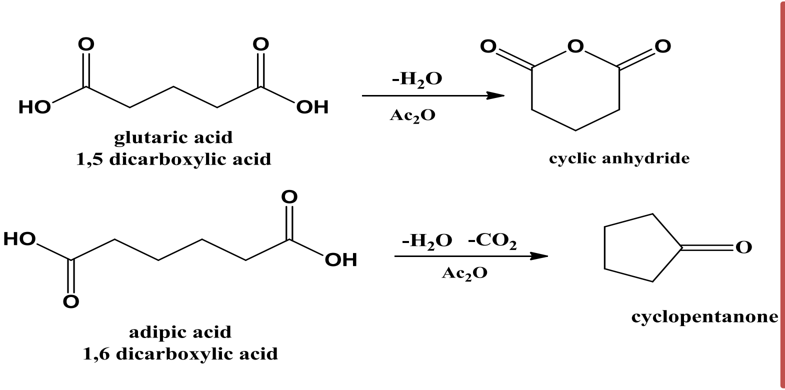
Heating with acetic anhydride,1,5-dicarboxylic acids forms cyclic anhydride and 1,6-dicarboxylic acids form cyclopentanones with elimination of carbon dioxide



Steriod (Cholesterol or bile acid) $\xrightarrow{\text{oxidation}}$ Dicarboxylic acid $\xrightarrow{\text{Acetic anhydride}}$

$\xrightarrow{-H_2O}$ cyclic anhydride $\overset{\text{from}}{\Longrightarrow}$ 1,5dicarboxylic acid

$\xrightarrow{-H_2O}$ cyclopentanone der, + CO_2 $\overset{\text{from}}{\Longrightarrow}$ 1,6dicarboxylic acid



glutaric acid
1,5 dicarboxylic acid

cyclic anhydride

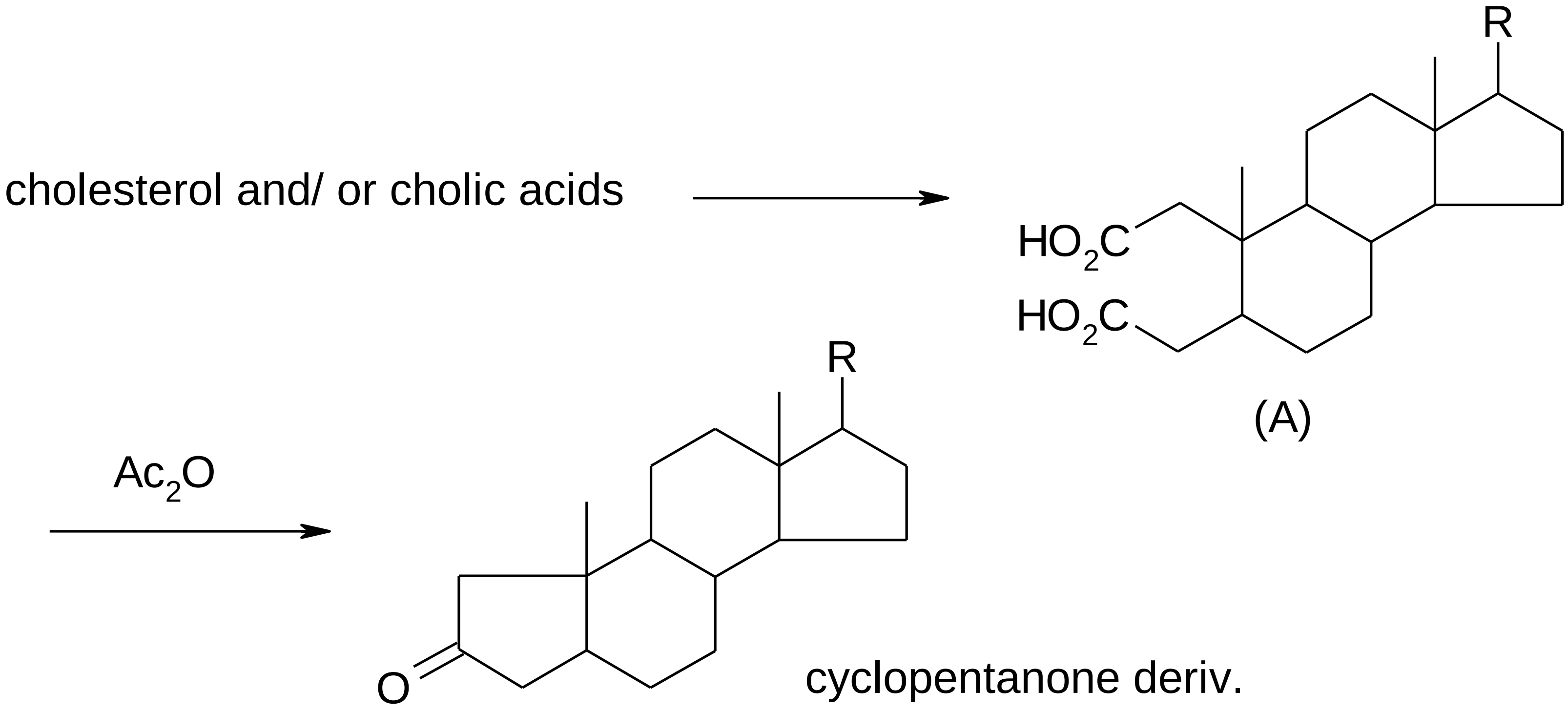
adipic acid
1,6 dicarboxylic acid

cyclopentanone

كل الستيرويدات تتكون من هيكل كربوني رباعي الحلقة (سيكلوبنتان بيرهيدرو فينانثرين) وهذا تم اثباته عند تسخين الستيرويد مع السيلينيوم ليعطي مشتق سيكلوبنتينوفينانثرين . ولإثبات حجم كل حلقة في الستيرويدات تجري الاكسدة للستيرويد فتفتح الحلقات لتعطي احماض ثنائية الكربوكسيل ولمعرفة طبيعة هذه الاحماض تطبق قاعدة بلانك والتي تنص علي :

عند التسخين مع اسيتيك انهيدريد الاحماض ١،٥ داي كربوكسيليك تكون انهيدريد حلقي مع فقد ماء اما الاحماض ١،٦داي كربوكسيليك فتكون سيكلوبنتانون مع فقد ثاني اكسيد الكربون بالإضافة لفقد الماء.

Determination of ring A in cholesterol and cholic acid



cholesterol and/ or cholic acids

(A)

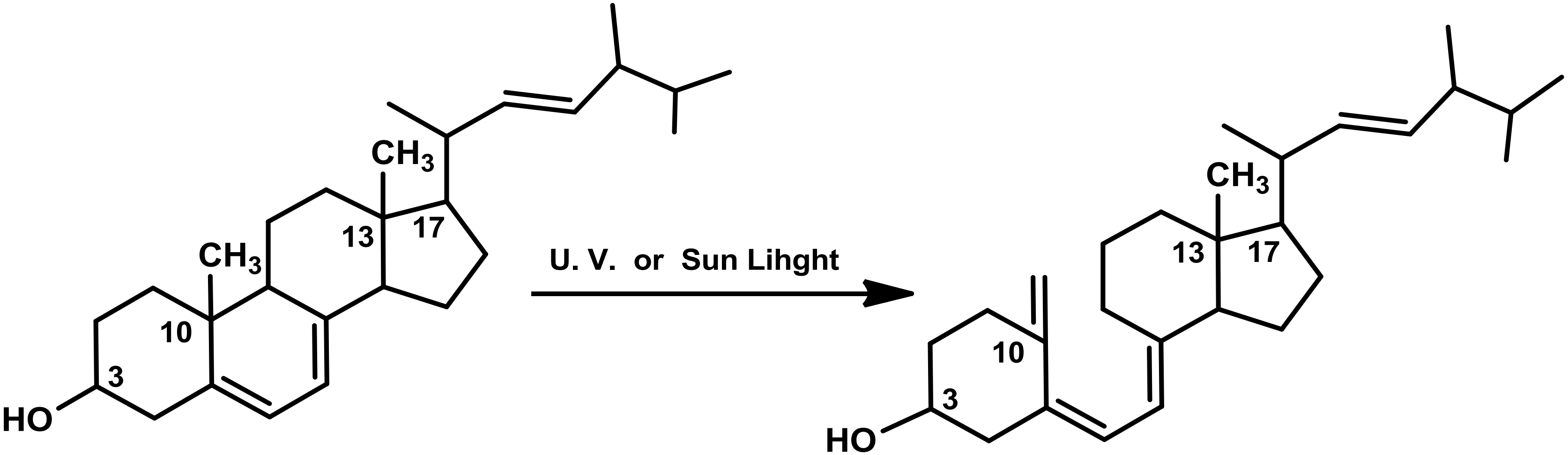
$\xrightarrow{Ac_2O}$

cyclopentanone deriv.

Cholesterol and cholic acid were converted into the dicarboxylic acid by oxidation which gave a cyclopentanone derivative by heating with acetic anhydride according to blanc rule and the acid 1,6 dicarboxylic acid and ring A is six membered ring (R is the appropriat side chain).

Ergocalciferol
Vitamin D2

Conversion of Ergosterol into VitaminD_2

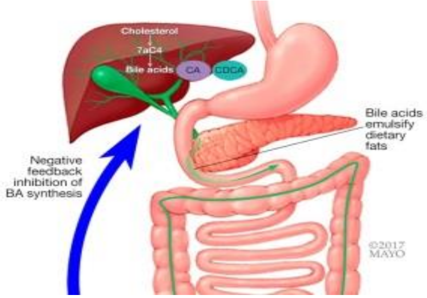


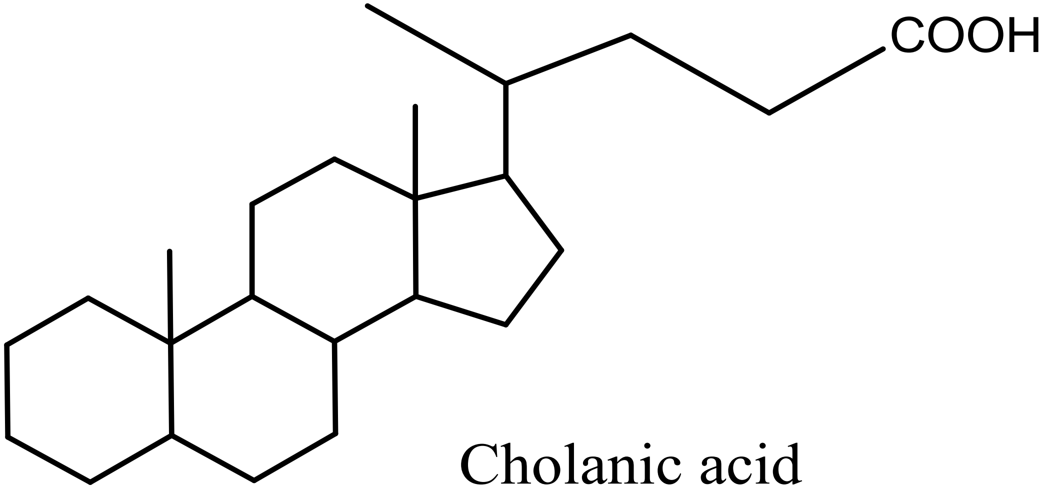
Ergosterol

Vitamin D_2

Vitamin D is anthracitic vitamin They are about seven compounds (Vitamin D1 - D7) with the ring B being opened. Vitamin D2 (or calciferol) is formed from ergosterol by the sunlight irradiation

Bile acids

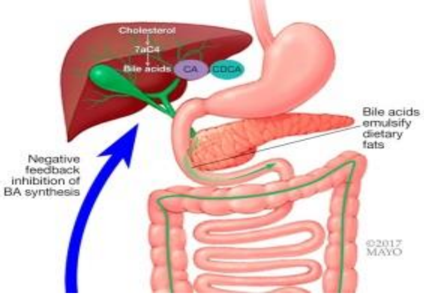


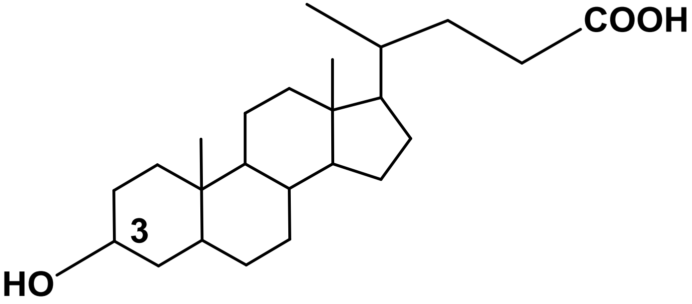


Cholanic acid

The natural bile acids are generally hydroxy derivatives of cholanic acid .They are produced in the liver either synthetically or by degradation of cholesterol and occur in bile as water soluble sodium salts of peptide conjugate with glycine or taurine.

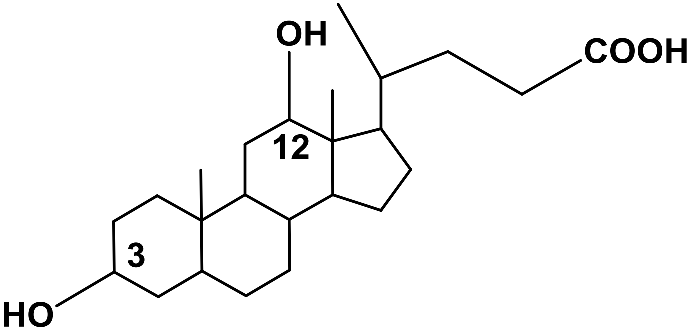
Bile acids





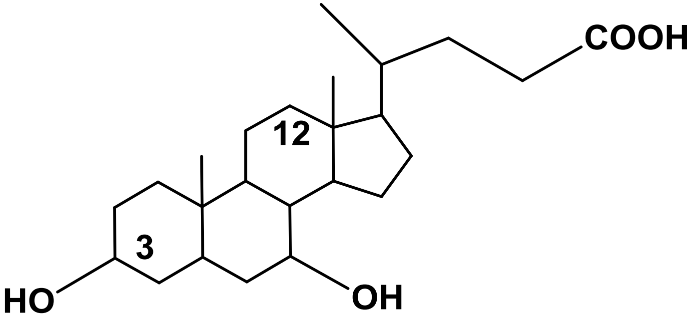
3-Hyrdroxycholanic acid

Lithocholic acid



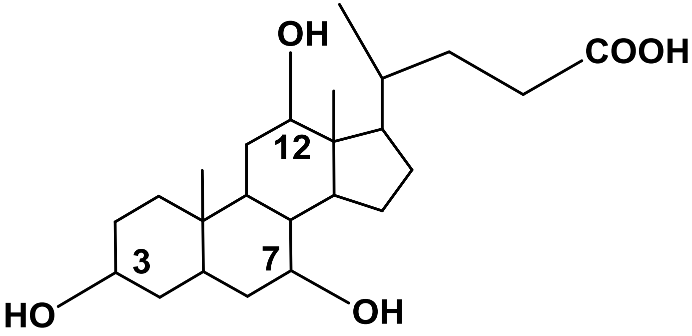
3,12-dihyrdroxycholanic acid

Deoxycholic acid



3,7-Dihyrdroxycholanic acid

Chenodeoxycholic acid

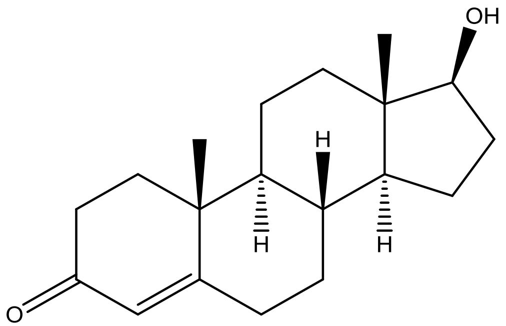


3,7,12-Trihyrdroxycholanic acid

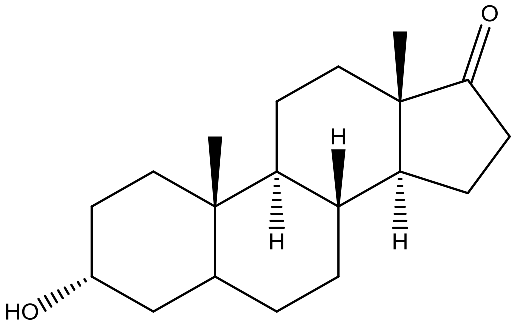
Cholic acid

Sex Hormones

1-Androgens (Male Hormones)(androsterone –testosterone)

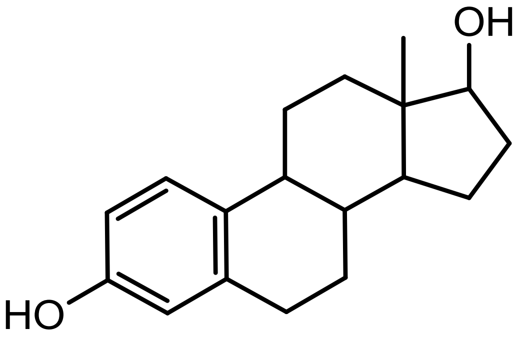


Testosterone

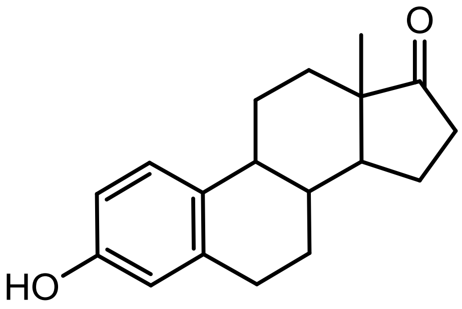


Androsterone

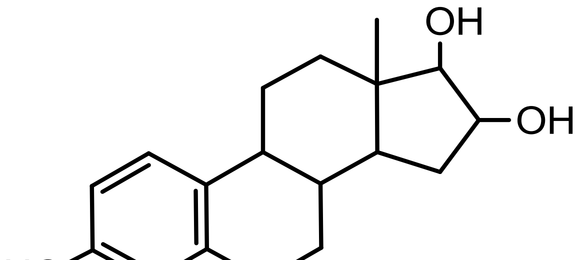
2-Oestrogens (Female Hormones)



Oestradiol



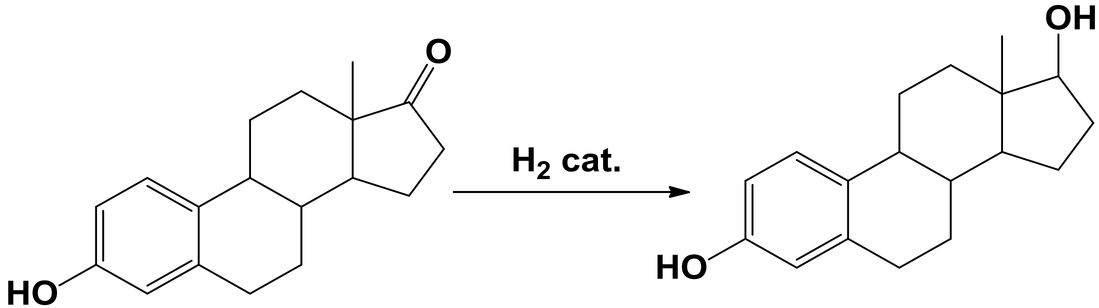
Oestrione



Oestriol

Oestrogens (Female Hormones) all of them contain phenolic hydroxyl group at C3 and may be prepared from dehydroepiandrosterone(D.E.A) which can be synthesized from cholesterol.

(Oestrogens)

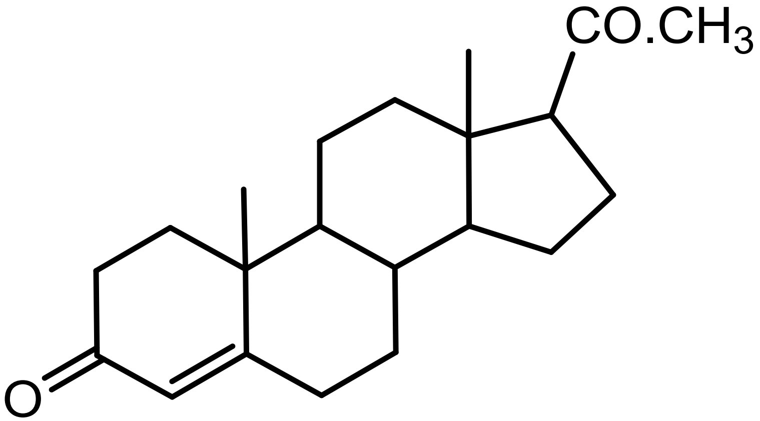


Oestrone

Oestradiol

Oestrone may be reduced to oestradiol by catalytic hydrogenation or by lithium aluminium hydride .

3- (Gestogens)
Progesterone



Progesterone

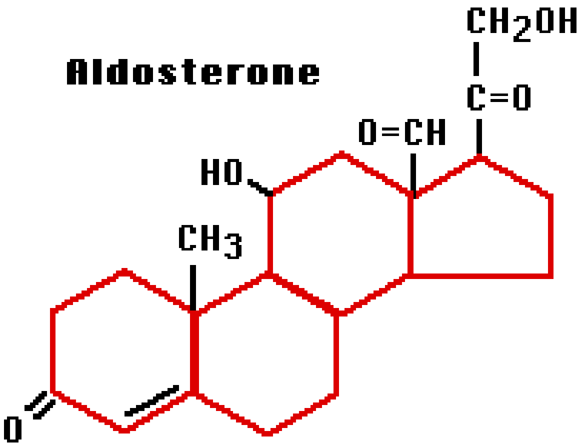
These are essential hormones which responsible for pregnancy.

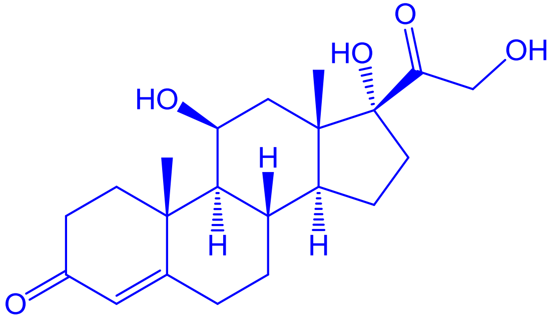
Progesterone is α,β-unsaturated ketone and synthesized from both D.E.A and Ergosterol .

Adrenocortical hormones

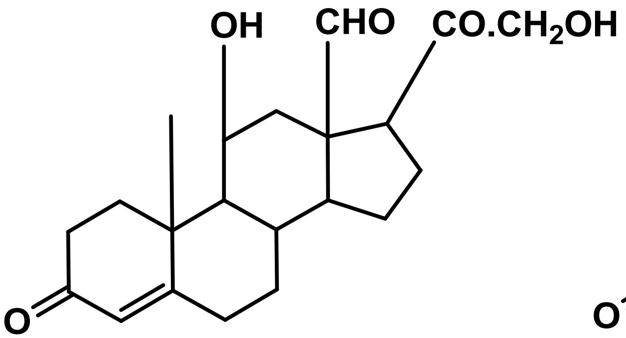
They are produced by the cortex of the adrenal glands ,their main functions are the control of carbohydrate and protein metabolism and control of balance of water and electrolytes.

Cortisone is also used in the treatment of allergies and immune diseases.

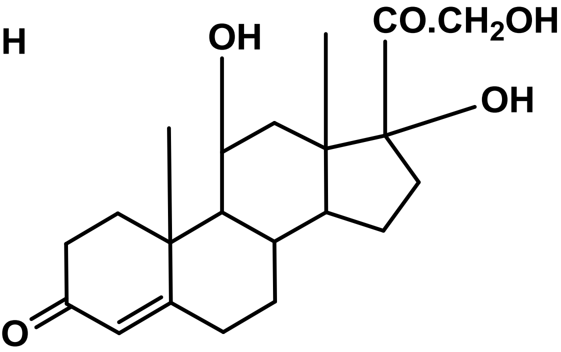




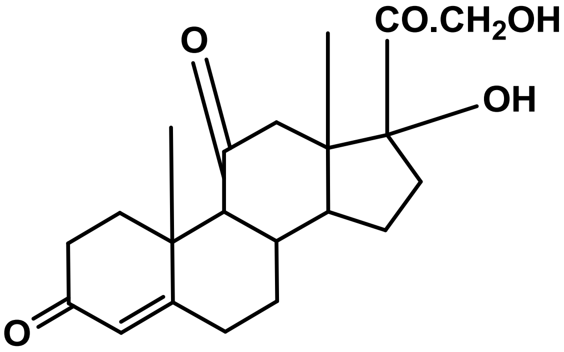
cortisol (stress hormone)



Aldosterone



Cortisol



Cortisone

References

1- I.L.FINAR Organic Chemistry VOL2

SOUTH VALLY UNIVERSITY

FACULTY OF SCIENCE
AT QENA

Chemistry of Dyes and Fiber

اعداد
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كلية العلوم – قسم الكيمياء
العام الجامعي
٢٠٢٢-٢٠٢٣

المحتوي :-

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

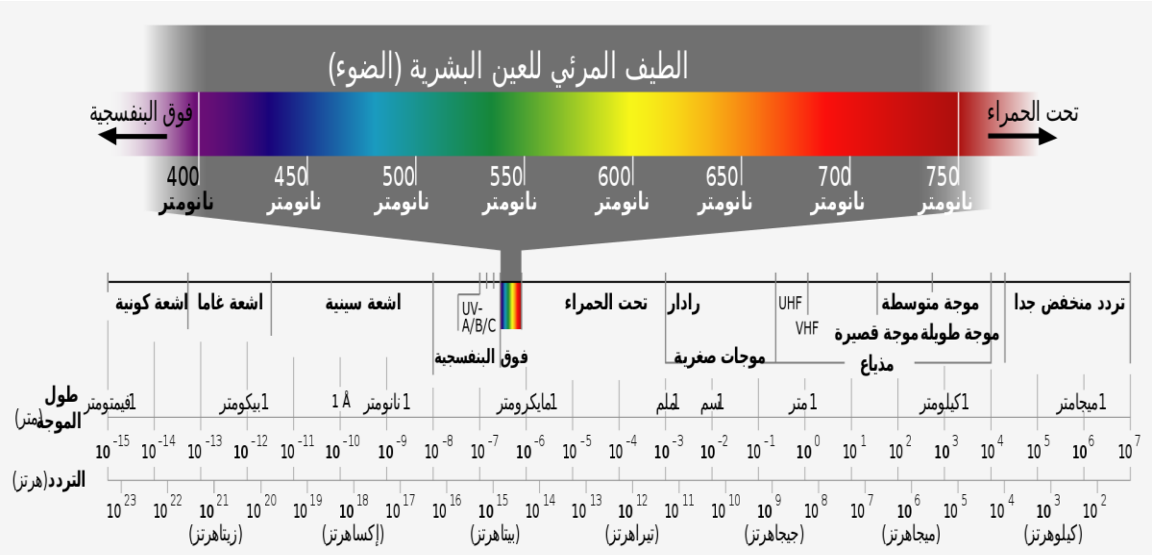
Definition of dyes

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

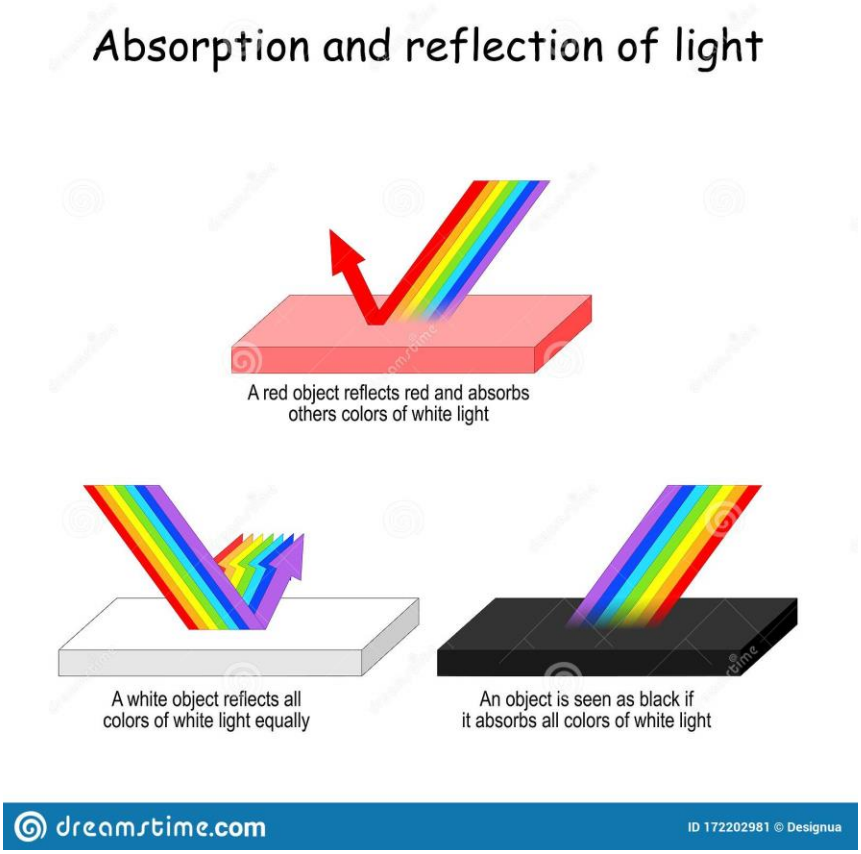
Interpretation of color ?

- 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

General characters of the dye molecule:

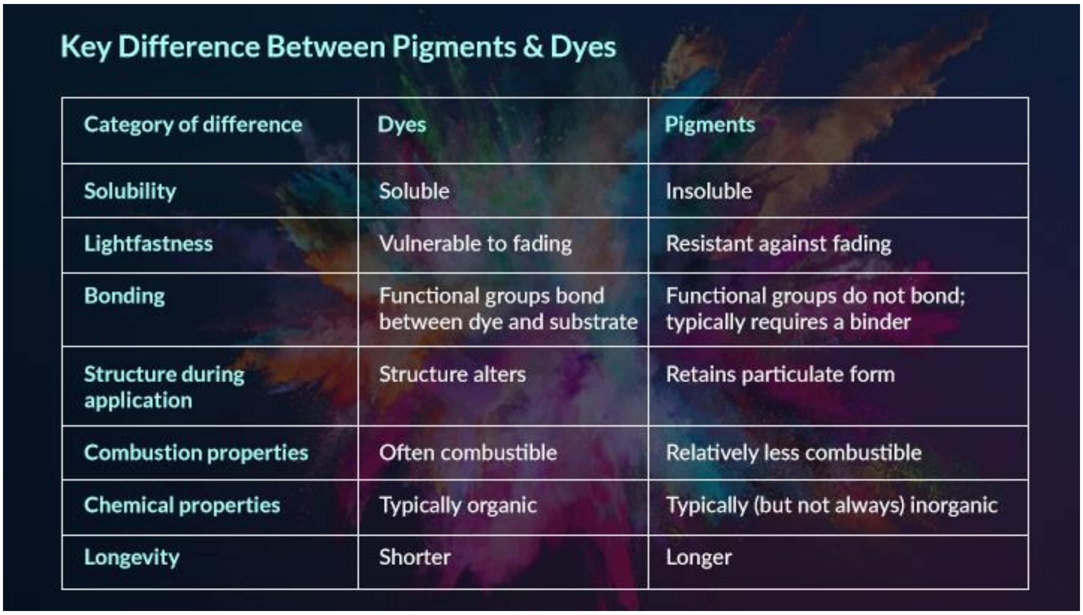
Substance to be used as a dye it must have the following characters

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

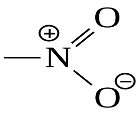
a) Chromophores.

b) Auxochromes.

c) Quinoid structure.

A) Chromophores:

- Chromophores are these groups with multiple bonds examples of chromophores



nitro

$N{=}O$

nitroso

$—N{=}N—$

azo

$\overset{O}{\overset{\|}{C}}$

$\overset{S}{\overset{\|}{C}}$

$C{=}C$

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

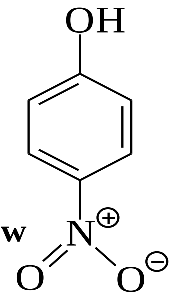
***Single conjugated is not sufficient to produce color but a number of conjugated must be attached with chromophores to produce color and as number of conjugated increase the degree of color increase.**

e.g. $CH_2{=}CH_2$

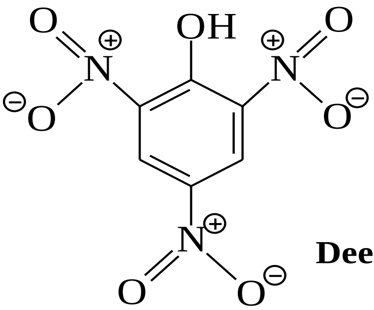
Colourless

$H_3C{-}(CH{=}CH)_6{-}CH_3$

Yellow



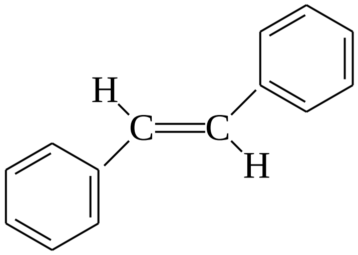
Yellow



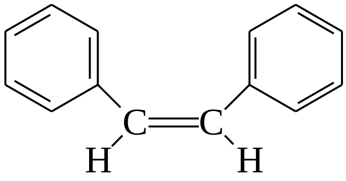
Deep Yellow

The position of groups in space can affect on color

e.g. stillbene



Trans
(Coloured)



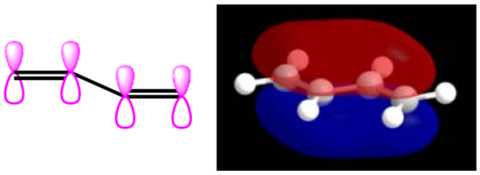
Cis
(Colourless)

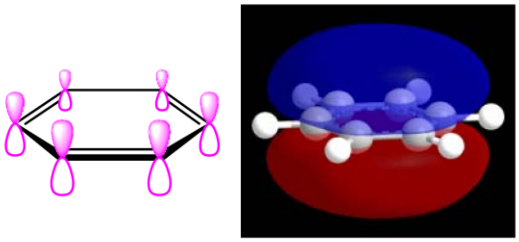
- In case of trans (colored) the molecule is planner so conjugation involves two benzene rings and one double bond.

-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

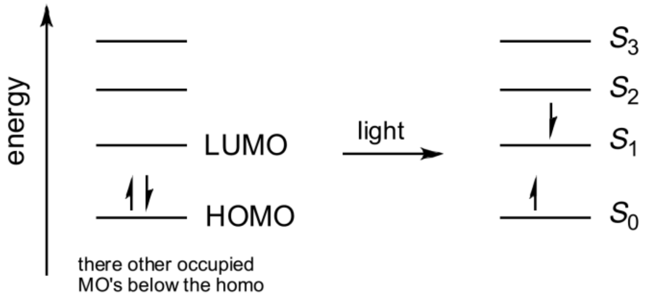
- The *p* orbitals of conjugated π bonds and aromatic compounds interact together to form a large orbital known as a *molecular orbital* (MO).



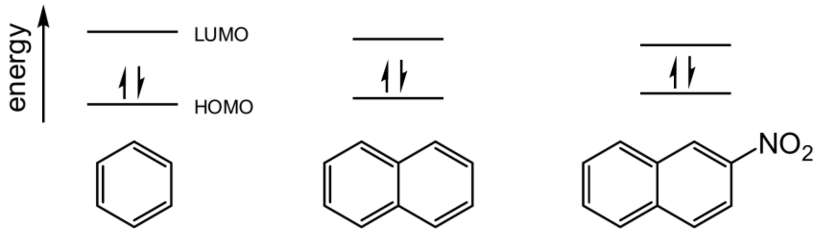


- π bonds are higher in energy than σ bonds. The MO derived from the π bonds is the one highest in energy that contains electrons, and it is termed the *highest occupied molecular orbital*, or HOMO. (MO theory is actually much more complicated!)
- MO's that are even higher in energy exist, but they are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

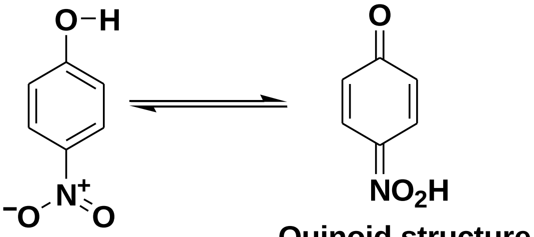
-Presence of auxochromes with chromogen make chromogen dye because it:

1- **Deepen the color.**

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

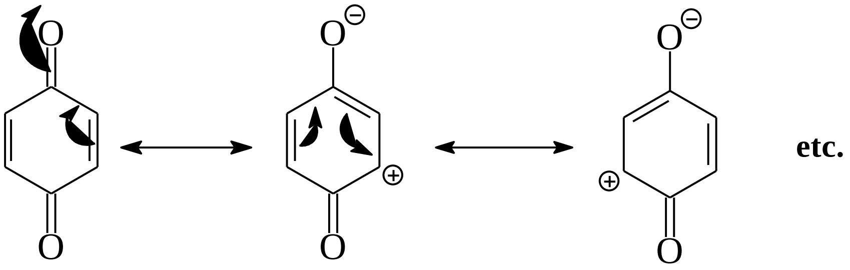
C) Quinonoid structure:

-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**

-Chemical classification of dyes:

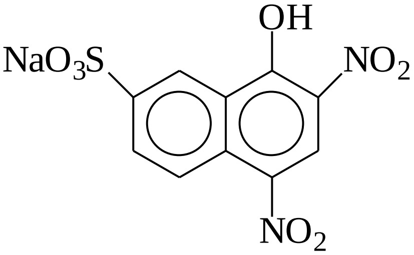
-It is classified according to the groups present or main nucleus

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

1) Nitro dyes:

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

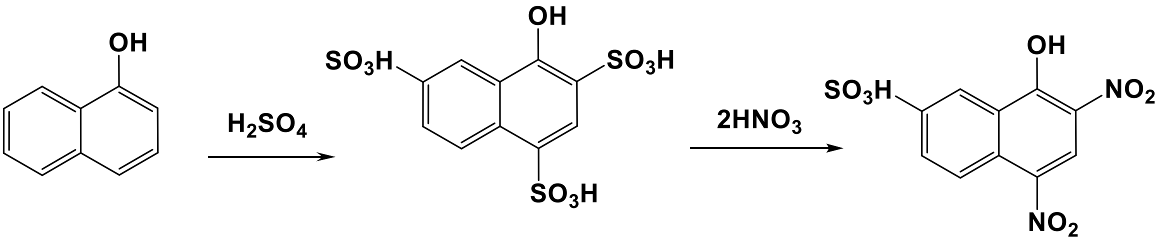
Used in dyeing wool and cotton.



Naphthol Yellow S

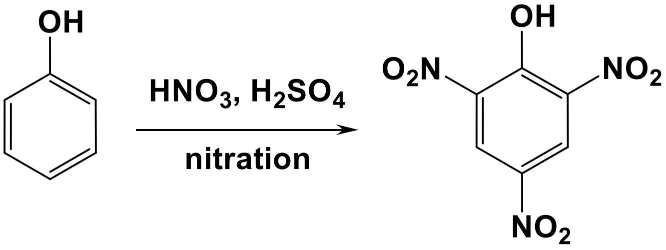
2,4-dinitro Naphthol-7-sulphonic acid sod. s

Preparation:



2-picric acid dye:-

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

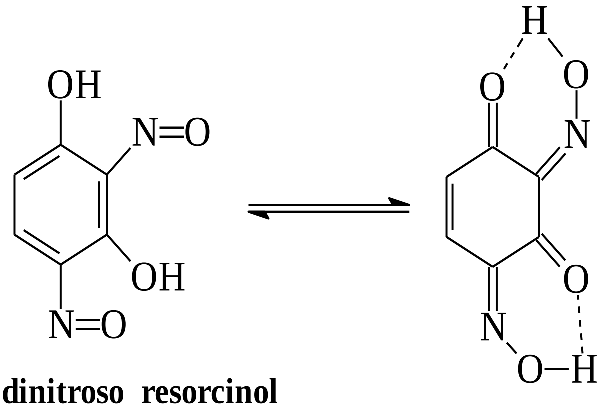


2) Nitroso dyes:

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

a-Resorcine green :-

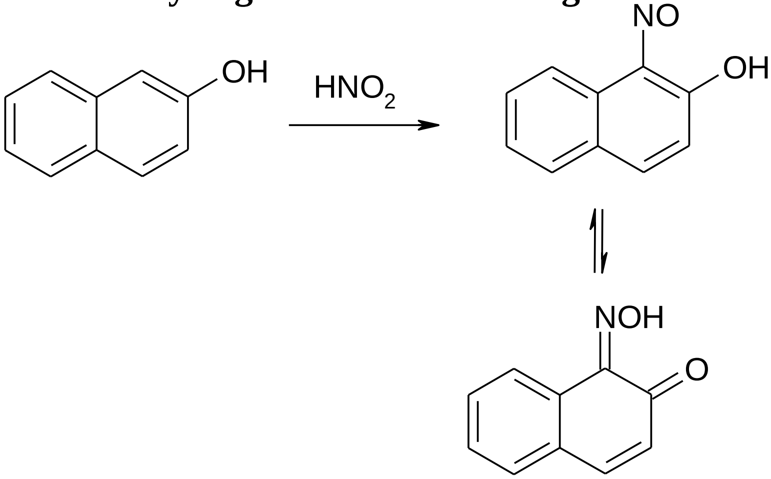
Used in dyeing silk and wool with green color.



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.

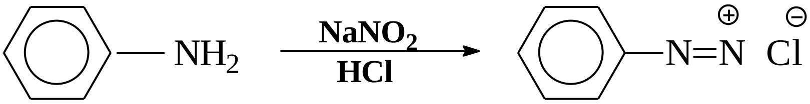
- Azo dye is prepared through two steps:

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.

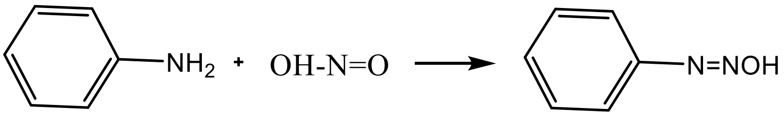
$\overset{\oplus}{NO}$, $NOCl$, $H_2\overset{\oplus}{O}-N=O$, N_2O_3

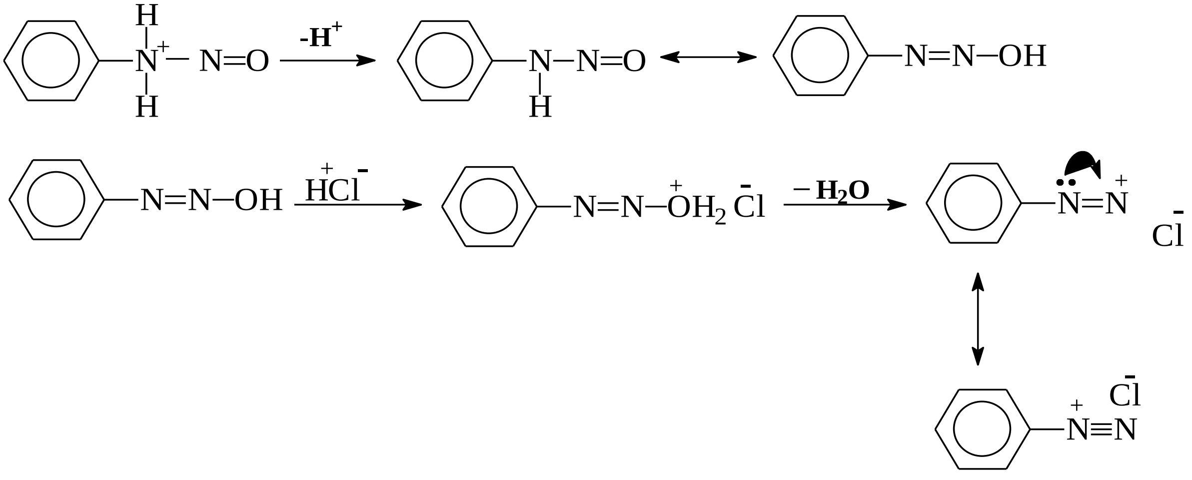
2-Conversion of N-nitroso to diazonism salt.

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

$NaNO2 + HCl \longrightarrow NaCl + HO\text{-}N=O$

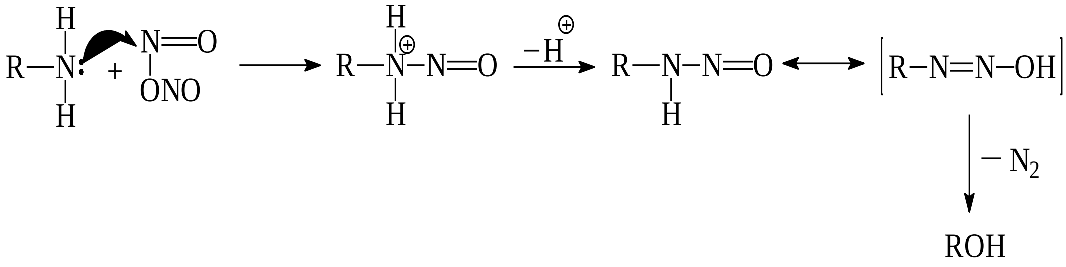
Nitrous acid





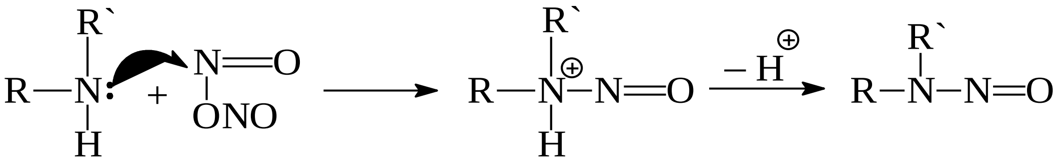
benzene diazonium chlorid

B) 1ry aliphatic amines:



i.e. No diazotization of aliphatic amines.

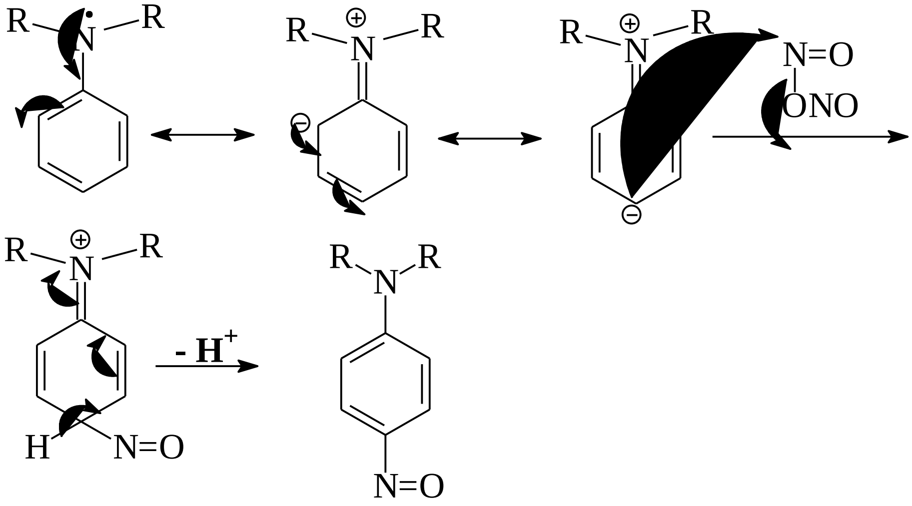
C) 2nd aromatic and aliphatic amines:



R may be aliphatic
or Aromatic

N Nitroso compoun

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:

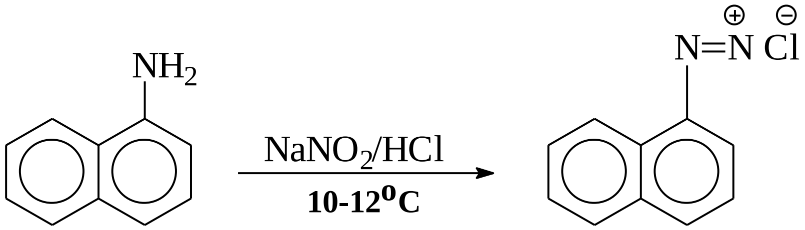
Diazotization of 1ry aromatic amines depends on nature and position of substituent groups.

1- for unsubstituted 1ry aromatic amine:

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

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

For amino naphthalene



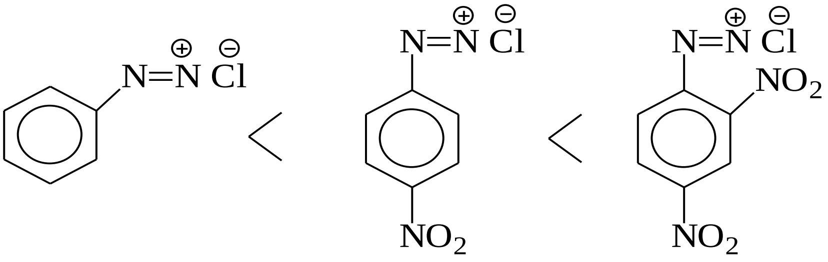
Secondary reaction can occur if some aniline is unreacted.

$$Ph{-}NH_2 + Ph\ N{=}\overset{\oplus}{N}\ \overset{\ominus}{Cl} \xrightarrow[-HCl]{} Ph\ NH{-}N{=}N{-}Ph$$

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:

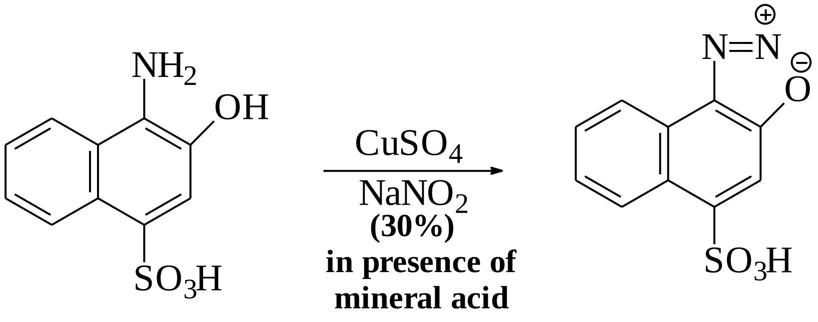
The presence of acidic group e.g. SO_3H make diazotization occur after dissolving amino sulphonic acid in $NaHCO_3$ solution and $NaNO_2$ is added to aqueous solution of aminosulphonic acid then diluted acid is added to make diazotization (this method is called reversed diazotization).

3- In case of aminophenol and aminonaphthol:

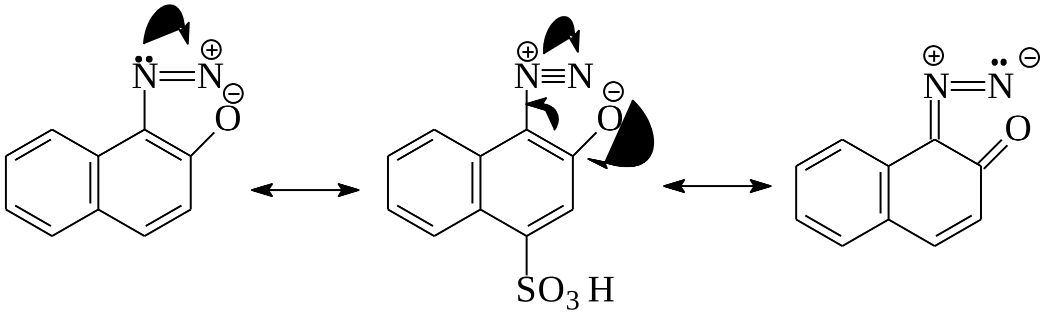
Amino phenol and amino naphthol in which NH_2 and OH are in position 1,2 or 1,4 for each other forming diazoxides.

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

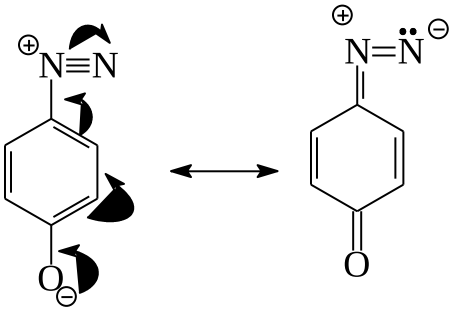
e.g.



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



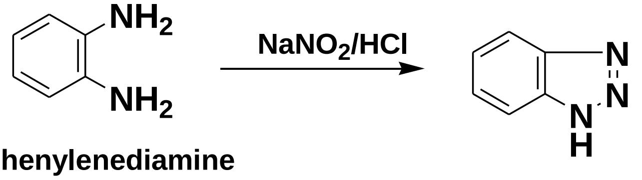
Also 1,4 aminophenol



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

5- for diamines:

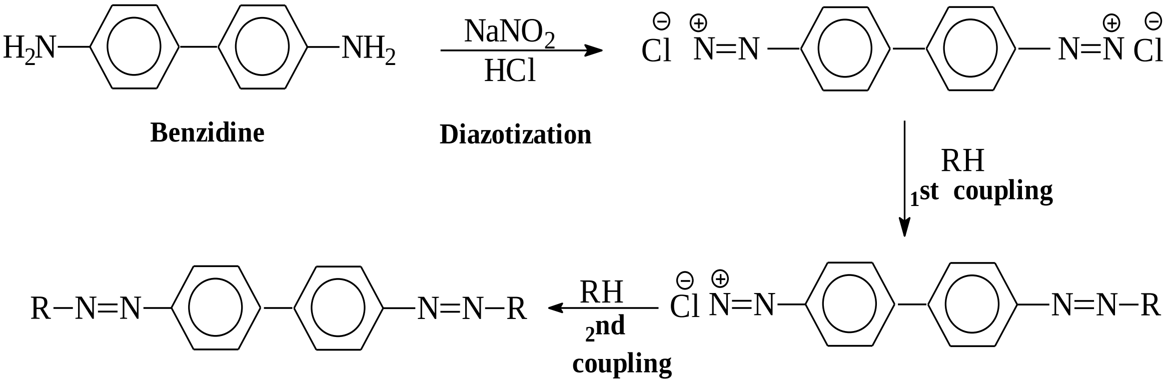
A) If two amino in o- position, no coupling occur due to ring closure.



O-Phenylenediamine

1*H*-Benzotriazole

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



The 2^{nd} coupling occurs slower than 1^{st}.

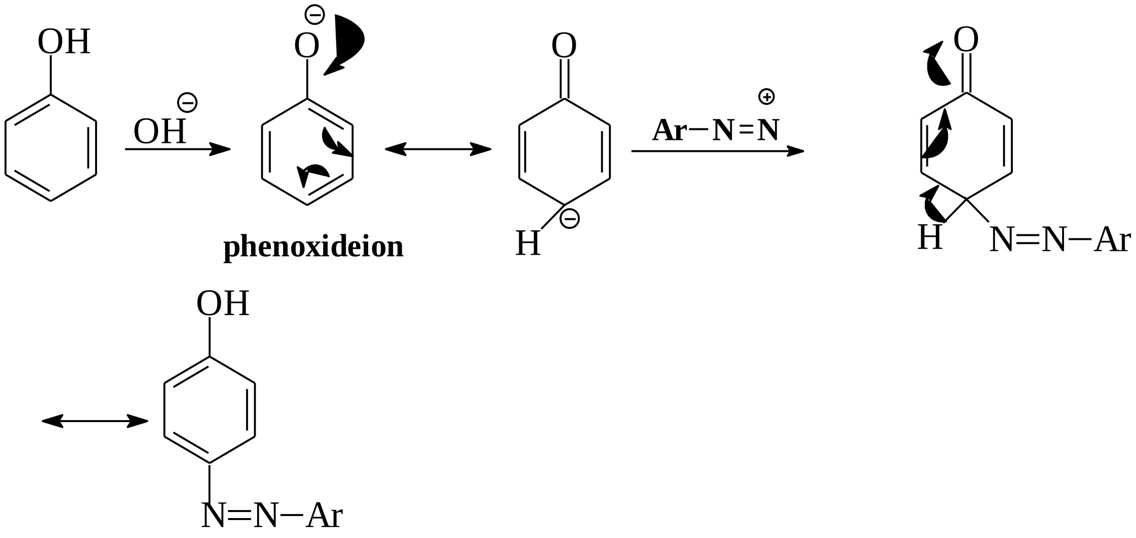
Diazo coupling

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

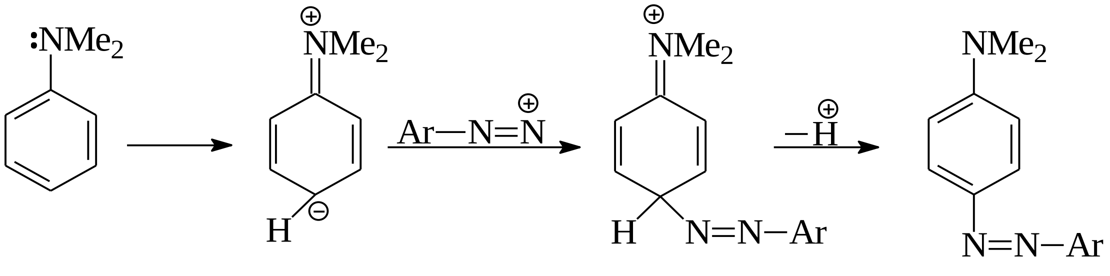
***It occurs often in para-position.**

***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:



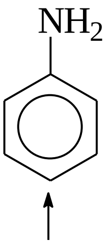
Coupling component:

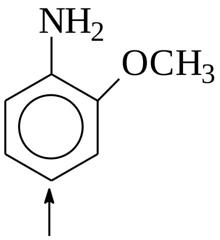
1) Benzene derivative:

A) Amines:

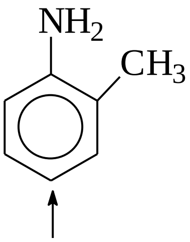
- **Medium of coupling: acidic medium**
- **Position of coupling: para-position of amino group.**

i- Primary amines:

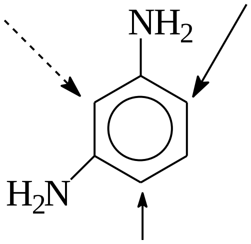




o-Ansidine



o-Toludine

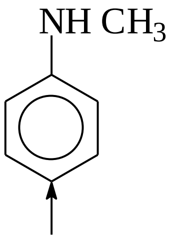


m– phenylenediamin

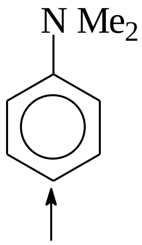
The arrow indicates the coupling position.

The arrow - - - - - - -➤ **indicate the less reactive position**

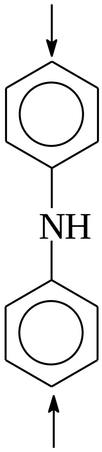
ii- Secondary and t–amines:



N–methyl aniline



N,N dimethyl aniline

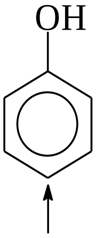


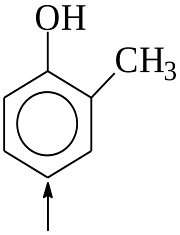
diphenyl amin

B) Hydroxy derivatives:

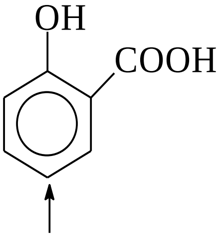
Medium of coupling: alkaline medium.

Position of coupling: para-position of –OH

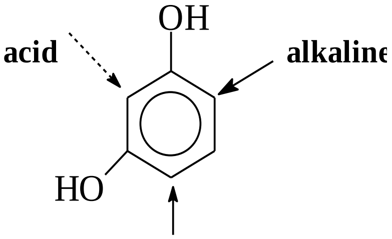




o- Cresol



Salicylic acid



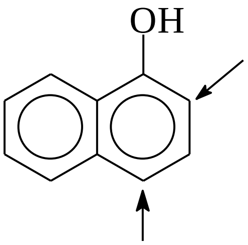
**alkaline
resoricnol**

2) Naphthalene derivatives:

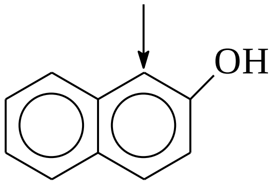
A) Naphthols:

Medium of coupling: alkaline

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



1 Naphtholor α–Naphthol

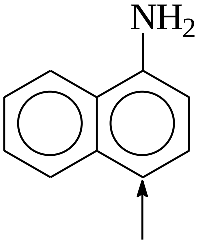


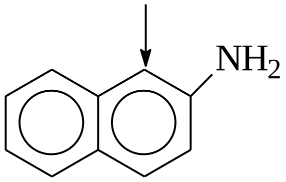
2-Naphthol or β-Naphtho

B) Naphthyl amines:

Medium: acidic

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

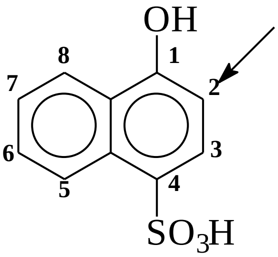




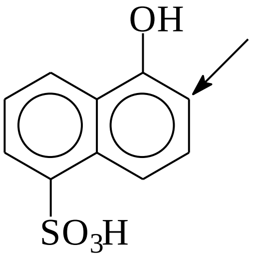
C) Naphthol sulphonic acid:

Medium: alkaline.

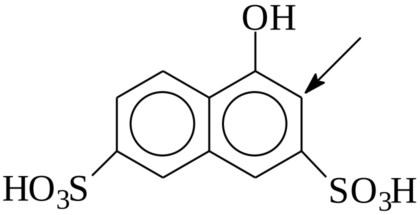
Position of coupling: ortho-position of OH.



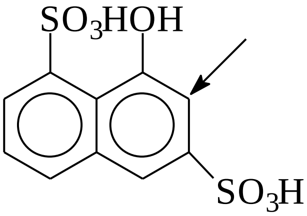
1-Naphthol-4-Sulphonic acid



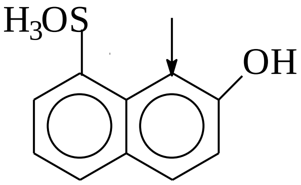
1-Naphthol-5-Sulphonic acid



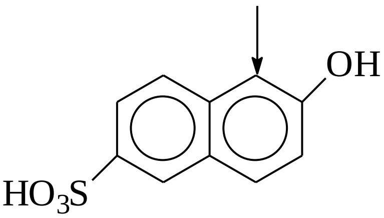
1-Naphthol-3,6-diSulphonic acid

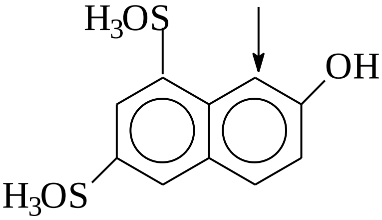


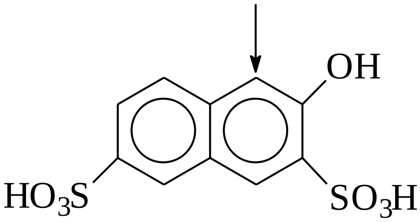
1-Naphthol-3,8-diSulphonic acid



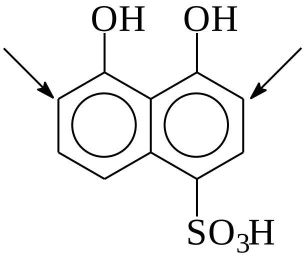
2-Naphthol-8-sulphonic acid



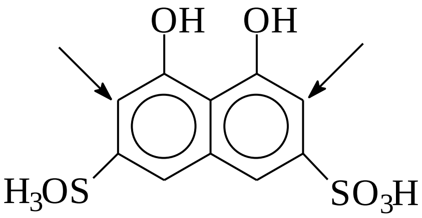




For dihydroxy naphthalene sulphonic acids



**4,5 dihydroxy Naphthalene
1- sulphonic acid**

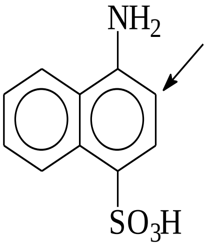


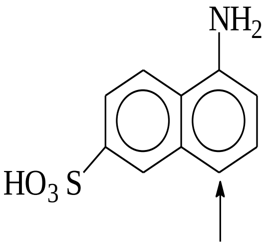
D) Naphthyl amine sulphonic acids:

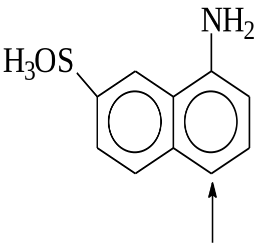
Medium: acidic

Position of coupling: position 4- for 1-Naphthylamine

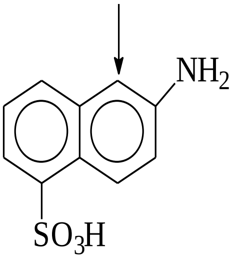
Position 1- for 2-Naphthylamine



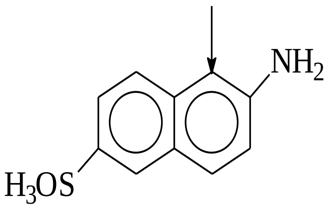




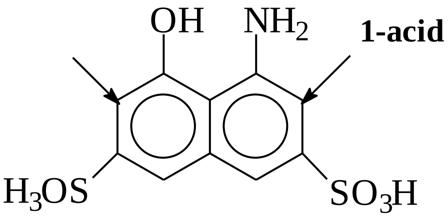
1-amino-7-Naphthalensulphonic acid ac



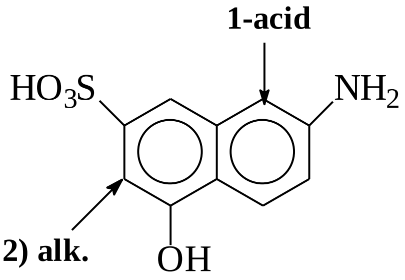
**2-amino 5-Naphthene
sulphonic acid**



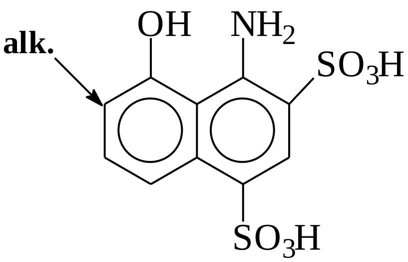
E) Amino naphthol sulphonic acids:

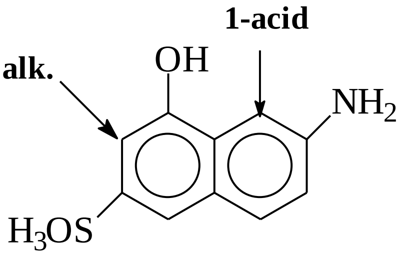


**1- amino- 8-Naphthol
3,6 disulphonic acid**



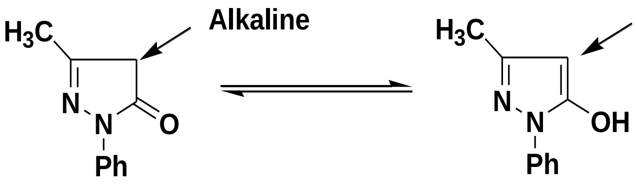
**2-Amino-5-hydroxy-
7-Naphthlene Sulphonic acid**



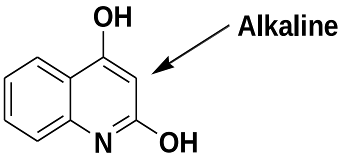


Active methylene component

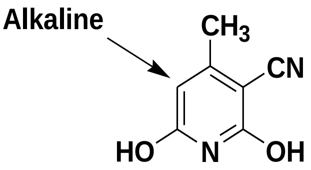
A) Hetero cyclic



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

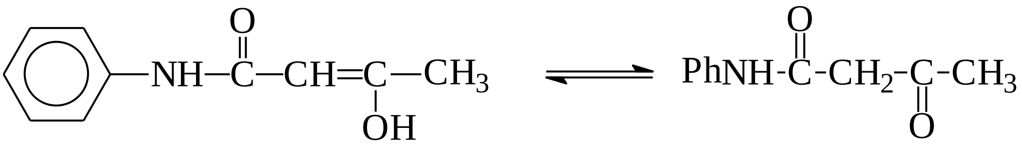


2,4-Dihydroxy-quinoline



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

Other example of active methylene acetoacetanilide



$$C_6H_5\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH{=}\underset{\underset{OH}{|}}{C}\text{-}CH_3 \rightleftharpoons PhNH\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_2\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_3$$

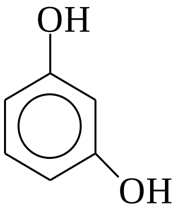
e.g of direct and acid dye

Questions

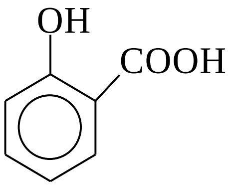
1- **Give structure of Azo dyes prepared from aryl diazonium cation (ArN_2^+) and the following coupling agent.**

- **a- Acetoacetanilide.**
- **b- 1- amino–8-naphthol-3, 6-disuphonic acid.**
- **c- 3- methyl-1-phenyl-2-pyrazolin-5-one.**

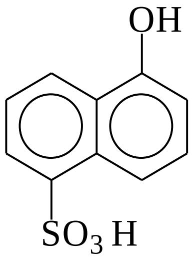
2- Give the structure of the following azo dyes which could be obtained from the interaction of diazonium cation (ArN_2^+) with the following coupling component



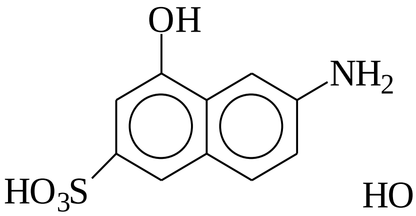
(1)



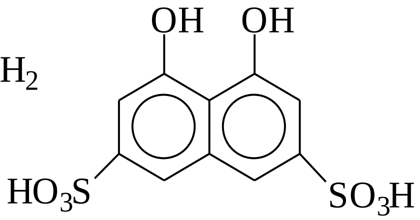
(2)



(3)



(4)



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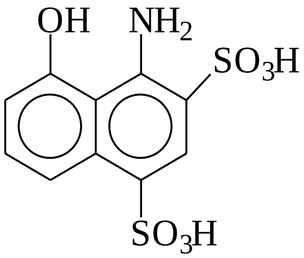
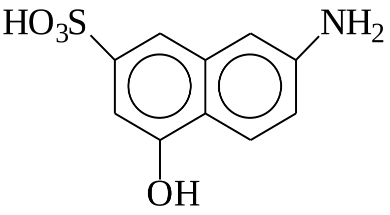


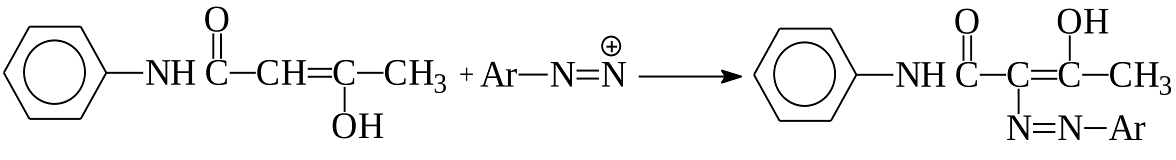
(6)



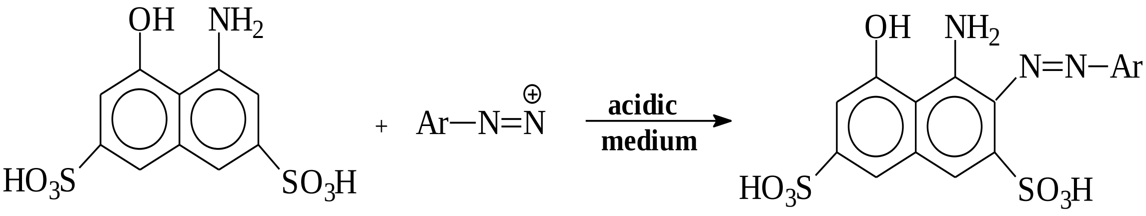
(7)

Answer of first question

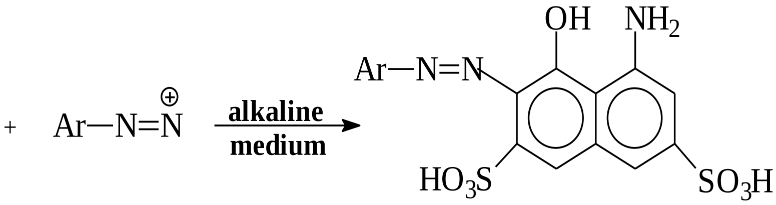
1) Acetoacetalide:



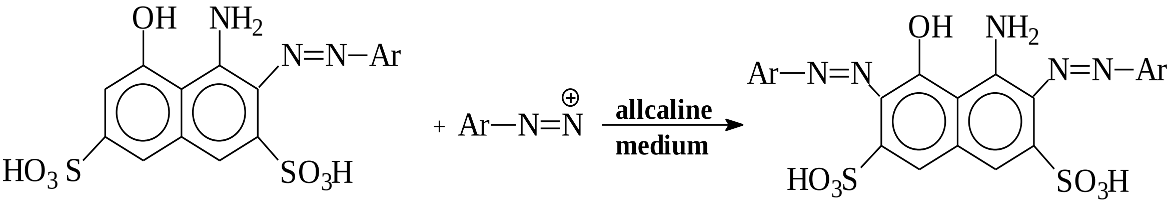
2) 1-amino–8-naphthol–3,6-disulphonic acid:



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

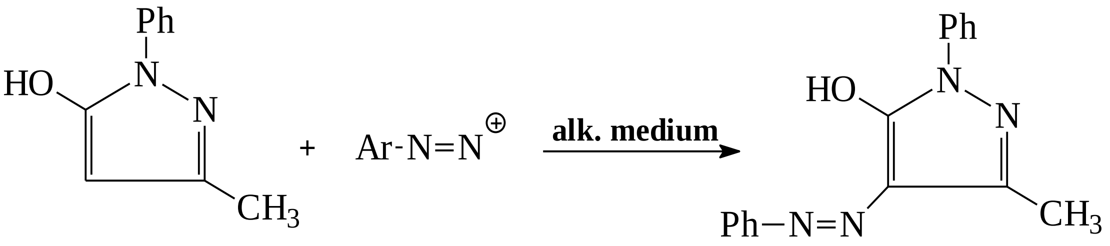


7-Arylazo-1- amio -8-naphthol- 3,6 disulphonic acid



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

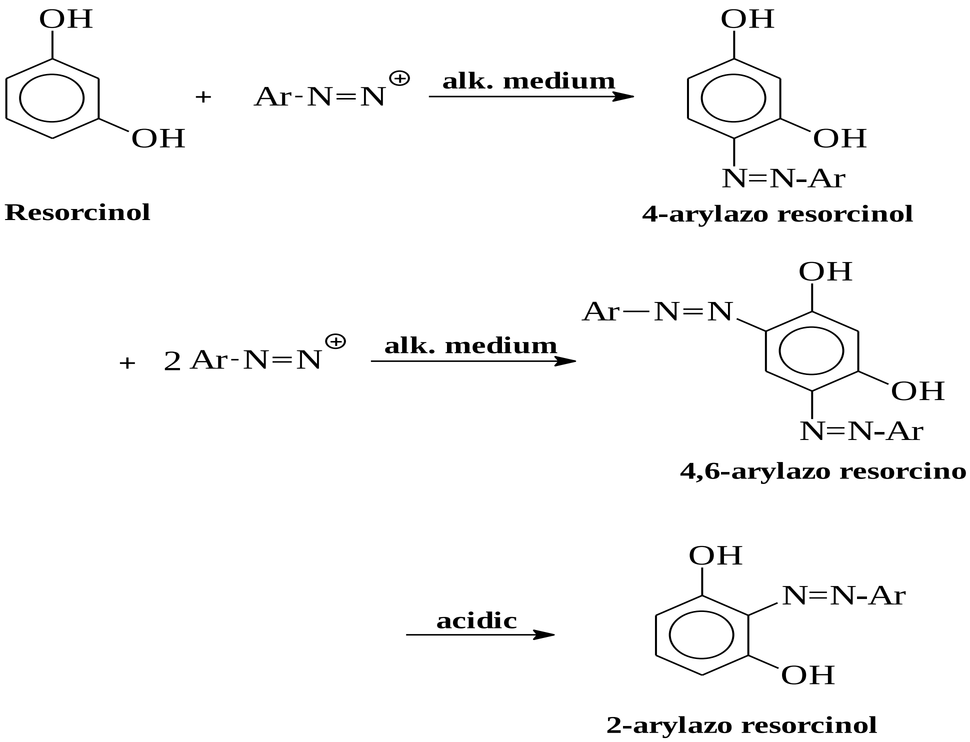
3) 3-methyl-1-phenyl-2-pyrazolin-5-one:



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

- إجابة السؤال الثاني

(1)



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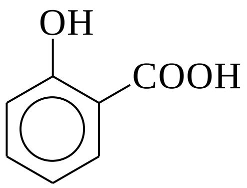
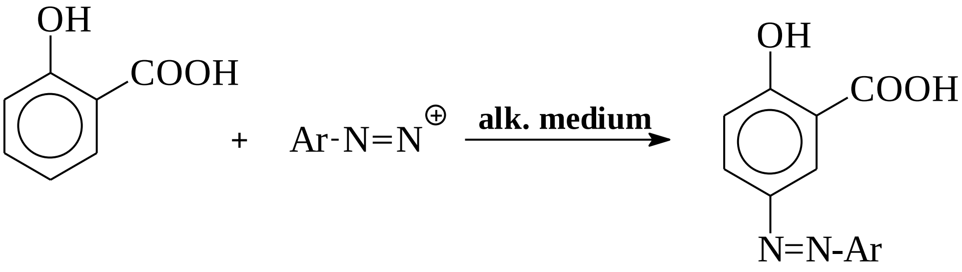
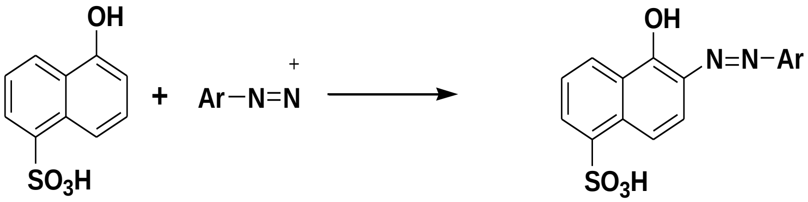




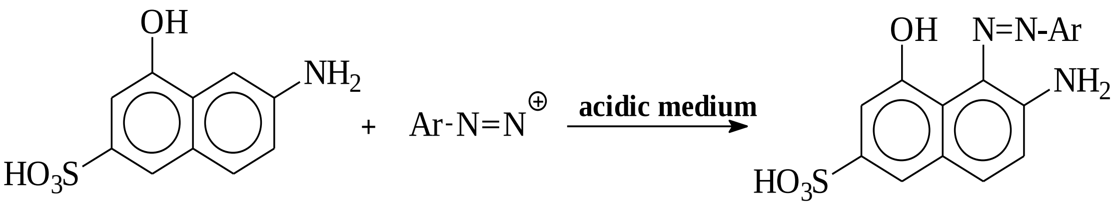
4-arylazo salicylic aci



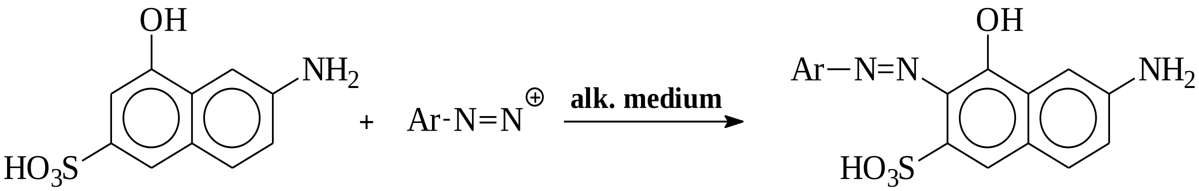
5-Hydroxy-naphthalene-1-sulfonic acid

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

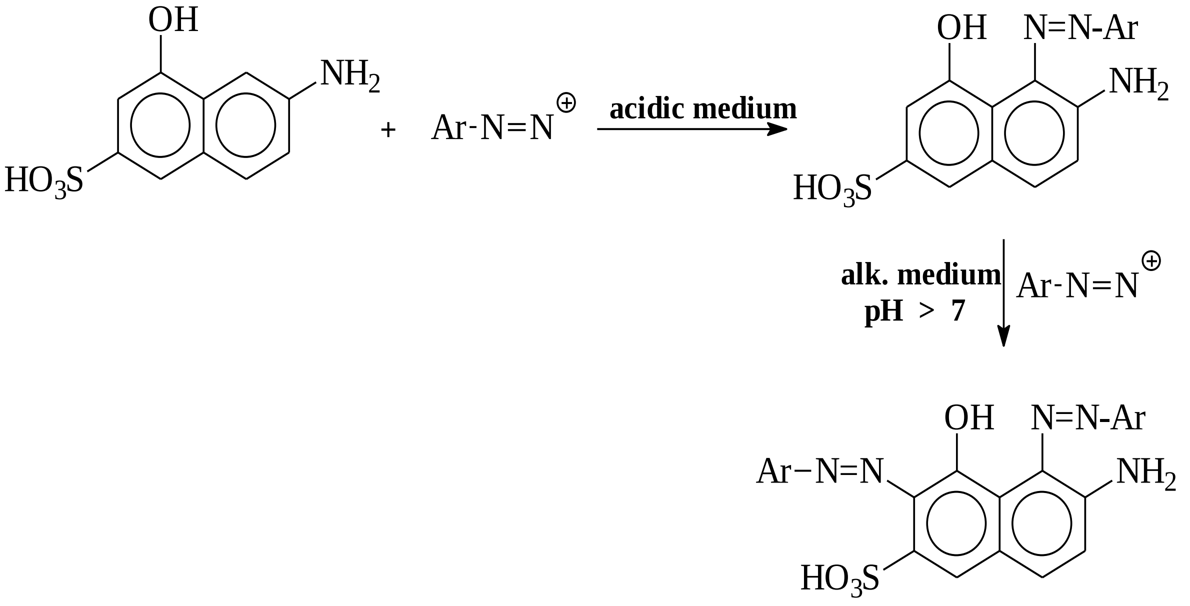
(a)



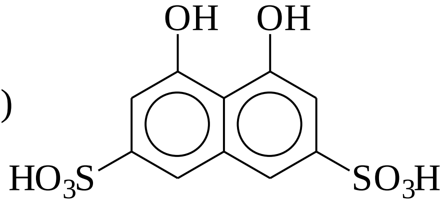
1-arylazo-2-amino-8-hydrox
naphthlene-6-sulphonic aci

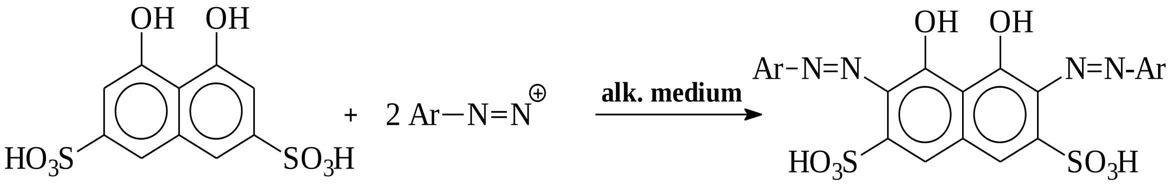


7-arylazo-2-amino-8-hydroxy naphthlene-6-sulphonic acid



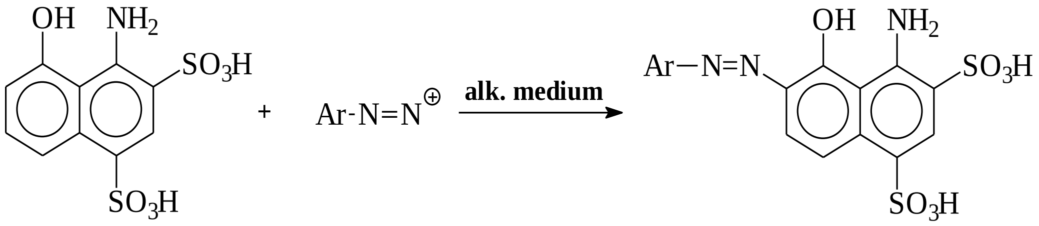
(5)





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

(6)



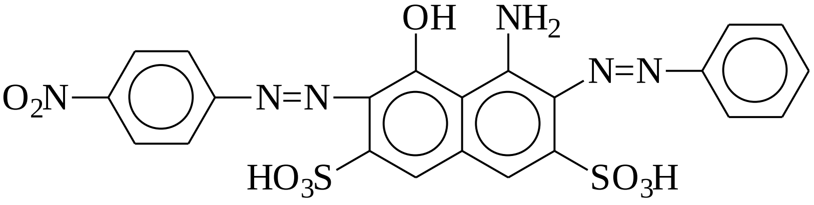
7-arylazo-1-amino-8-hydroxy naphthalnene 2,4-disulphoric aci

(7) Like (4).

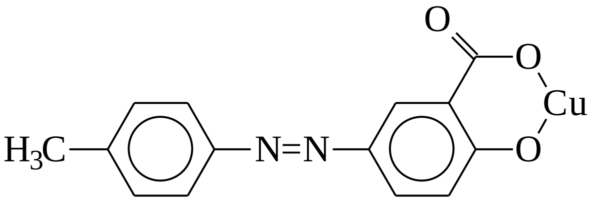
<u>Question:</u>

Synthesis of the following dyes:

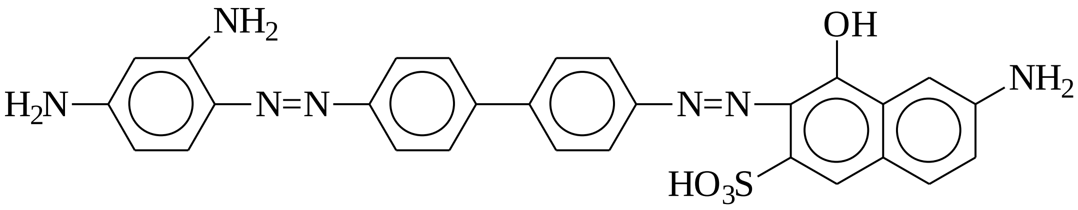
(1)



(2)

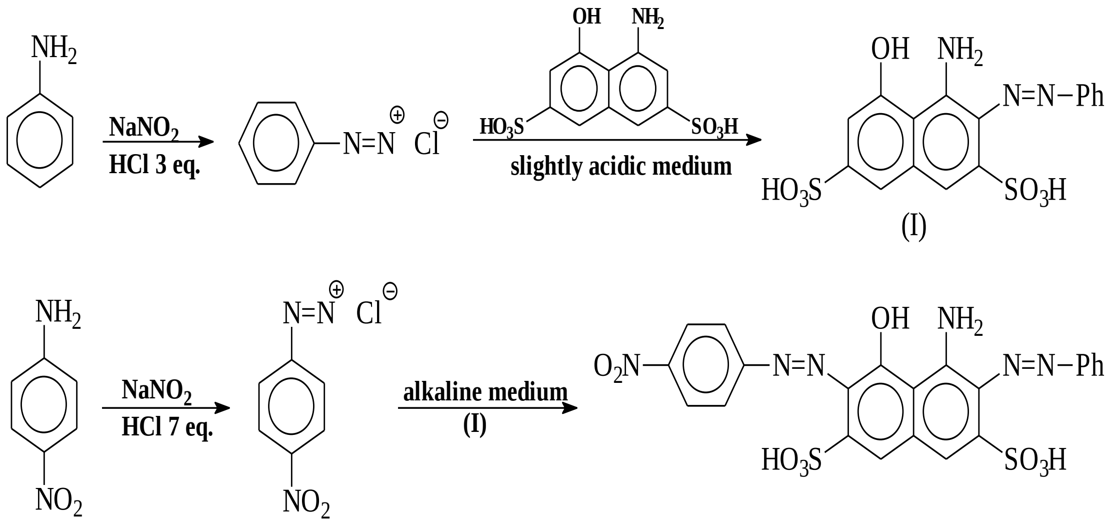


(3)

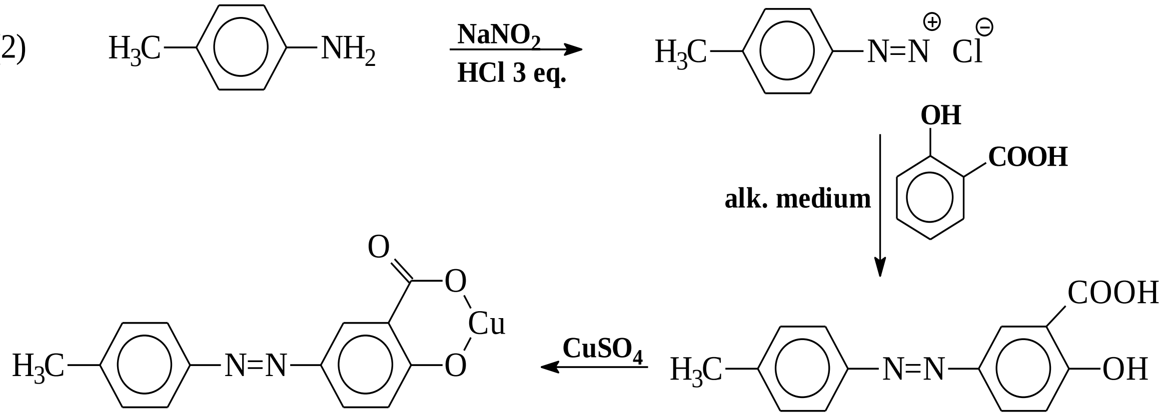


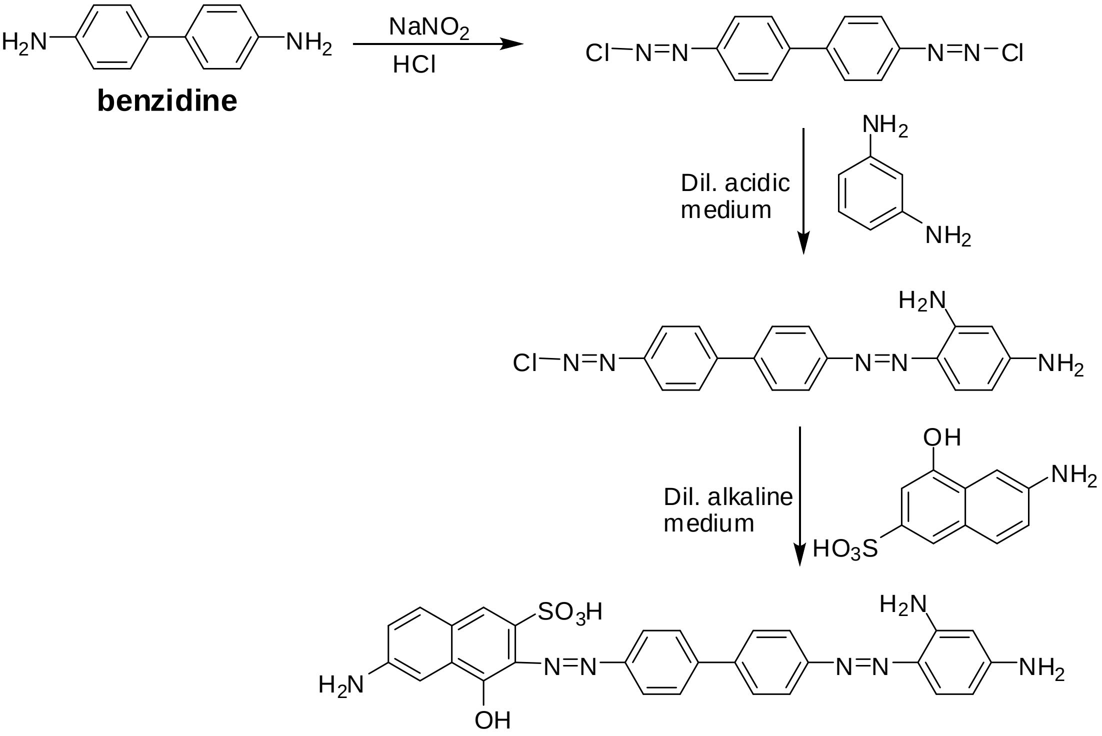
Solution:

(1)



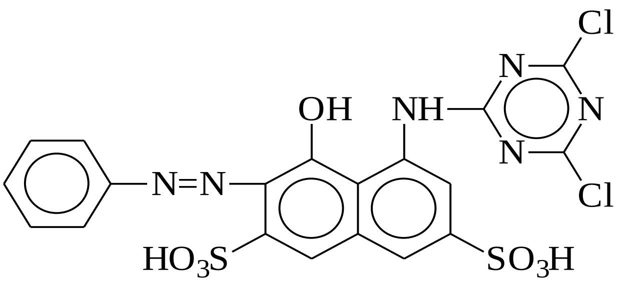
(2)


H3C
NH2
NaNO2
HCl 3 eq.
H3C
N=N
Cl
OH
COOH
alk. medium
COOH
H3C
N=N
OH
CuSO4
H3C
N=N
O
O
Cu
O

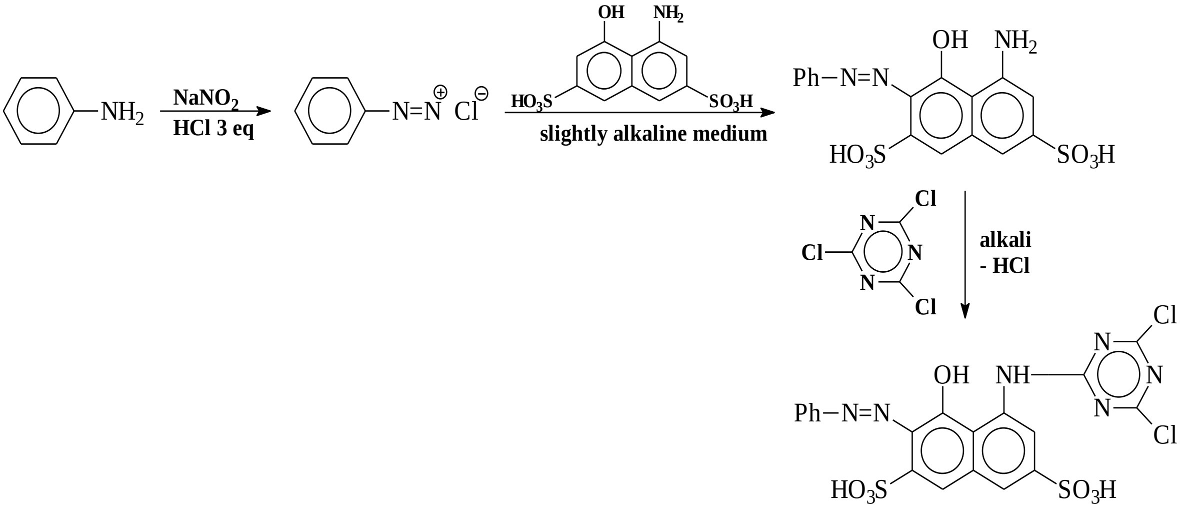

H2N
NH2
benzidine
NaNO2
HCl
Cl
N=N
N=N
Cl
NH2
Dil. acidic medium
NH2
H2N
Cl
N=N
N=N
NH2
OH
NH2
Dil. alkaline medium
HO3S
SO3H
H2N
N=N
N=N
H2N
NH2
OH

Question:

Synthesis



Solution:



Types of Disazo dyes

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

1. A→ E→ E\ or A→ M→ E

2. $$\begin{tikzcd}[row sep=small] & E \\ A \arrow[ur] \arrow[dr] & \\ & E^{\backslash} \end{tikzcd}$$

3. $A \rightarrow E \leftarrow A^{\backslash}$

4. $A \rightarrow E.X.E \leftarrow A^{\backslash}$

Where A is diazo component (amine)

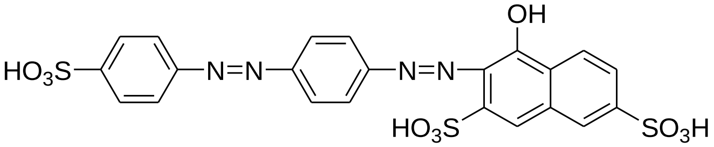
E is coupling component

X is agent used for binding two amines

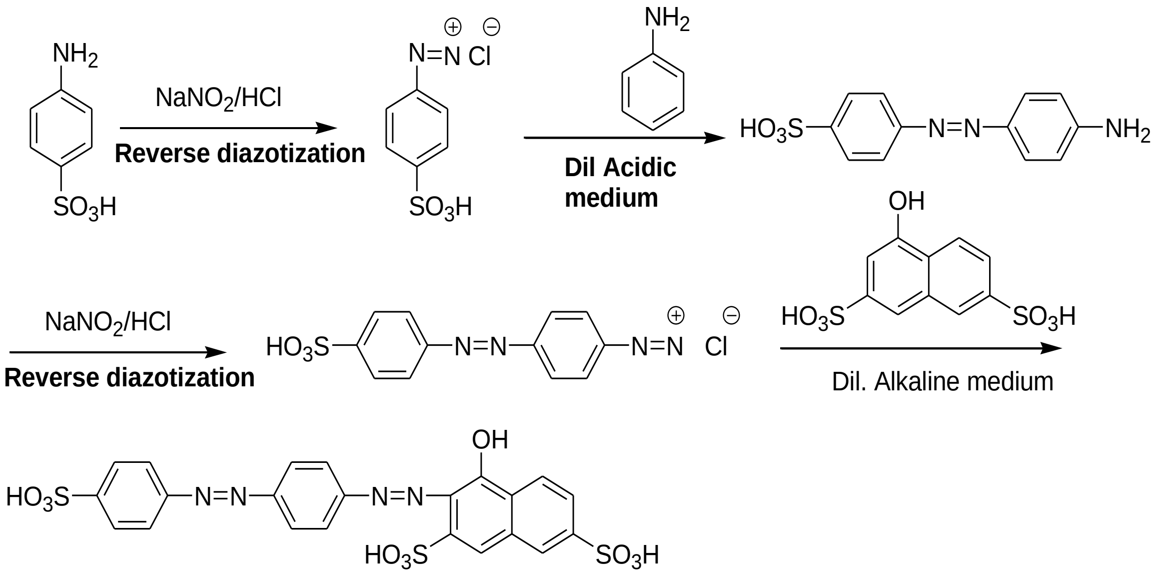
5. **<u>Type 1</u>** $A \rightarrow E \rightarrow E^{\backslash}$ **or** $A \rightarrow M \rightarrow E^{\backslash}$

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

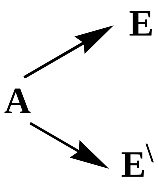
<u>e.g.</u>



<u>Synthesis</u>

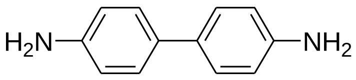


Type 2

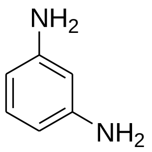


- **In this type we use Diamine as benzidine and couple it with two coupling component**

A as

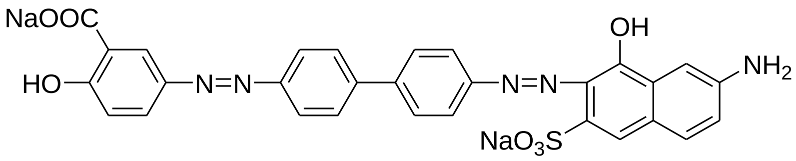


Benzidine

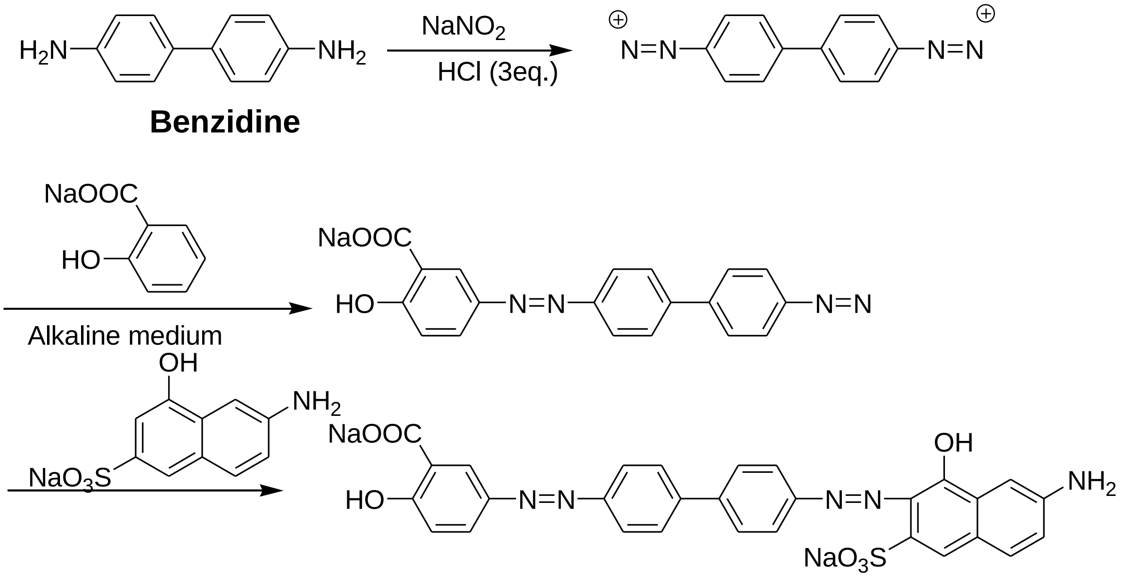


m-phenylenediamine

e.g.

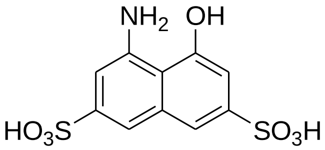


Synthesis



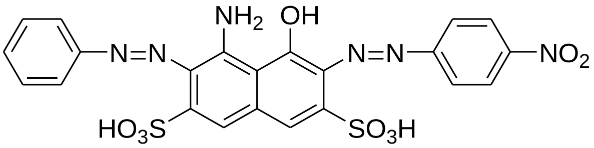
Type 3 **A→ E← A**

- **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**



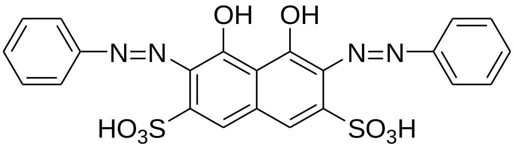
4-amino-5-hydroxynaphthalene-2,7-disulfonic acid

e.g.



See synthesis page 20

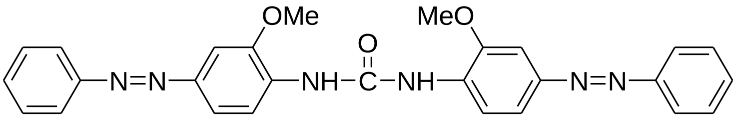
Example of A→ E← A



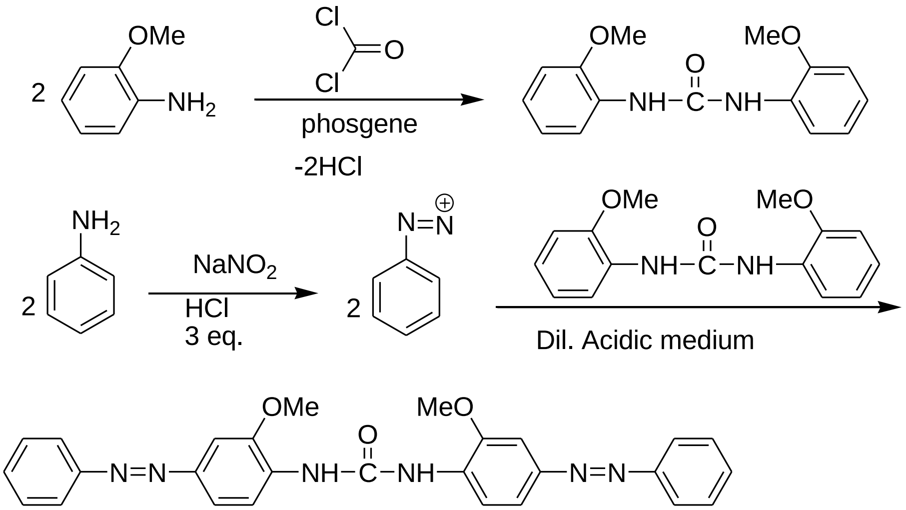
Type 4

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

E.g.



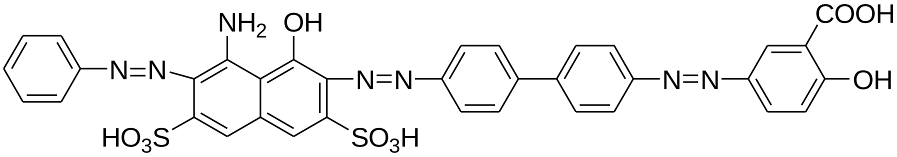
Synthesis



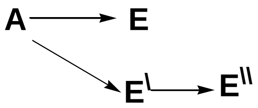
1. Triazodyes

$$\begin{tikzcd}
\mathbf{A} \arrow[r] \arrow[dr] & \mathbf{E} & \\
& \mathbf{E}^{\backslash} & \mathbf{A}^{\backslash} \arrow[l]
\end{tikzcd}$$

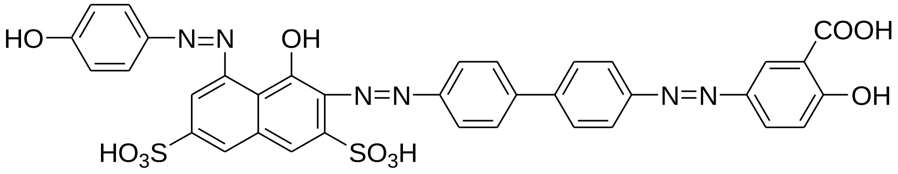
- **Like 3 but we introduce other coupling component on $E^{\backslash}$**



2.

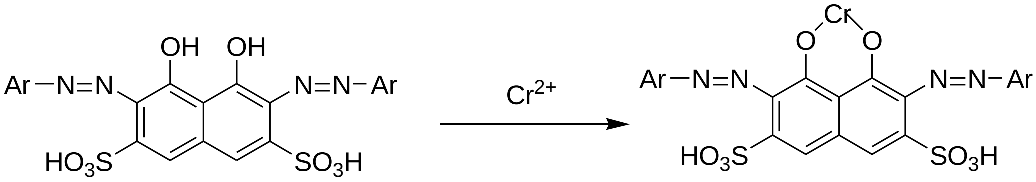


- **$E^{\backslash}$ must contain NH_2 which can be converted into diazonium salt can couple other coupling component**



<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.**



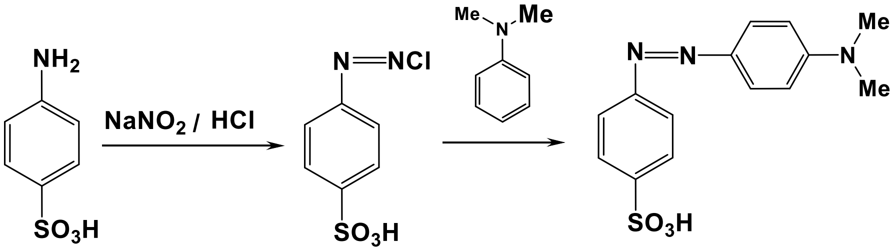
Some notes

- **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.

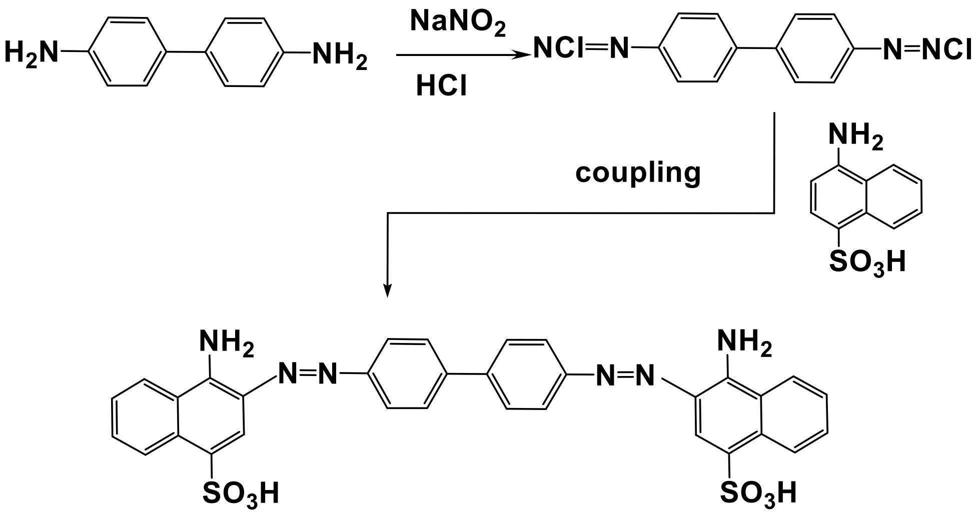
Used in dyeing wool and silk with orange color but it Can't fix on fibers so it is used only as indicator.



2-Congo red.

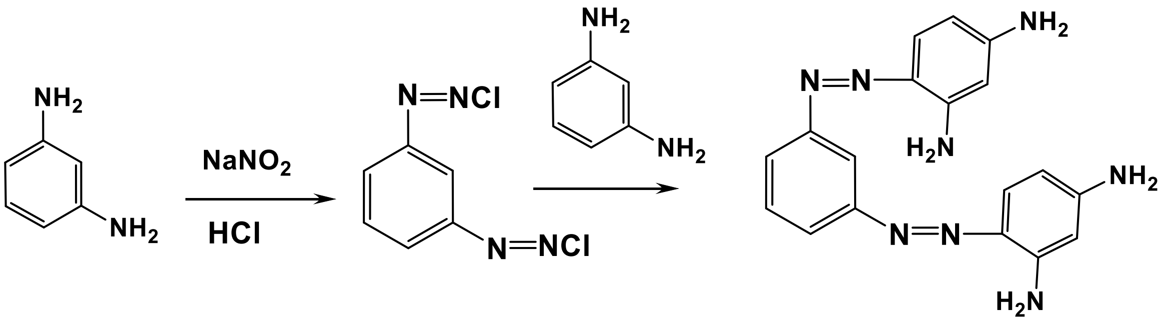
the sodium salt of 3,3′-([1,1′-biphenyl]-4,4′-diyl)bis(4-aminonaphthalene-1-sulfonic acid).in water yielding red colloidal solution. Used for dyeing cotton and as indicator (Due to a color change from blue to red at pH 3.0–5.2)

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.

$$\begin{array}{ccccc} \text{Leuco base} & \underset{\textbf{red.}}{\overset{\textbf{ox.}}{\rightleftharpoons}} & \text{Colour base} & \underset{\textbf{alkali}}{\overset{\textbf{acid}}{\rightleftharpoons}} & \text{Dye} \\ \textbf{colorless} & & \textbf{colorless} & & \textbf{colored} \end{array}$$

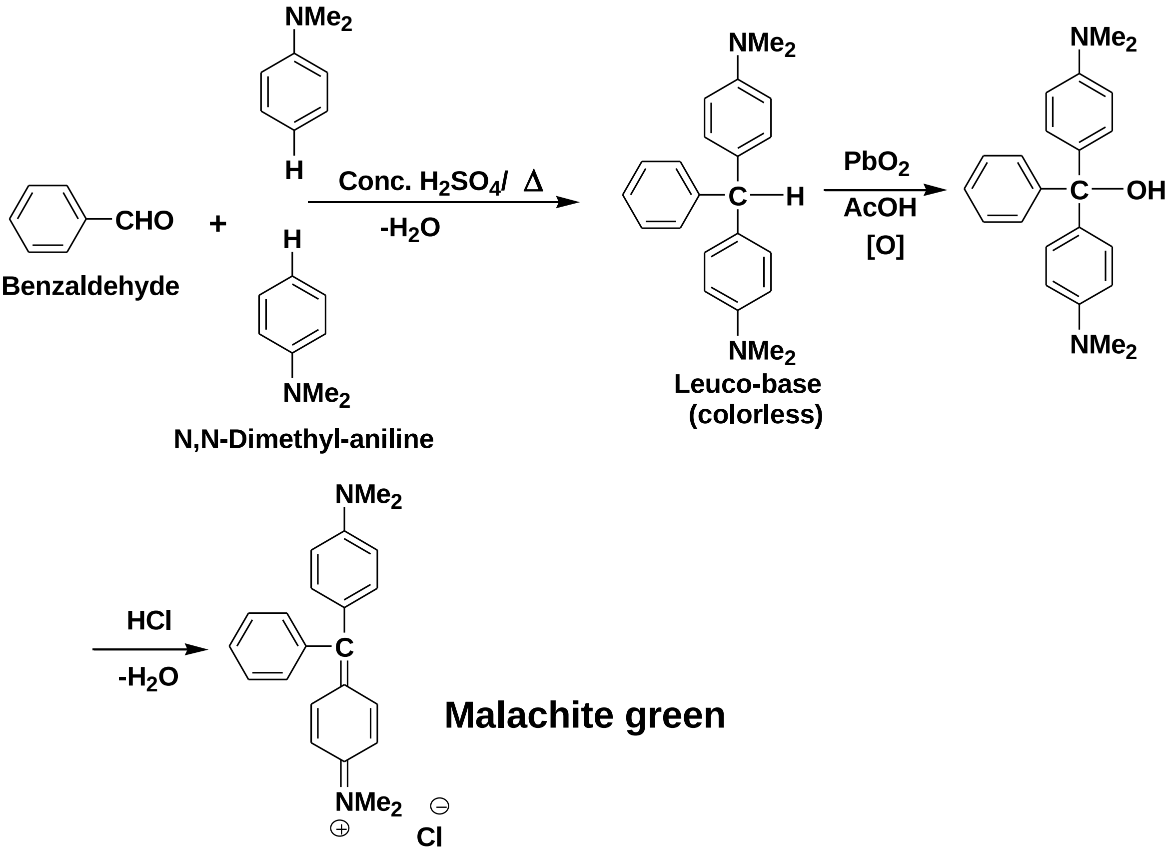
- Triphenyl methane dyes are classified into:

1- Base Dyes or cationic dyes.

2- Acid Dyes or anionic dyes.

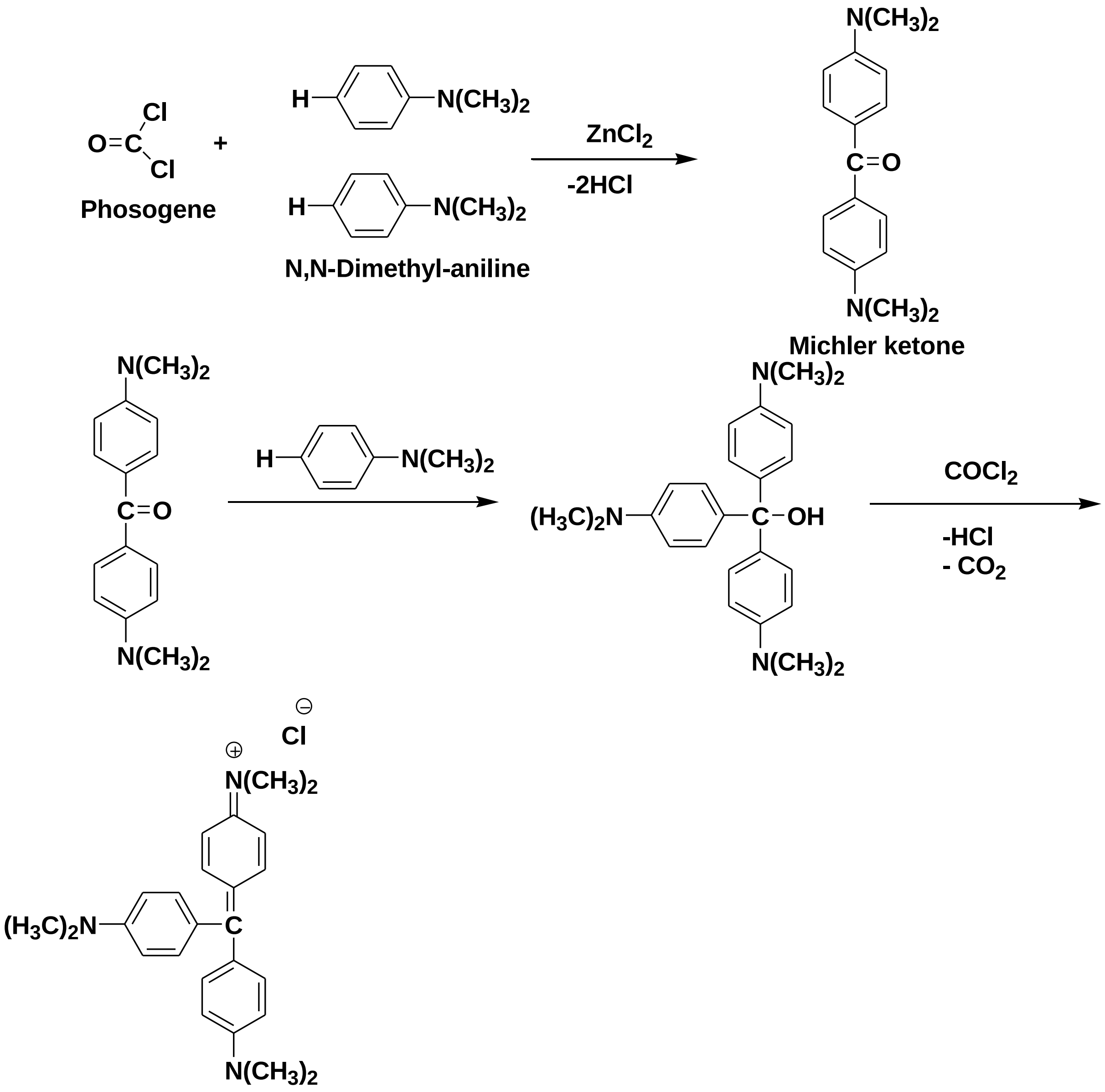
<u>1) Base Dyes or cationic dyes</u>

A) Malachite green



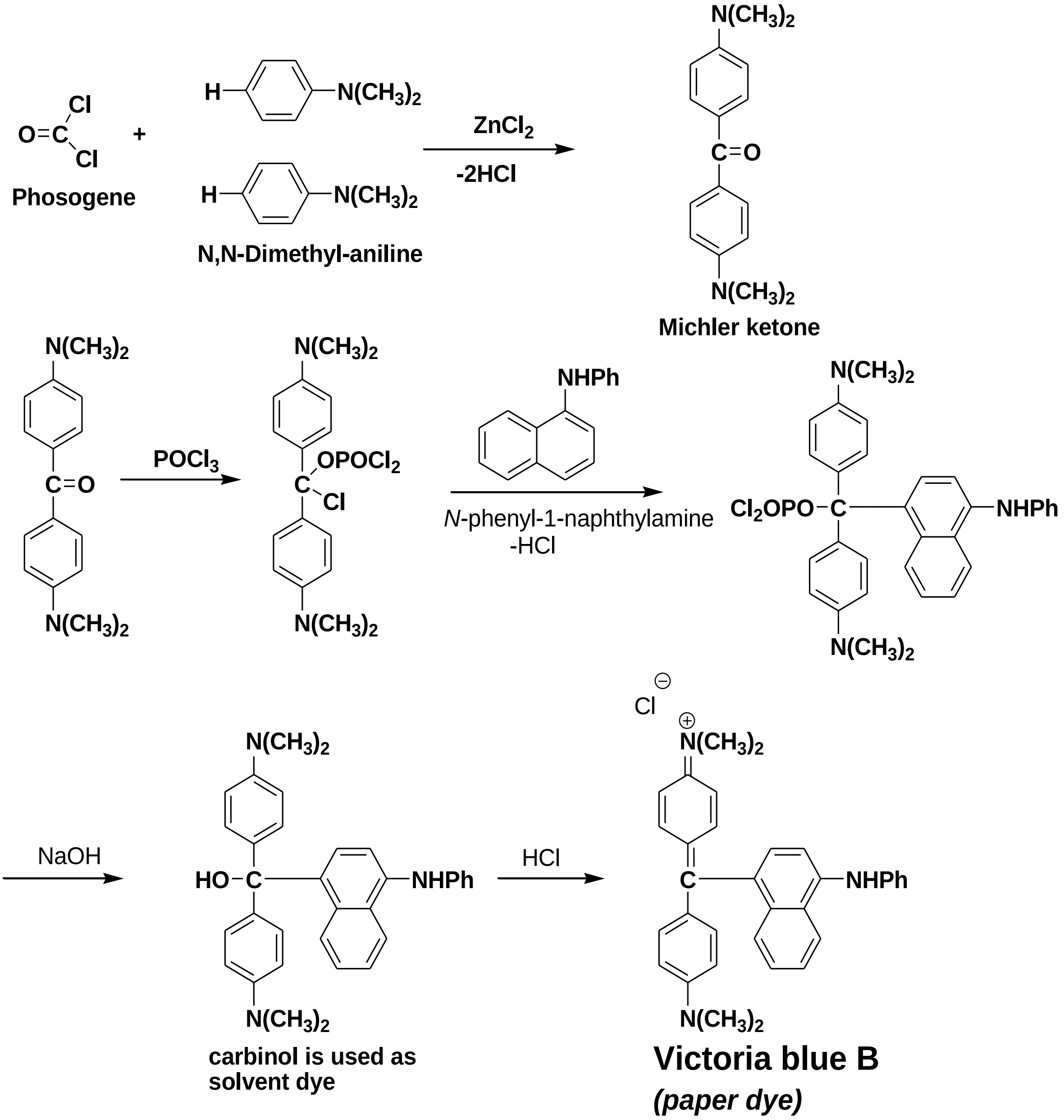
- ***Malachite green is used for dying cotton and polyacrylonitrile***

B) Crystal violet

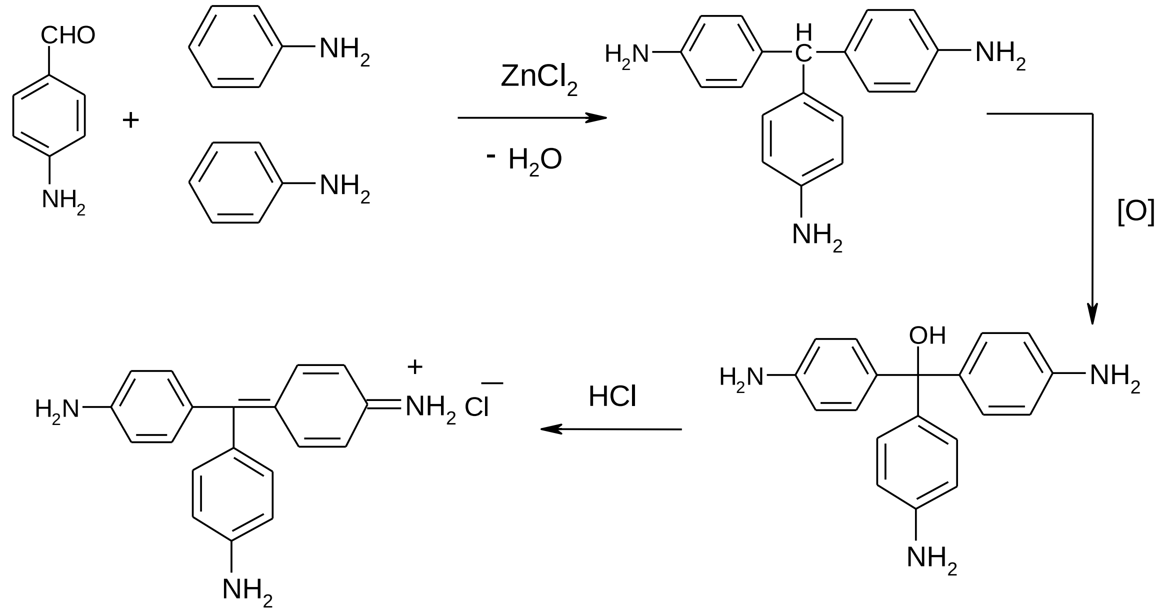


Crystal violet

C) Victoria blue B (paper dye)

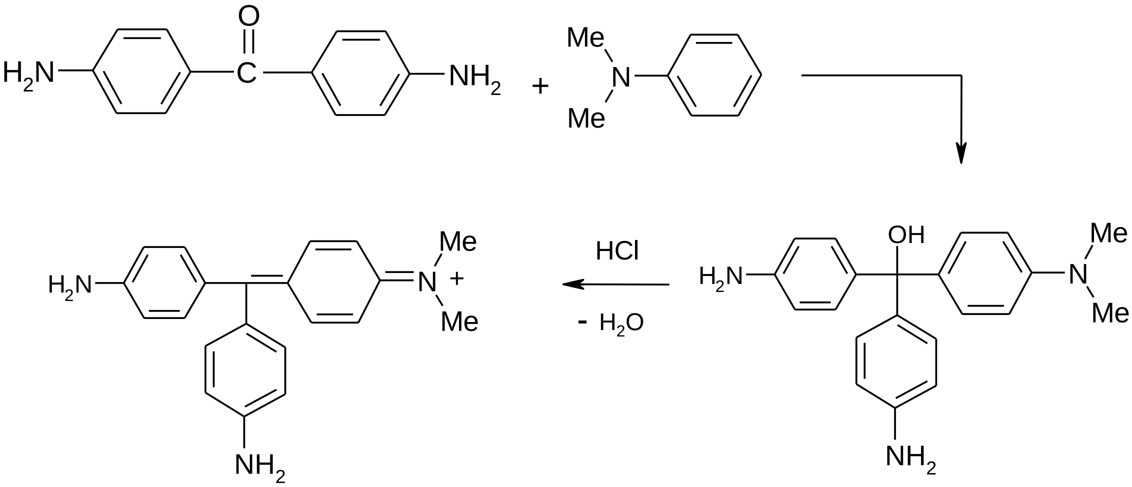


D)-Para rose aniline dye



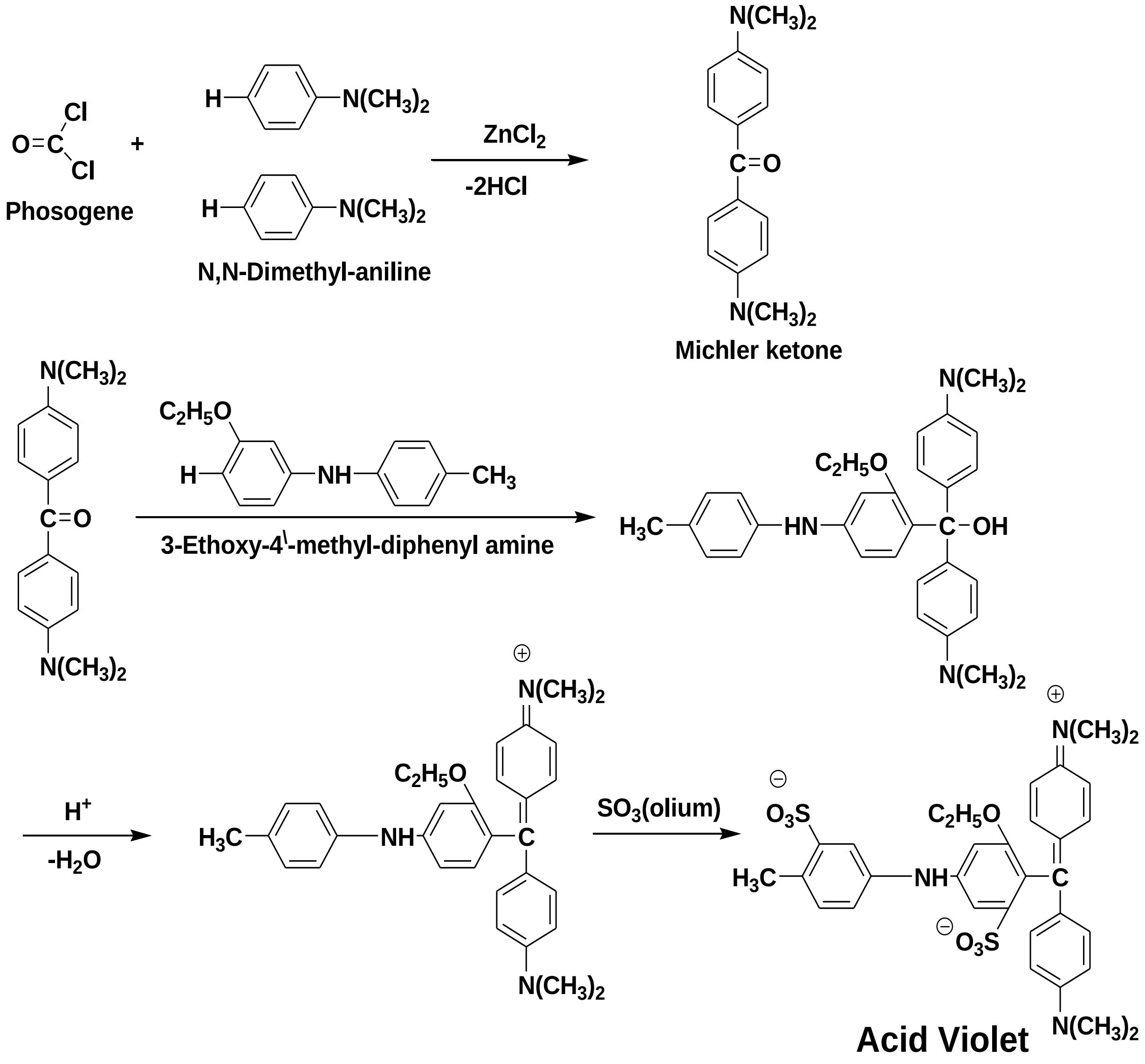
E) Gention violet dye

Used as antiseptic

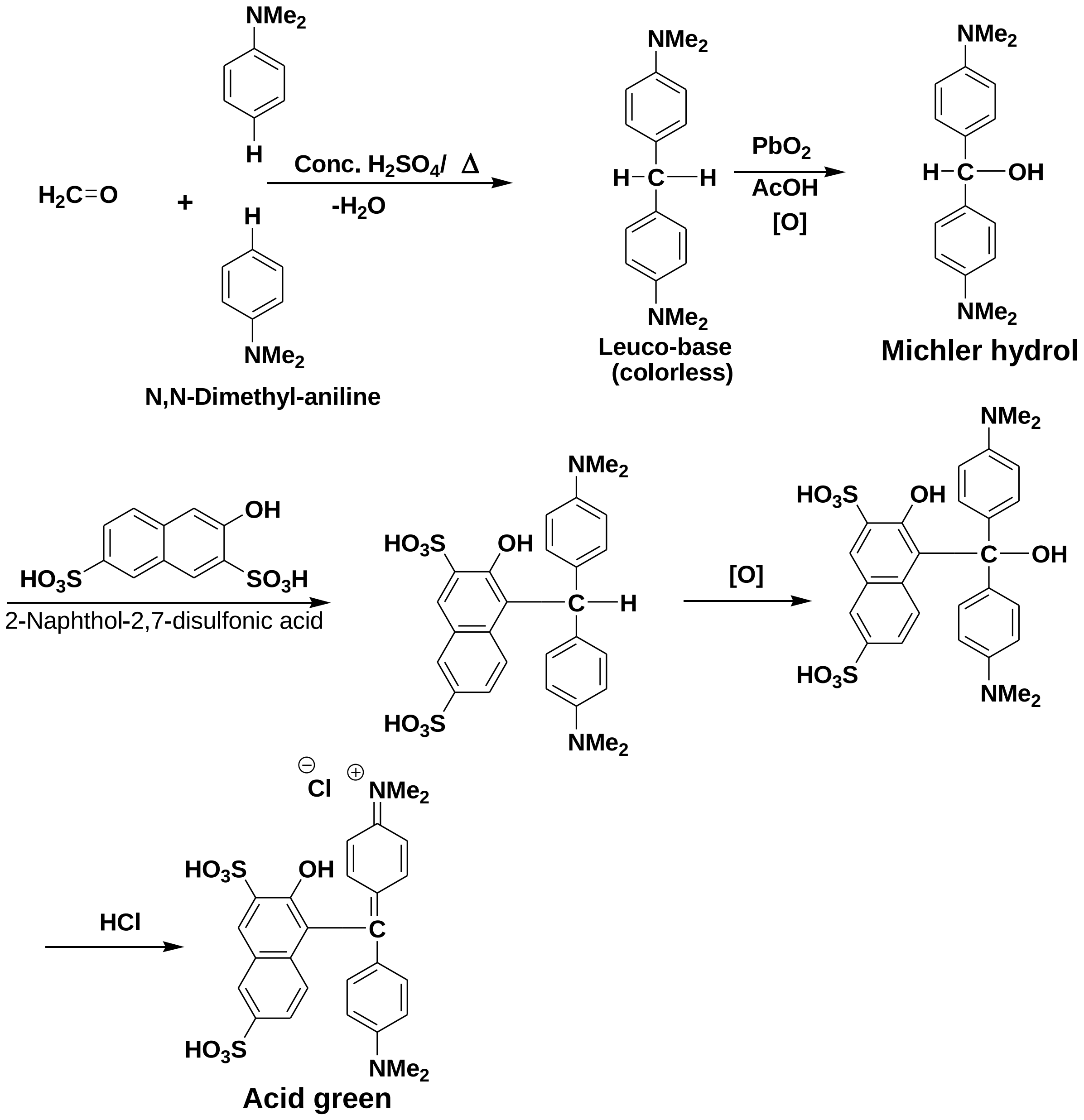


Acid dyes

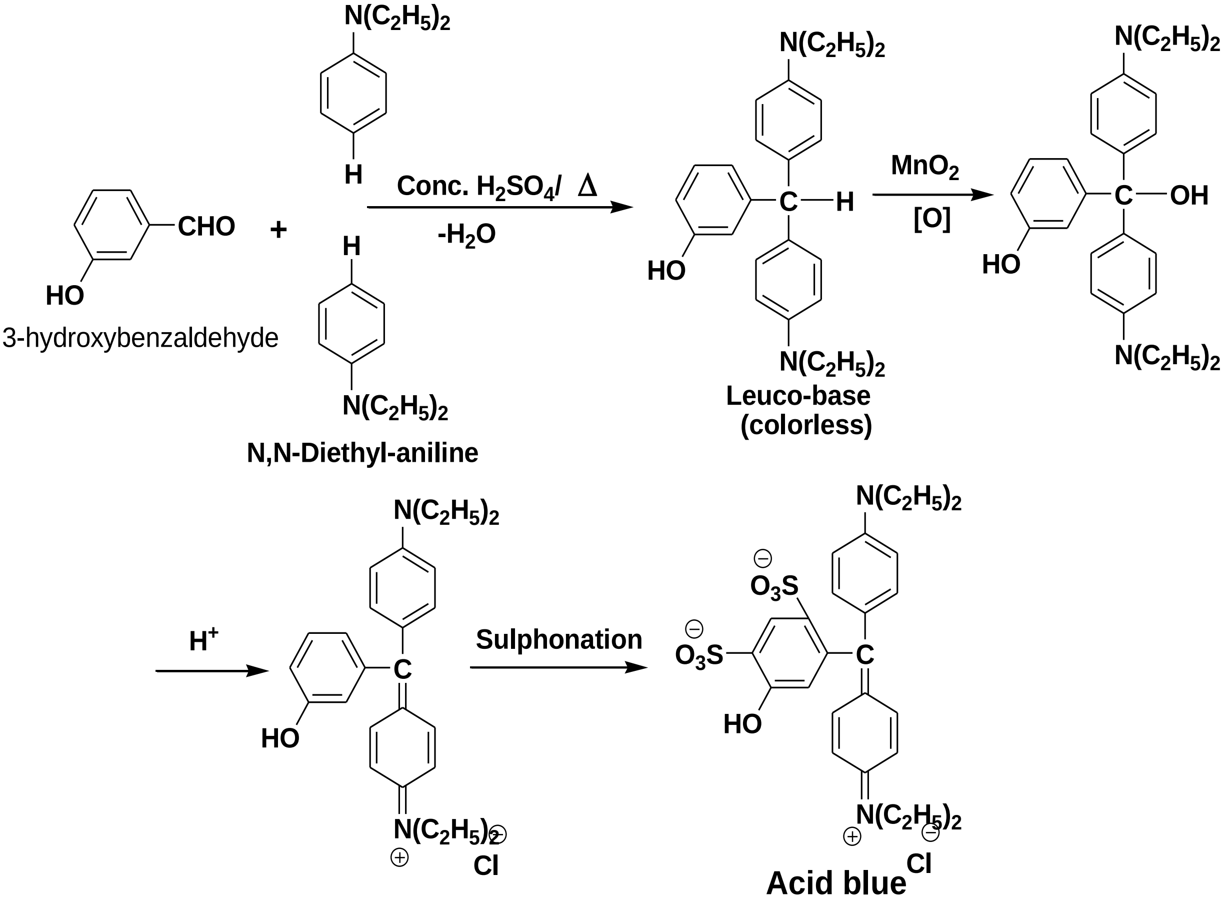
1) Acid violet :- used for **staining fingerprints and shoeprints .**



2) Acid green (wool green):

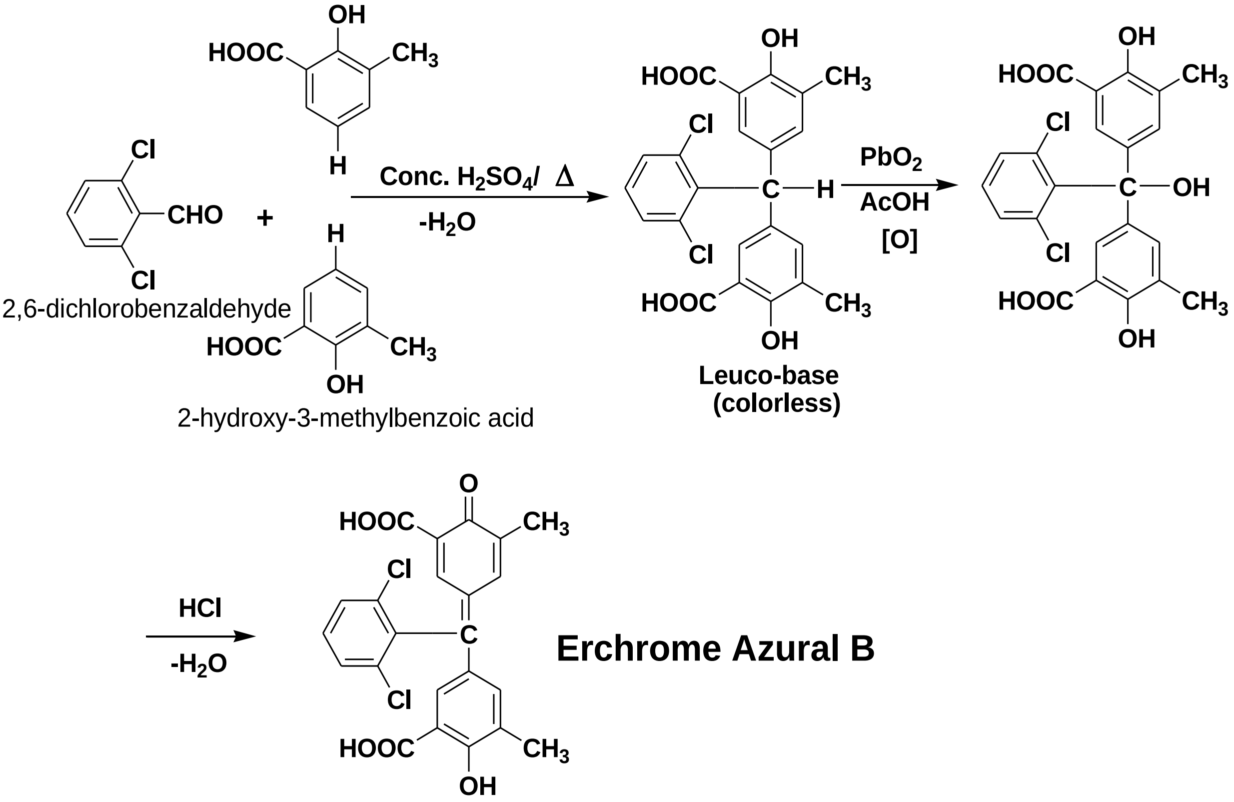


2) **Acid blue (patent blue):** patent blue is used for marking lymphatic vessels and arterial territories as well as for sentinel lymph node prior to biopsy in patients with operable breast cancer. Patent blue is also used in the textile, paper, agriculture and cosmetic industry

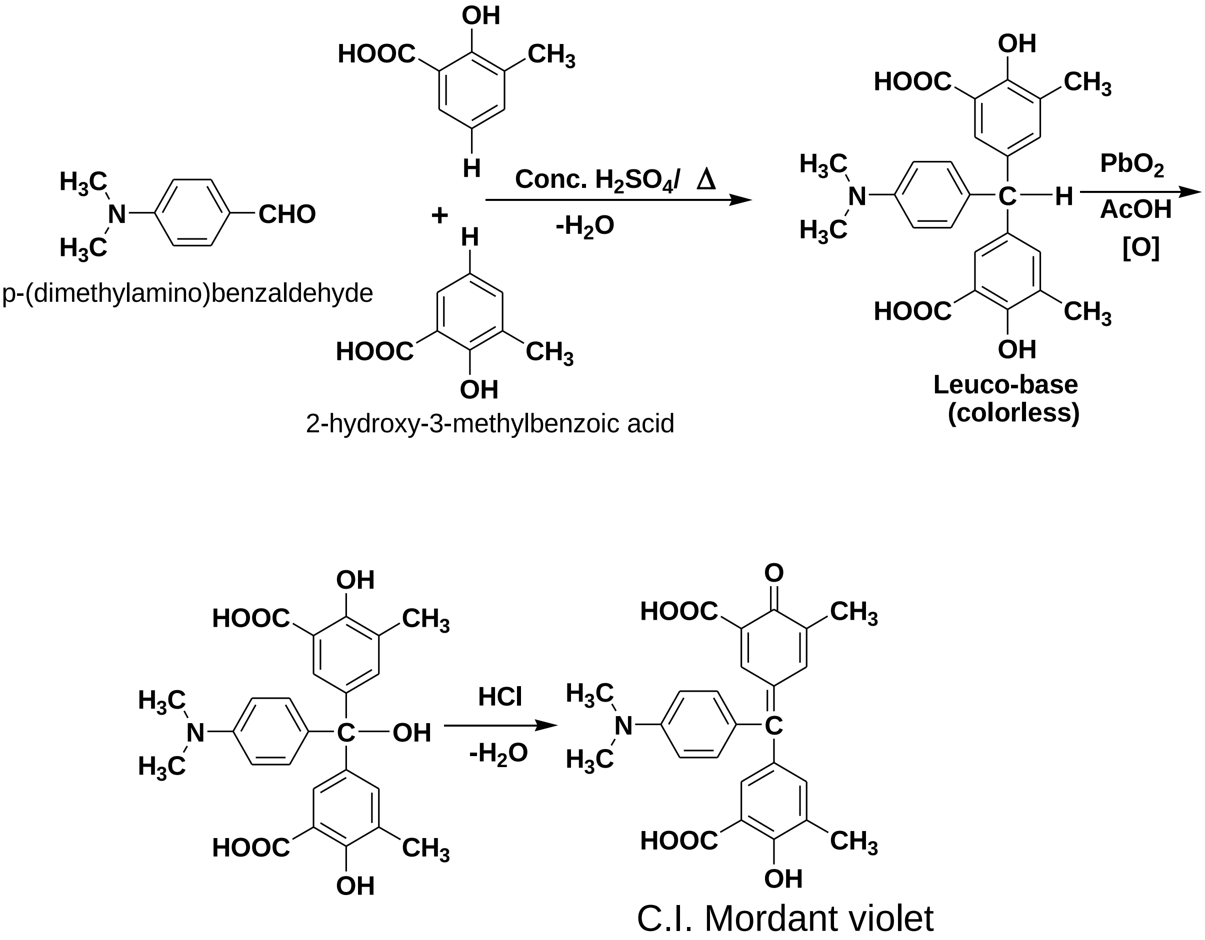


Hydroxy triaryl methane dye

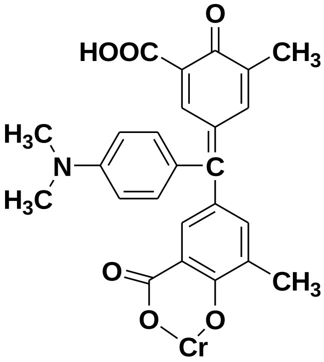
1-Erichrome azurol B:



2-C.I Mordant violet Dye



- **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:

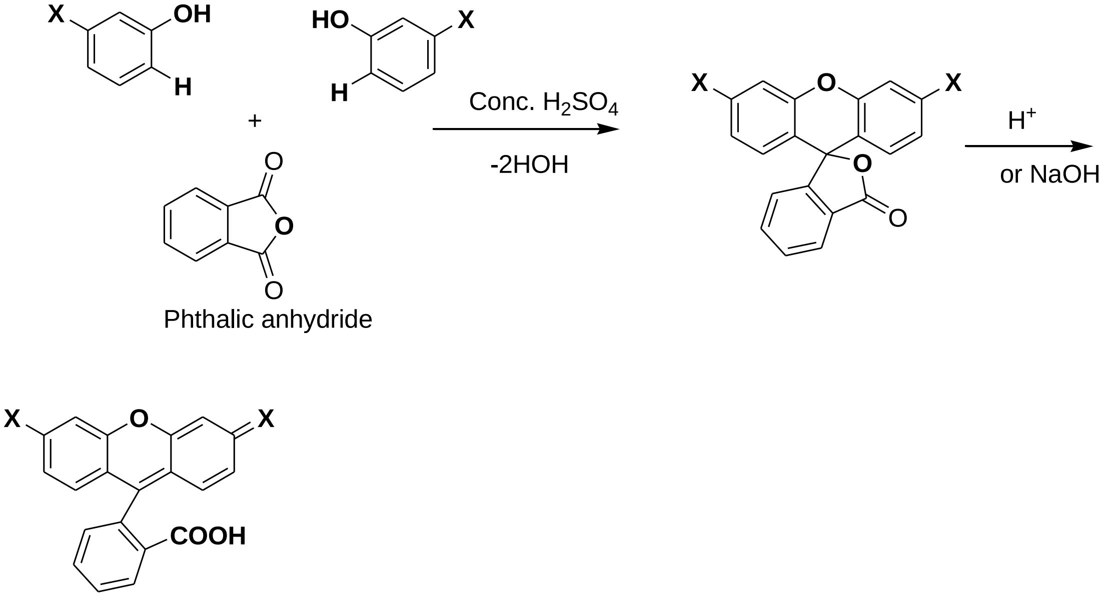
X = auxochromes (NH_2, NHR, NR_2, OH).

X must be in para-position to CR_2

- The color is due to formation of quinoid structure.

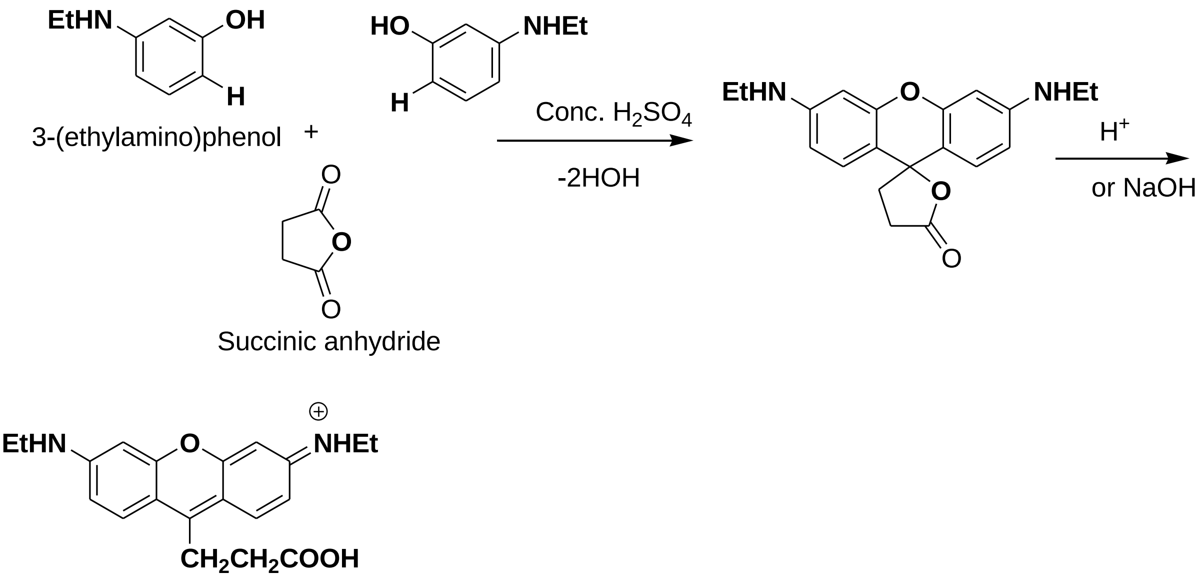
Xanthene dyes

General procedures



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

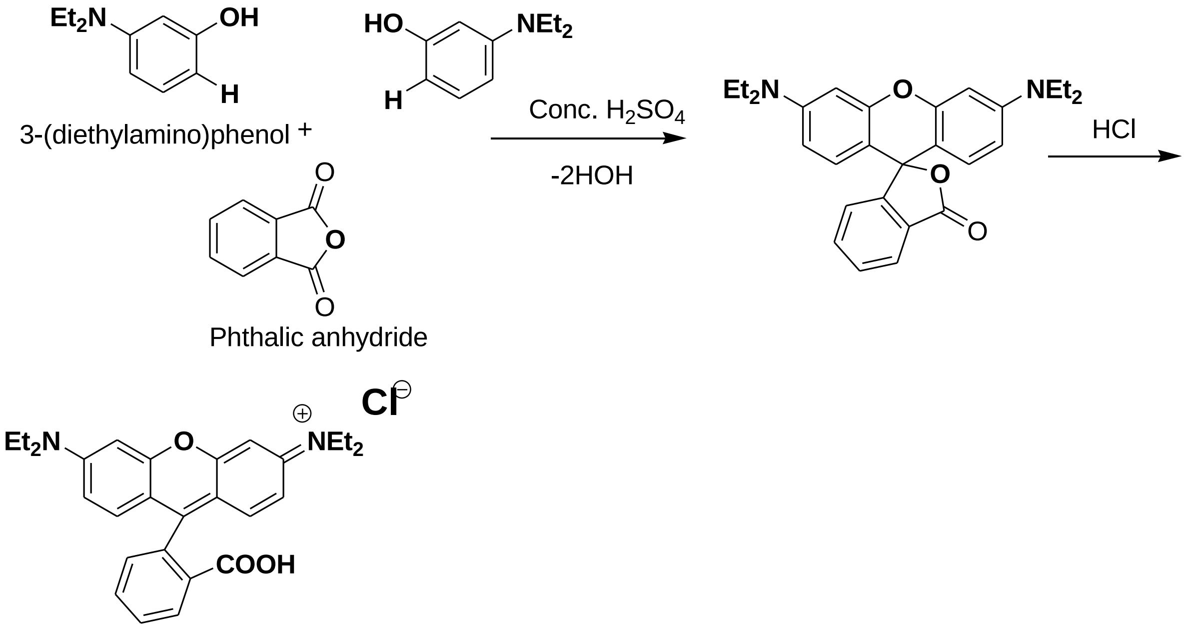
1- C.I. Basic red



C. I. Basic red

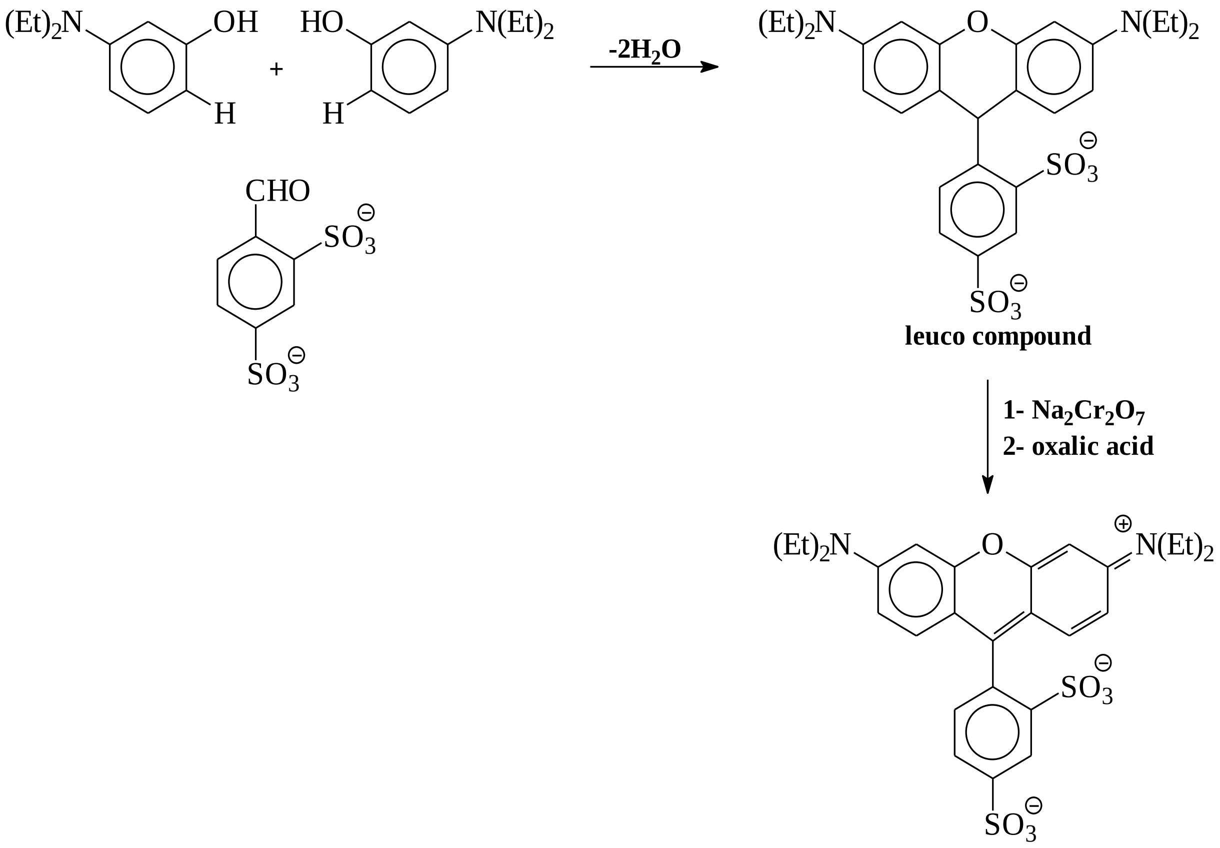
3) Rhodamine B

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.

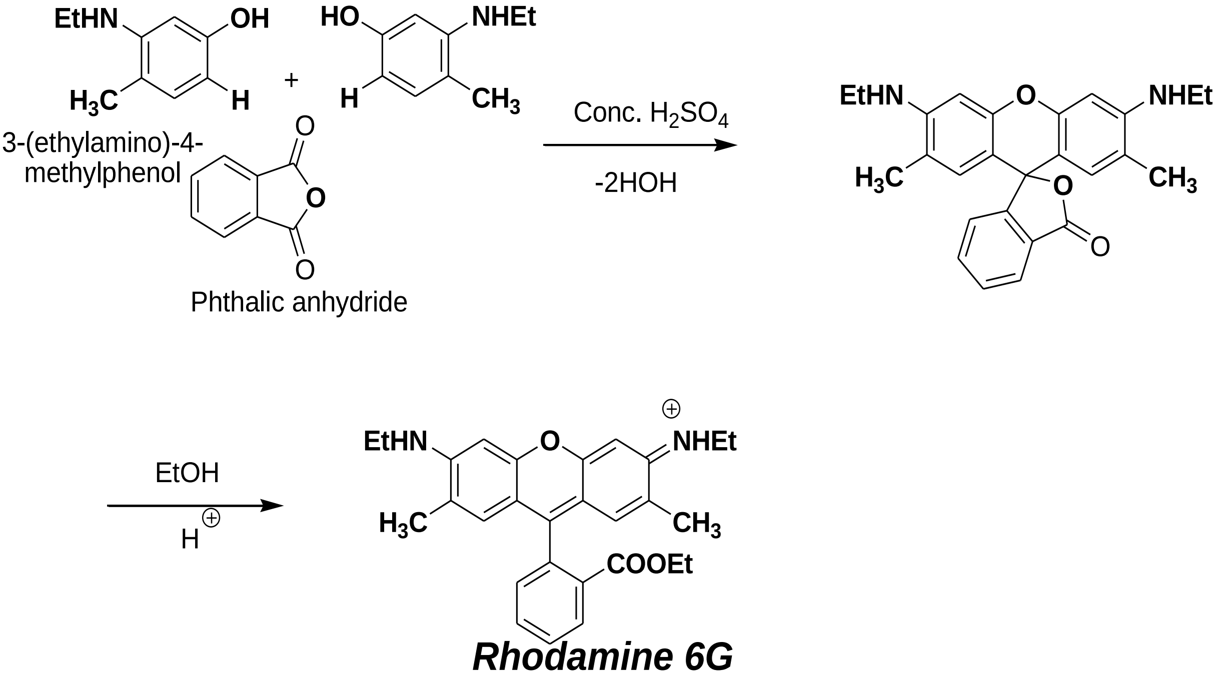


Rhodamine B

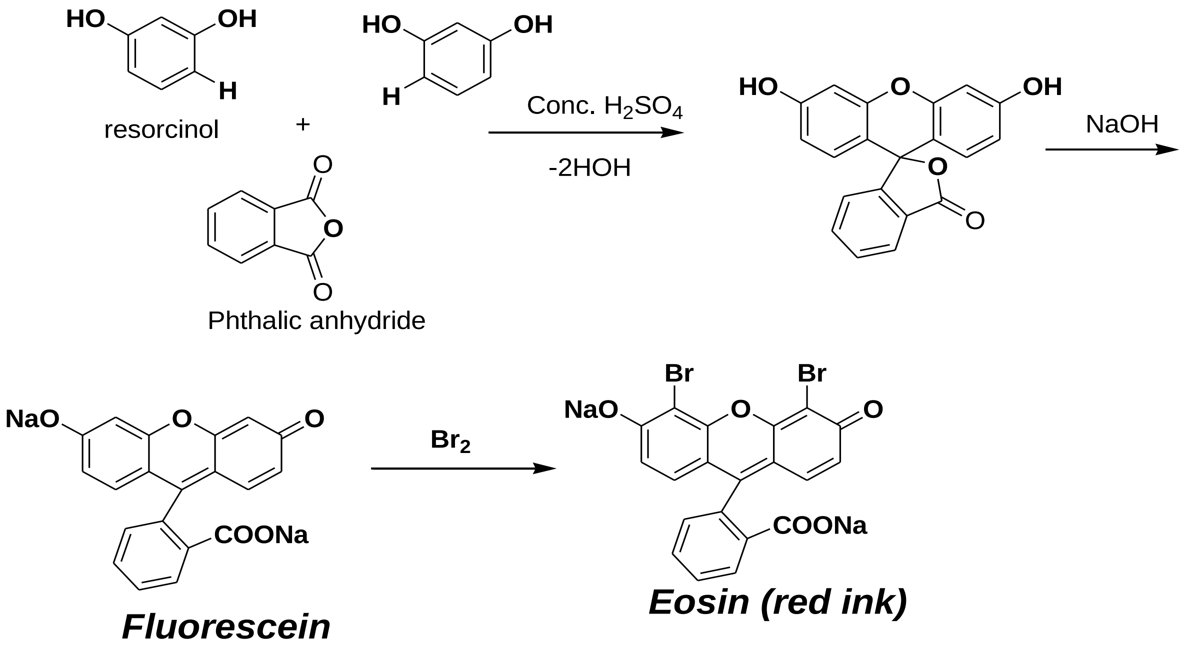
3) Sulphorhodamine (Rosamine dye)



4) Rhodamine 6G



5) Fluorescein dye and its derivative (Eosin)



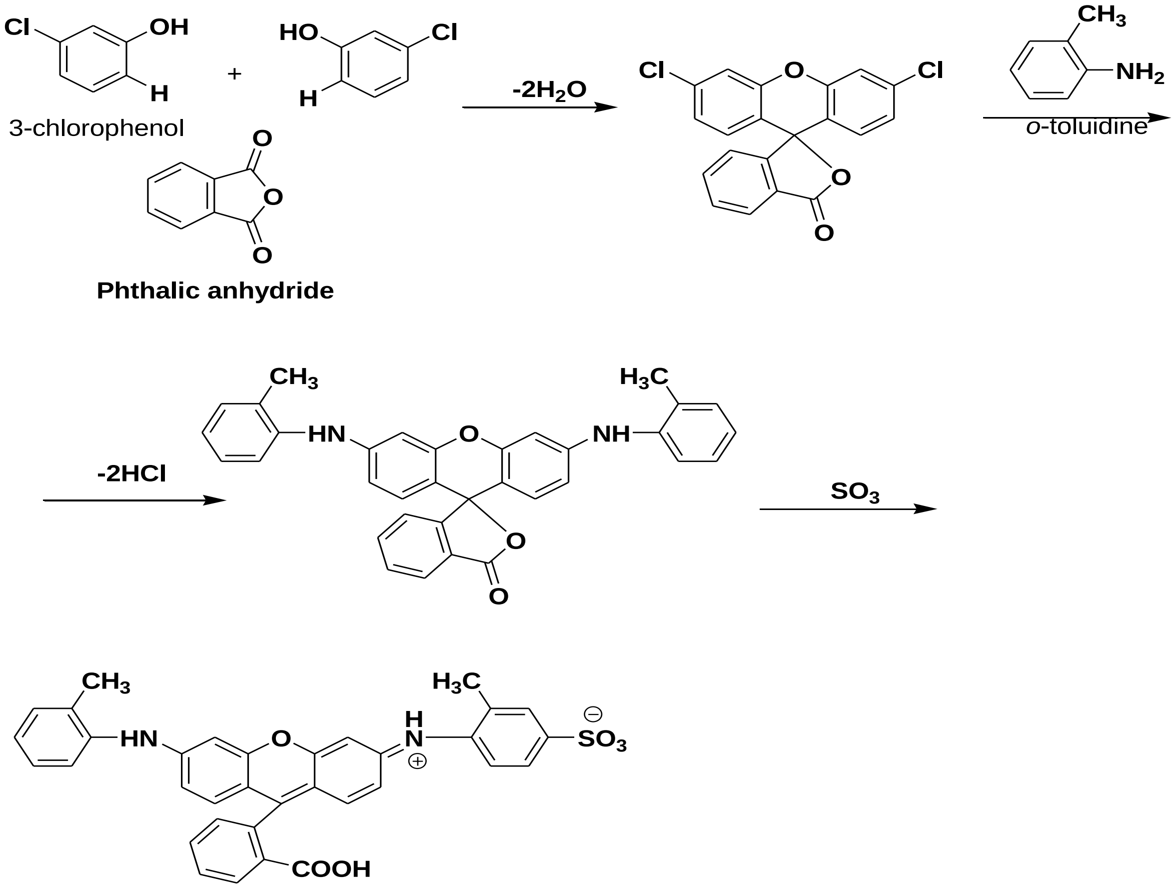
<u>3-Kiton fuchine A_2R:</u>

It is wool dye.

It is reddish violet dye with good fastness.

It can be used for paper coloration.

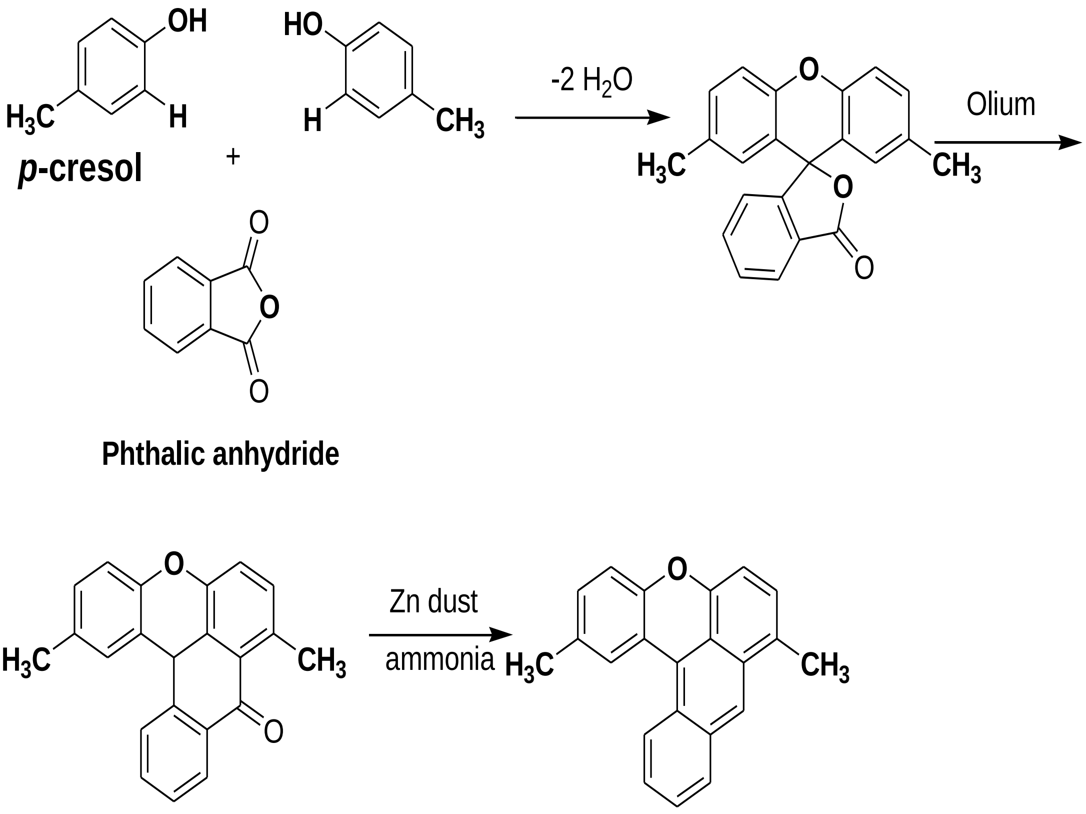
It can be prepared as follow.



Kiton Fuchine

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

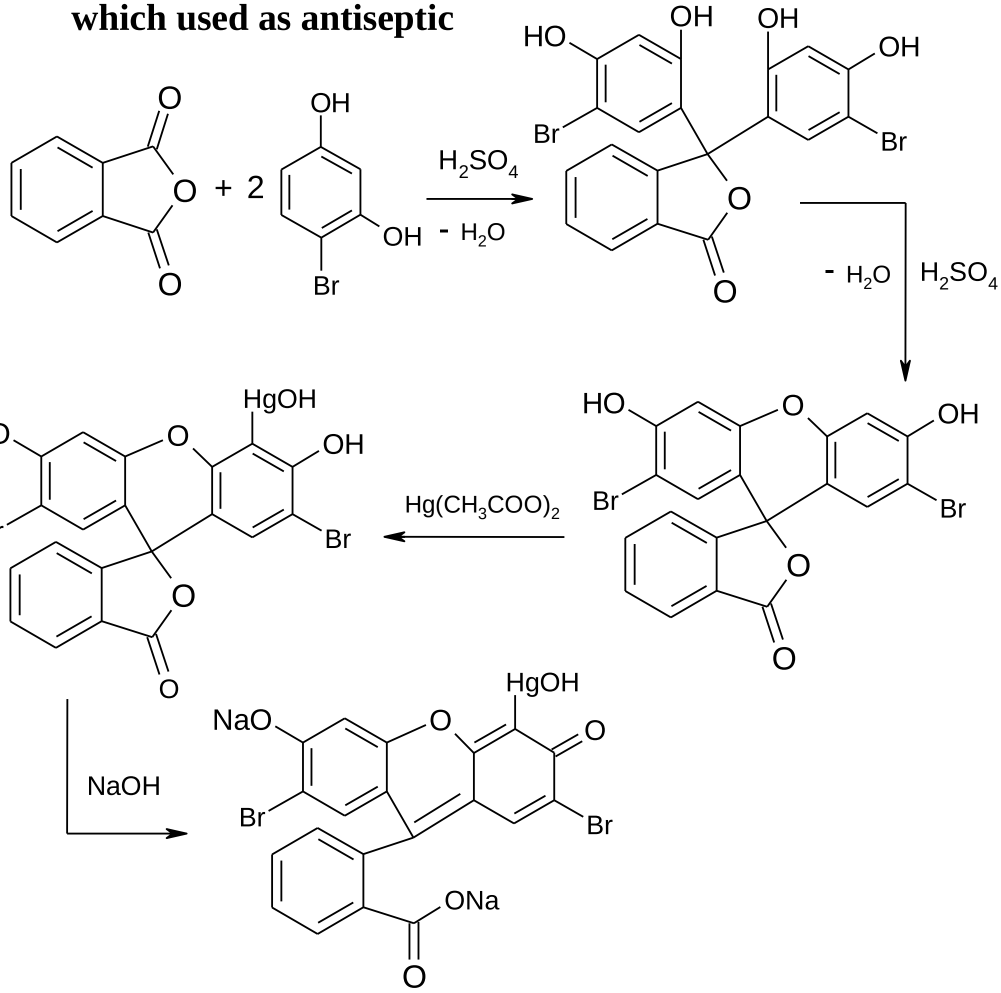
Fluorol Yellow 088 is a polyaromatic organic dye used to stain cells of suberin lamellae in plant tissue



Fluorol 5G
Coloring mineral oil)

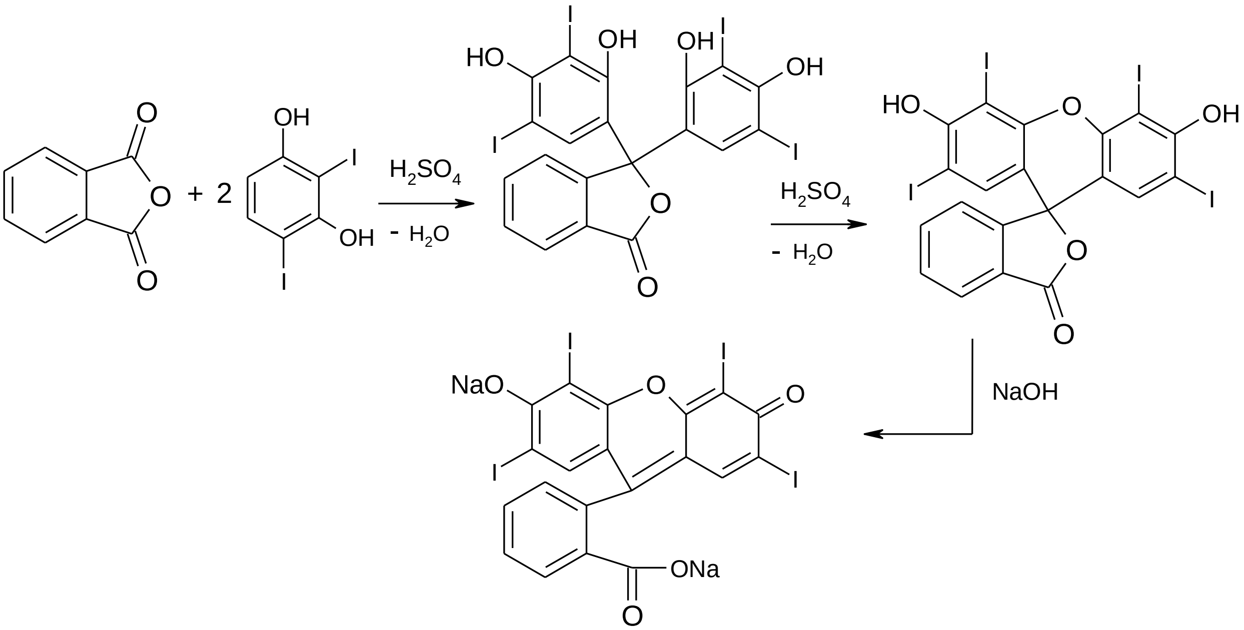
5- Merchrochrom dyes:

which used as antiseptic



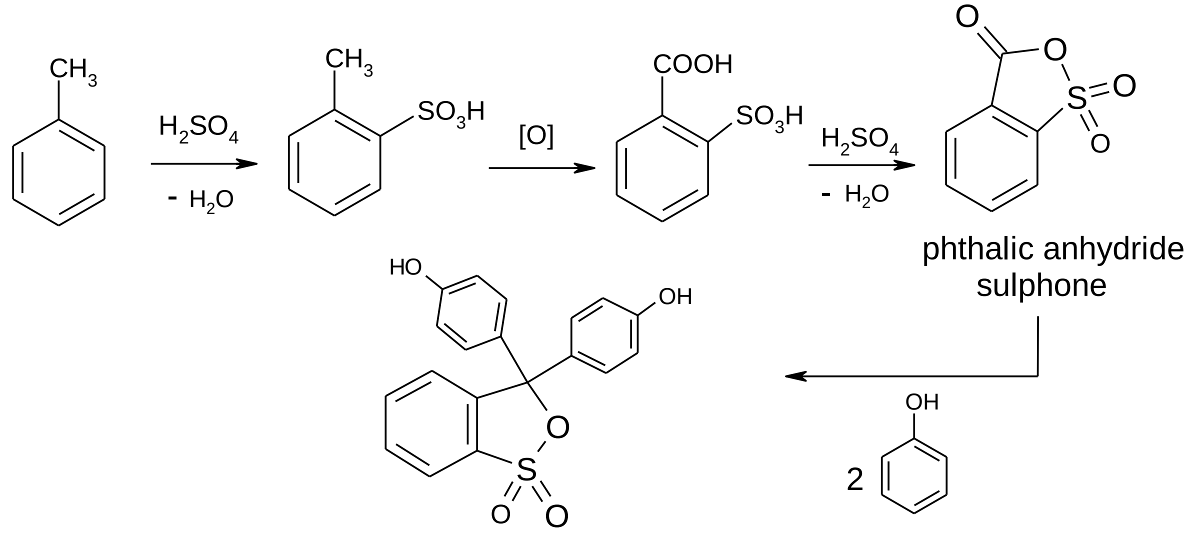
6- Erthorocine:-

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



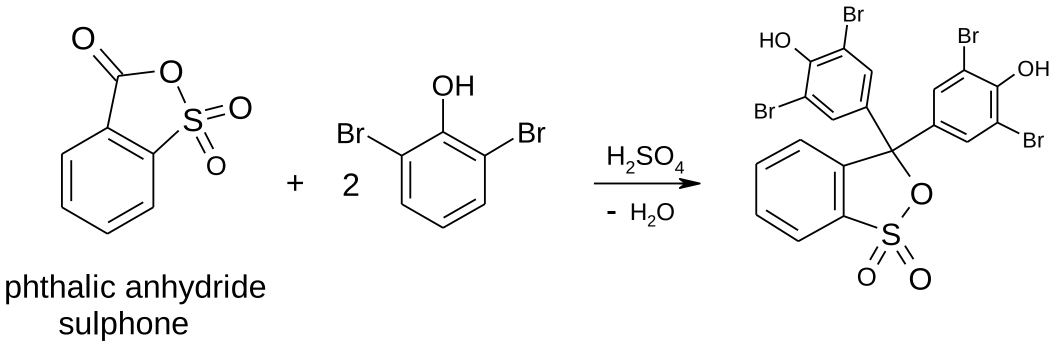
phthaleine sulphone dyes (phenol red)

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



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.**

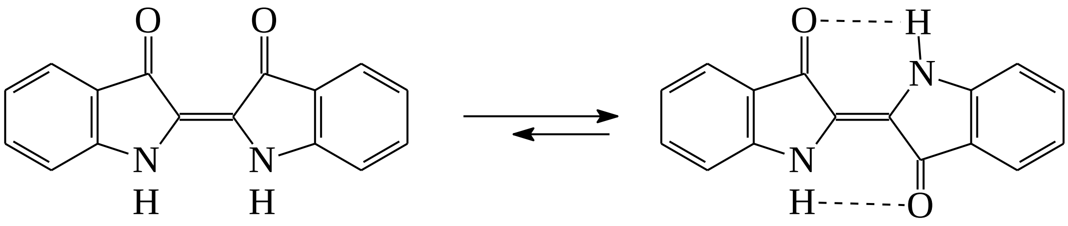
$$\text{Vat dye (insol. dye)} \xrightarrow{\textbf{Reduction}} \text{Leuco compound (soulble colorless)}$$

$$\downarrow \textbf{[O]}$$

$$\text{Colored insoluble dye}$$

Structure of indigotin:

Indigotin can exist in both cis and trans form.

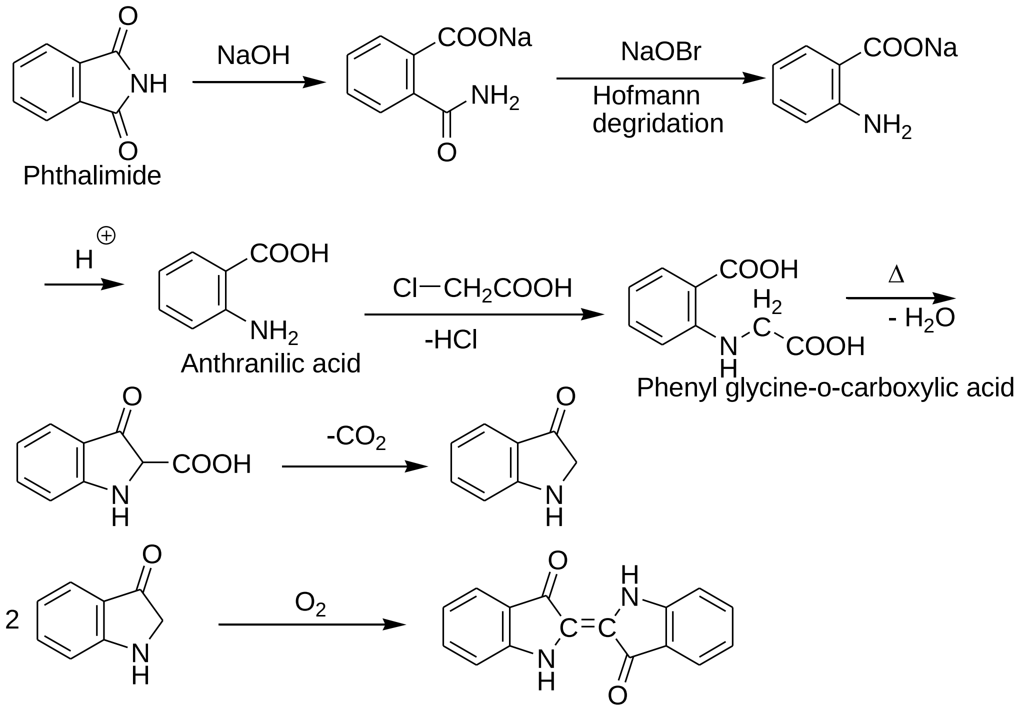


cis form
less stable

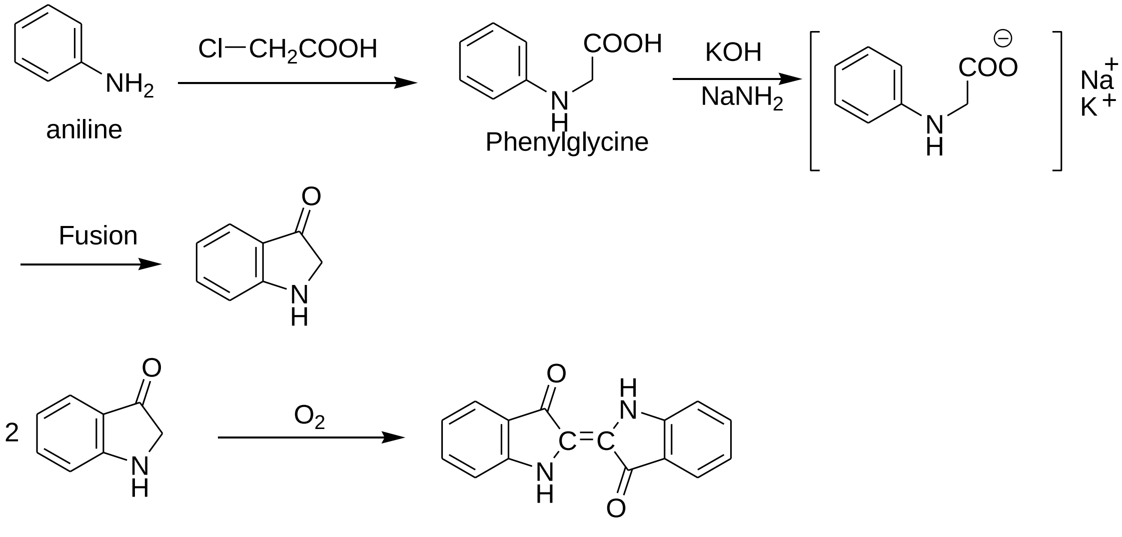
trans form
more stable due to formation of H.b.

Synthesis of Indigo

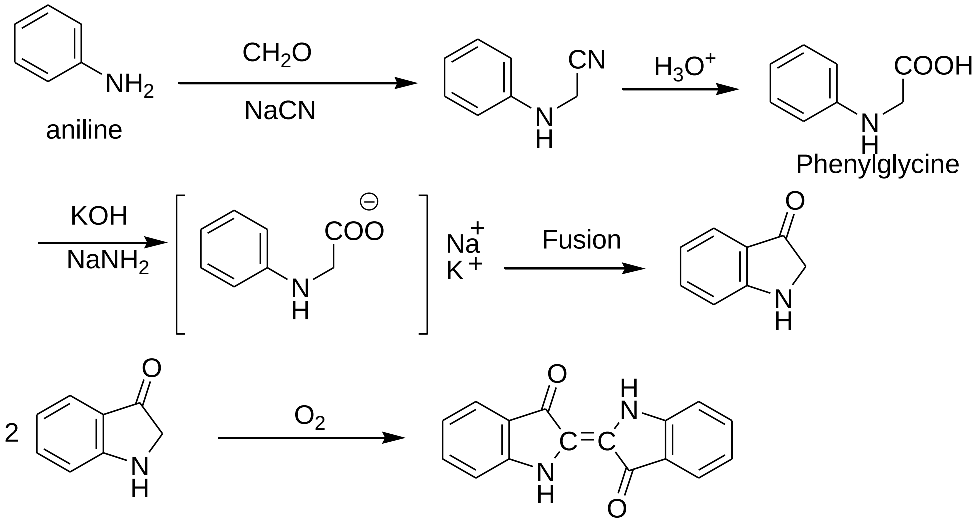
1. **Heumann process**



2. Sodamide process

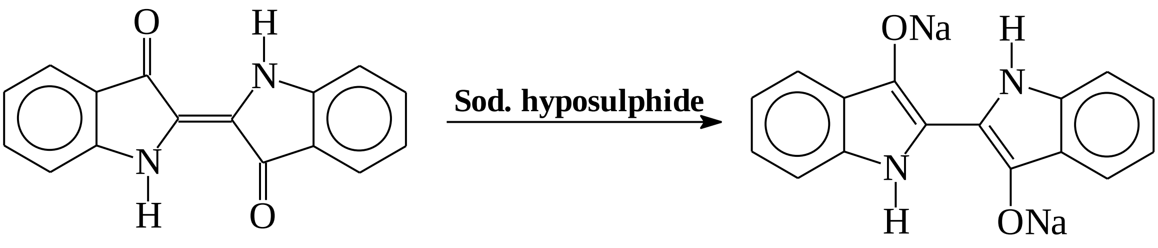


3. From aniline and sodium cyanide



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).



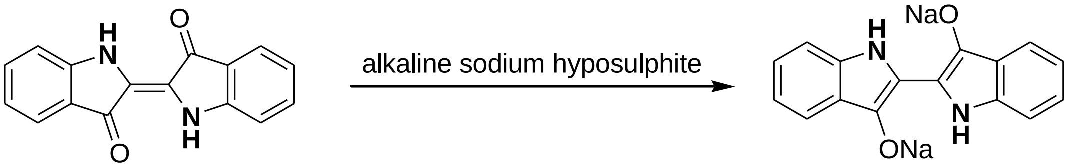
indigotin blue oxidized form water insol.

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

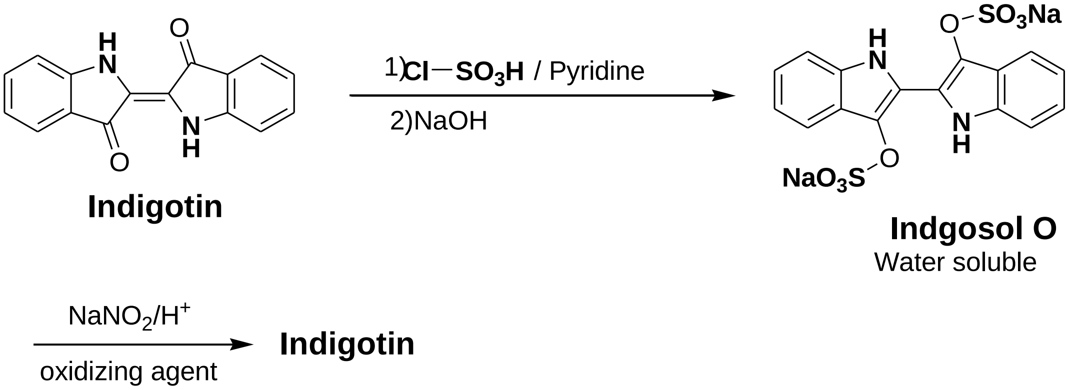


Indigotin
dark blue
water insoluble

White Indigotin
colorless
water soluble

2) Indigosol O

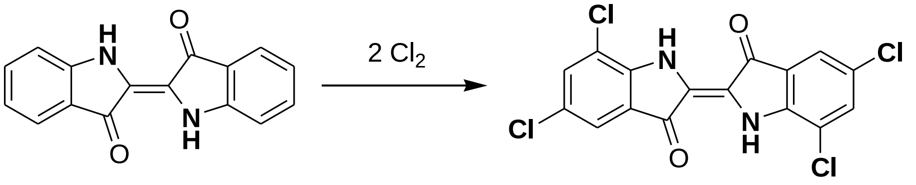
- **It is used for dying wool**



Application of Indigosol on fibres

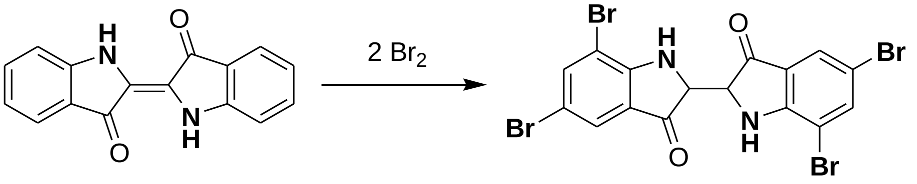
Indigosol O is applied on both animal and vegetable fibres by soakin the fabic in the solution, and then oxidizing the indigosol O in acid solution (with $NaNO_2$) to the original insoluble vat dye.

3) Brilliant indigo B and Brilliant indigo 2B



Indigotin

Brilliant Indigo B



Indigotin

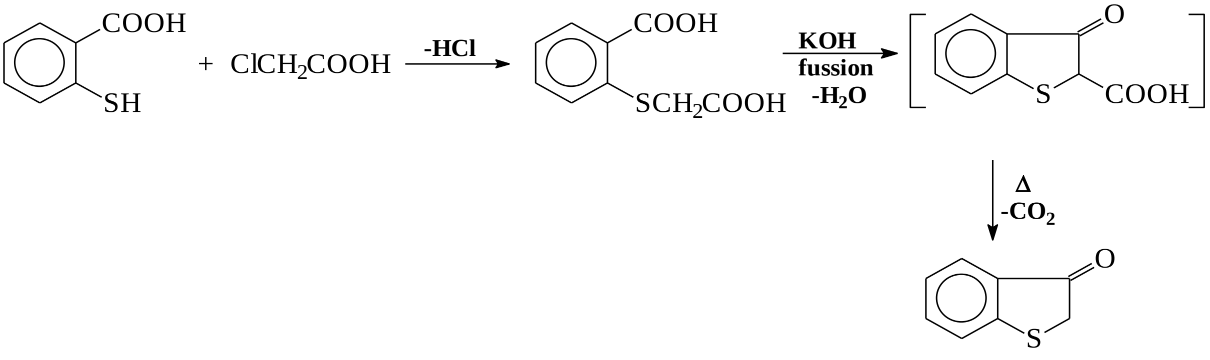
Brilliant Indigo 2B

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

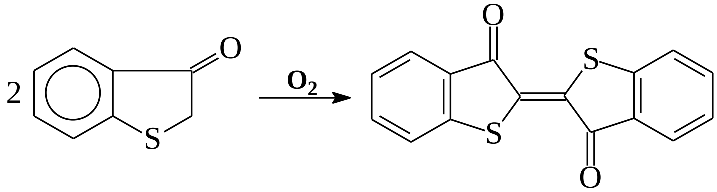
Preparation of thio-indigo:

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

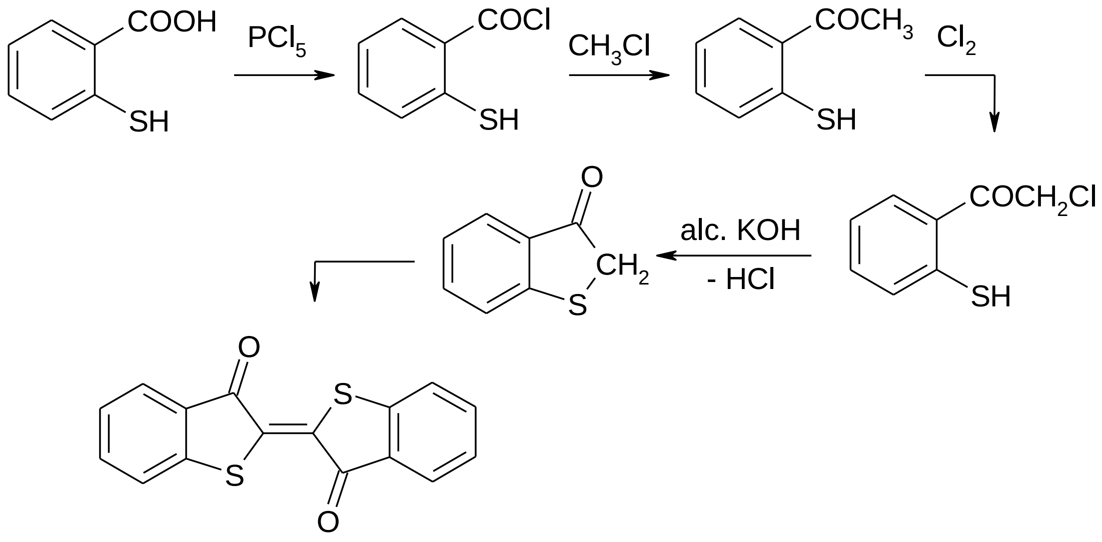


thioindoxyl

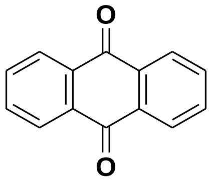


Thioindig red

Second method

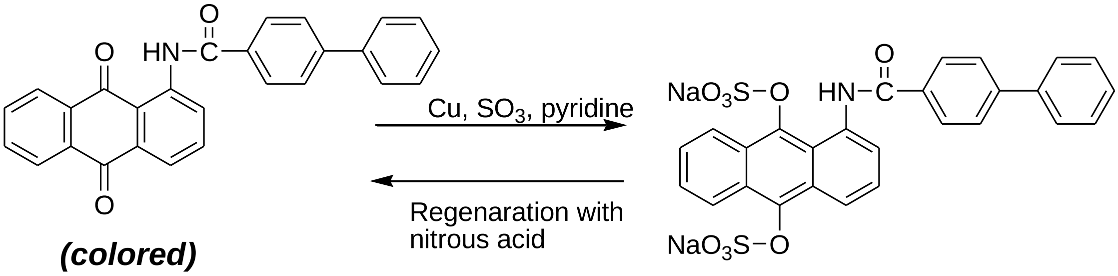


Anthraquinone dyes:



Anthraquinone

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

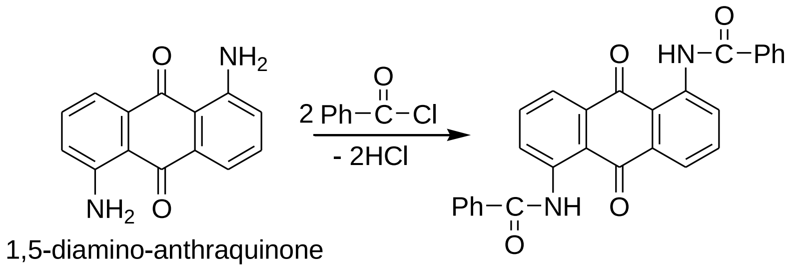


(colored)

Leuco form (colorless)

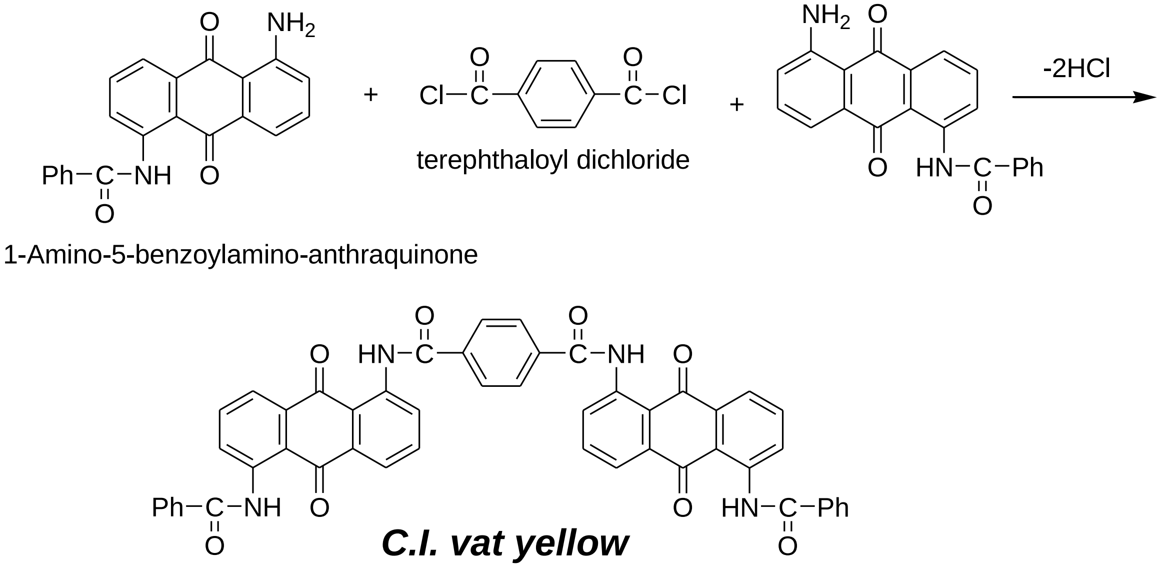
1) Indanthrone dyes:

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



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

Synthesis of C.I vat yellow (Caledon yellow)

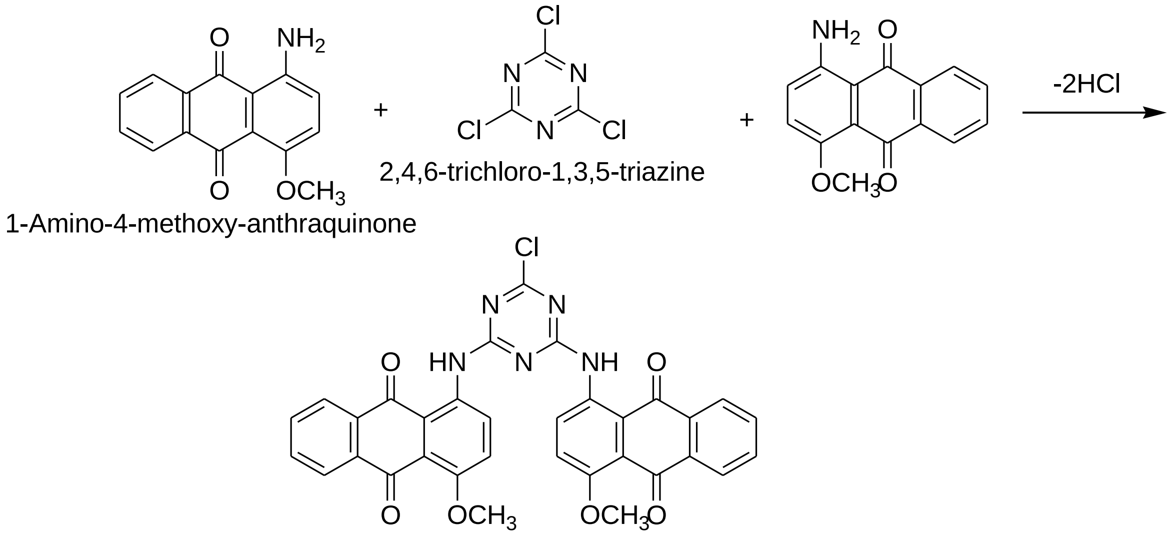


C.I. vat yellow (Caledon yellow)

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

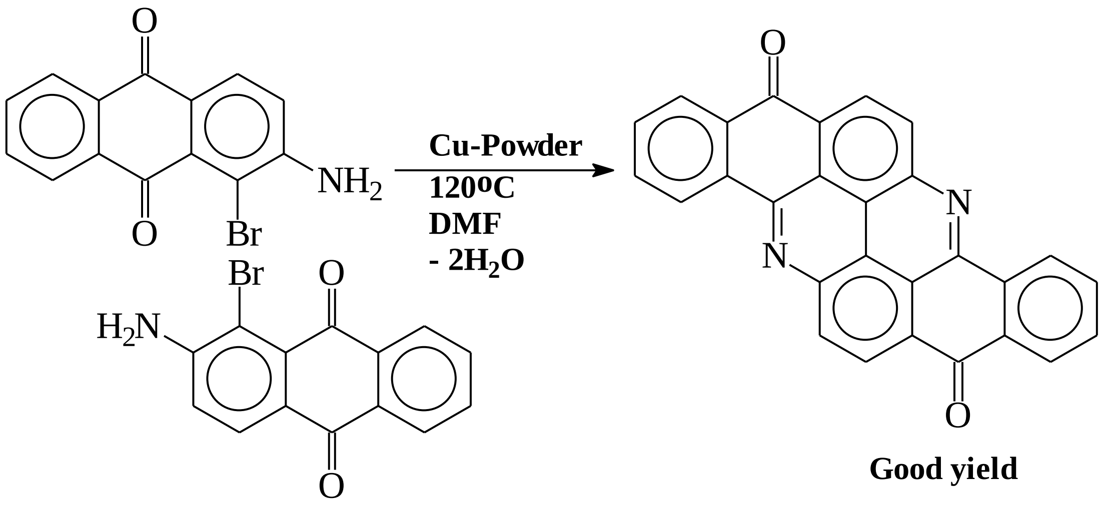
- **Cibanone Orange 6R is an example of reactive dye which is used for dying cellulosic fibres**

- **It is type of reactive dye**



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

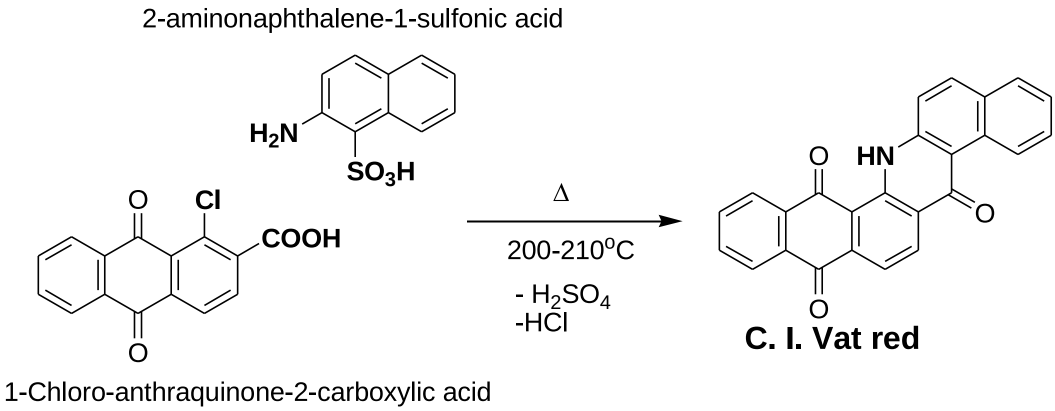
C) Flavanthrone (Indanthrone yellow G):



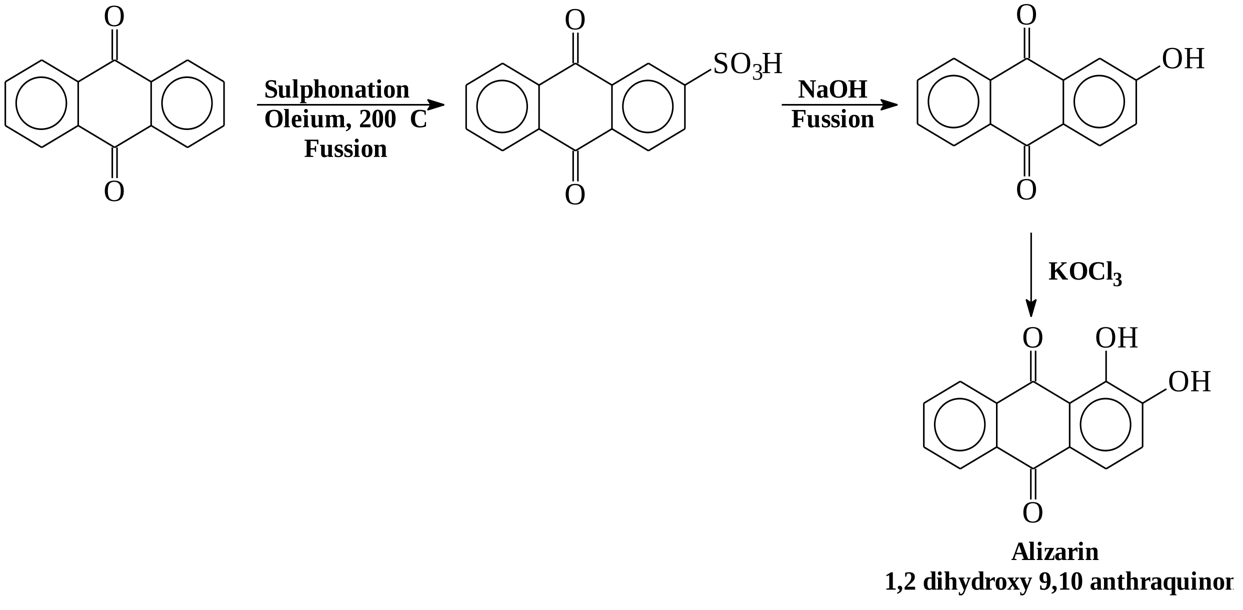
Good yield

Anthraquinonacridine

Synthesis of C.I Vat red



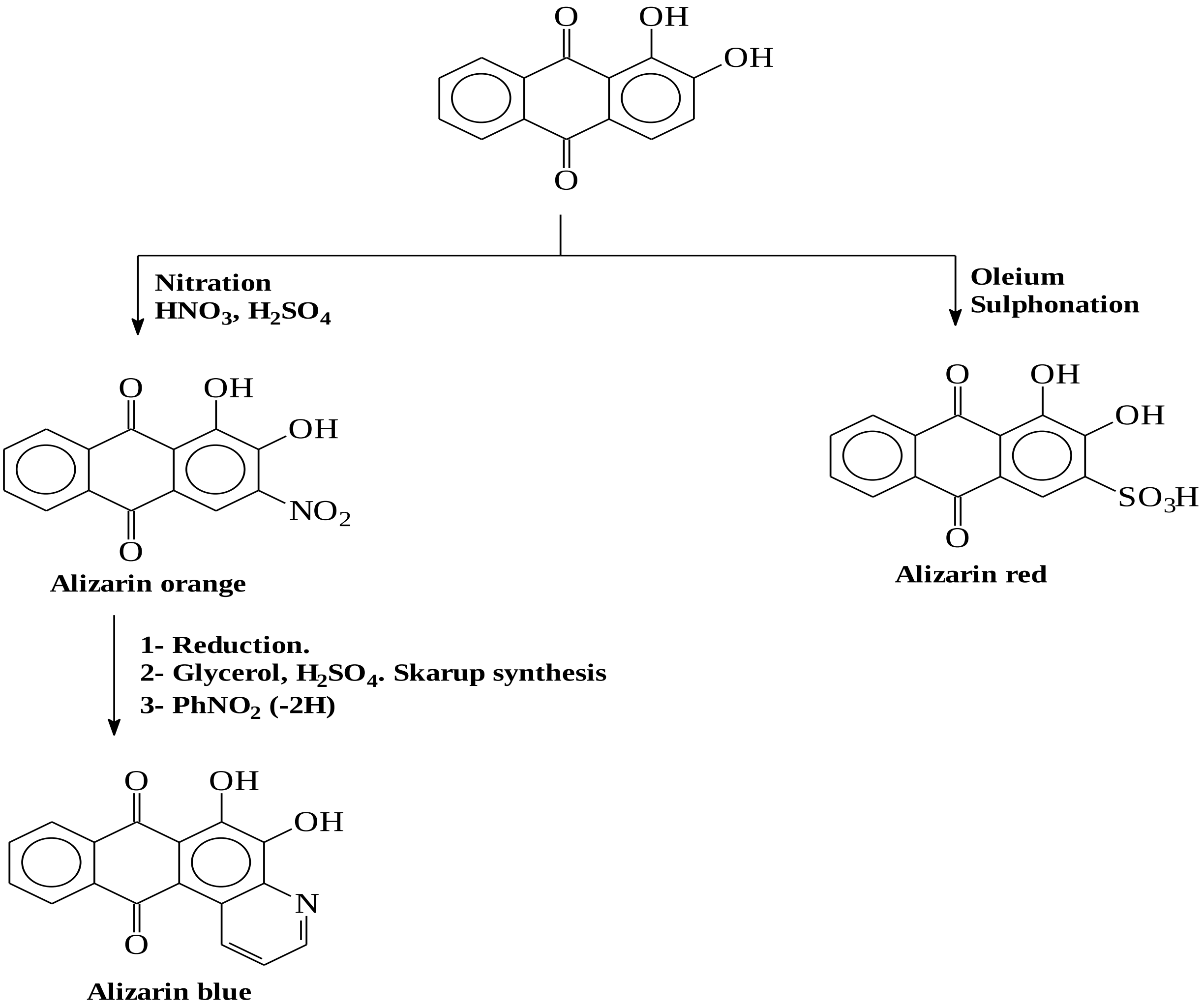
Alizarine



Alizarin is used to prepare:

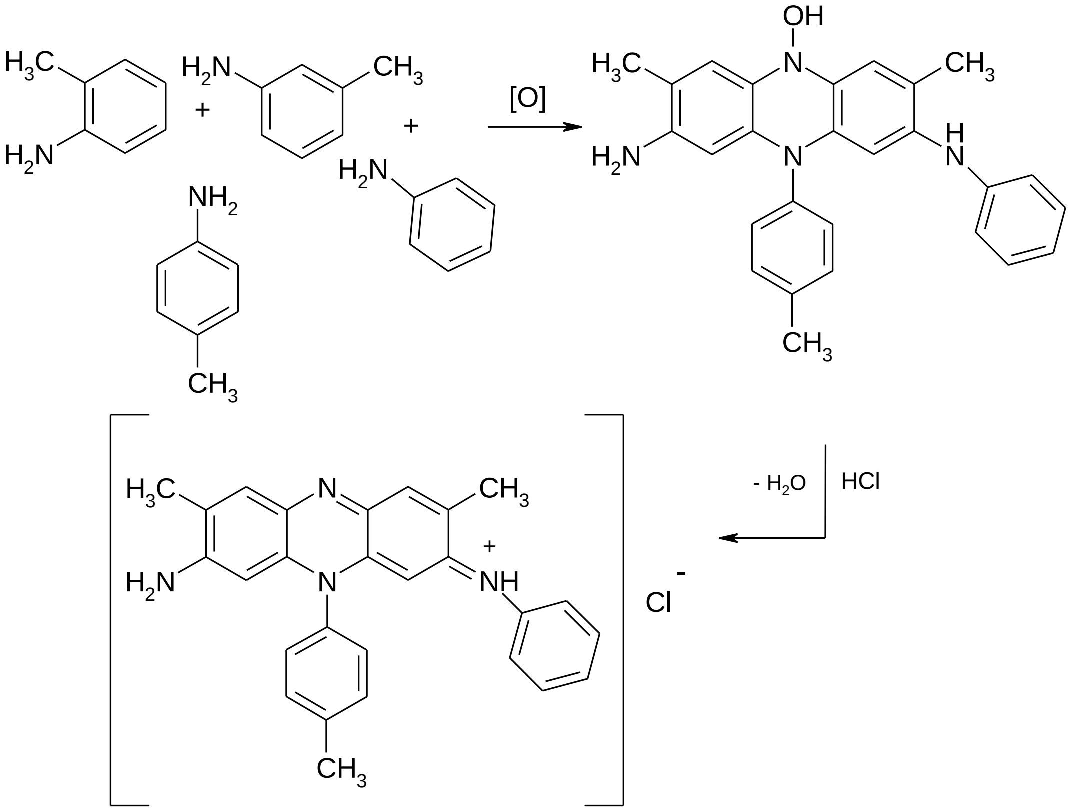
- **a- Alizarin orange.**
- **b- Alizarin red.**
- **c- Alizarin blue.**

As the following:

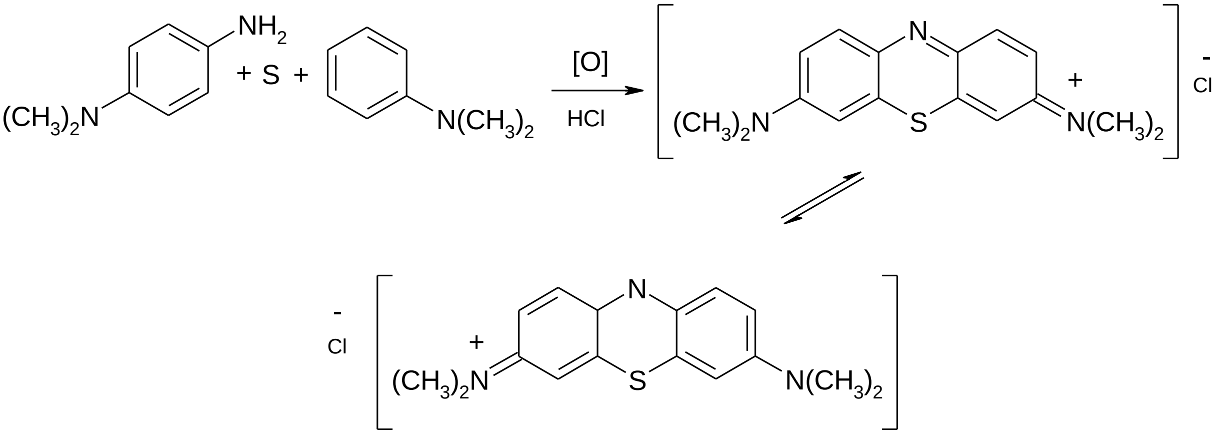


Azine dyes

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:

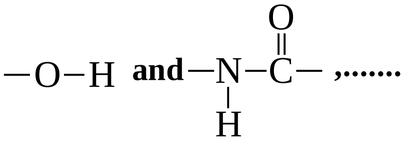
Vander Waal forces are due to interaction between π-orbitals of dye and fiber. The Van der Waal forces are effective in linear dyes i.e. long and flat. Van der Waal forces are very weak forces. It is present in certain wool dye and majority polyester and

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



$$-O-H \text{ and} -\underset{\displaystyle H}{\underset{|}{N}}-\overset{\displaystyle O}{\overset{\|}{C}}- \text{ ,.......}$$

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

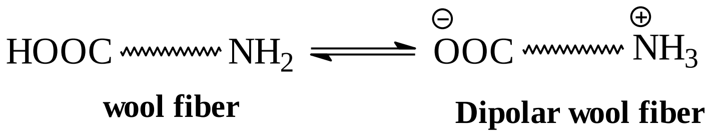
- Examples of fiber, which are bound by hydrogen bond, are silk, wool, synthetic Fibres.

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

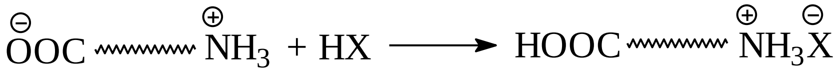
3-Ionic bond

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

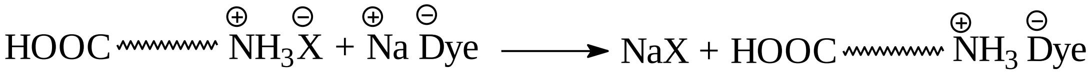
- Wool fiber is bound with ionic bond with sodium salt of dye. The ionic bond is formed when dyeing process occur in diluted acidic medium as follow:



$$\mathrm{HOOC}\sim\sim\sim\mathrm{NH_2} \rightleftharpoons \overset{\ominus}{\mathrm{O}}\mathrm{OC}\sim\sim\sim\overset{\oplus}{\mathrm{N}}\mathrm{H_3}$$



$$\overset{\ominus}{\mathrm{O}}\mathrm{OC}\sim\sim\sim\overset{\oplus}{\mathrm{N}}\mathrm{H_3} + \mathrm{HX} \longrightarrow \mathrm{HOOC}\sim\sim\sim\overset{\oplus}{\mathrm{N}}\mathrm{H_3}\overset{\ominus}{\mathrm{X}}$$



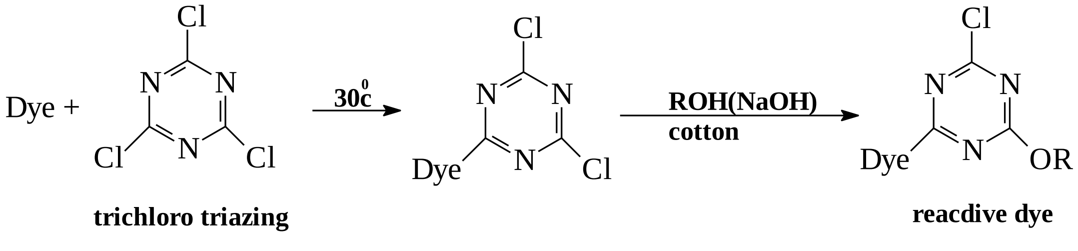
$$\mathrm{HOOC}\sim\sim\sim\overset{\oplus}{\mathrm{N}}\mathrm{H_3}\overset{\ominus}{\mathrm{X}} + \overset{\oplus}{\mathrm{Na}}\,\overset{\ominus}{\mathrm{D}}\mathrm{ye} \longrightarrow \mathrm{NaX} + \mathrm{HOOC}\sim\sim\sim\overset{\oplus}{\mathrm{N}}\mathrm{H_3}\,\overset{\ominus}{\mathrm{D}}\mathrm{ye}$$

4- Covalent bond:

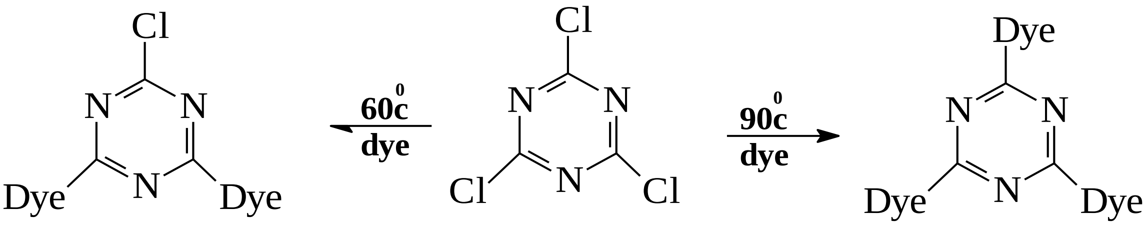
It is actual chemical bond between fiber and dye through crosslinkage agent such as 2,4,6-trichloro triazine.

It is called reactive dye

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

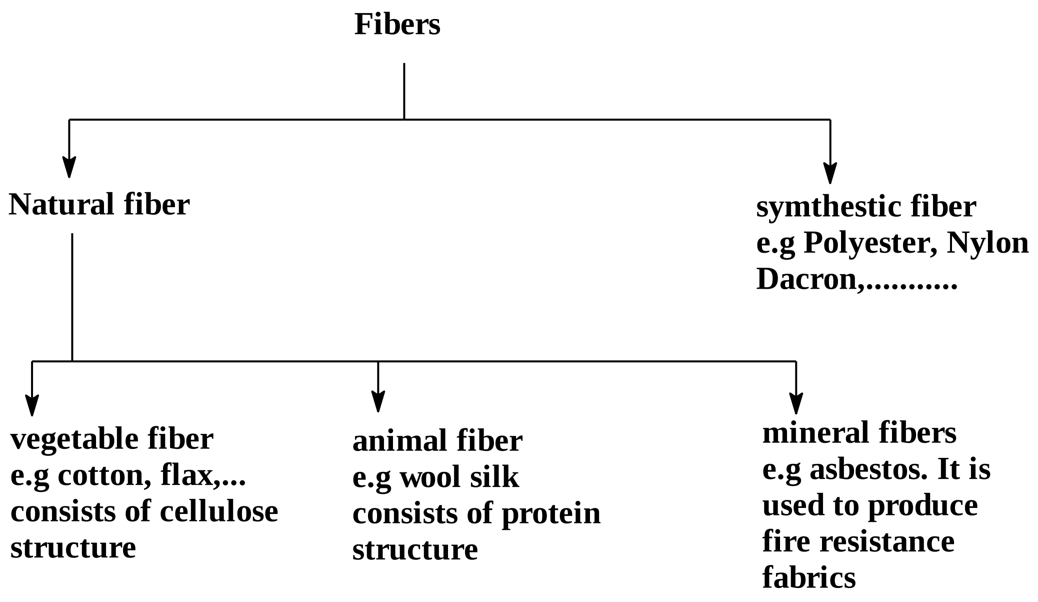


- The number of dye molecules is affected by temperature



not attach with fibr

- Classification of fibers:



Fibers

Natural fiber

symthestic fiber
e.g Polyester, Nylon
Dacron,..........

vegetable fiber
e.g cotton, flax,...
consists of cellulose
structure

animal fiber
e.g wool silk
consists of protein
structure

mineral fibers
e.g asbestos. It is
used to produce
fire resistance
fabrics

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.

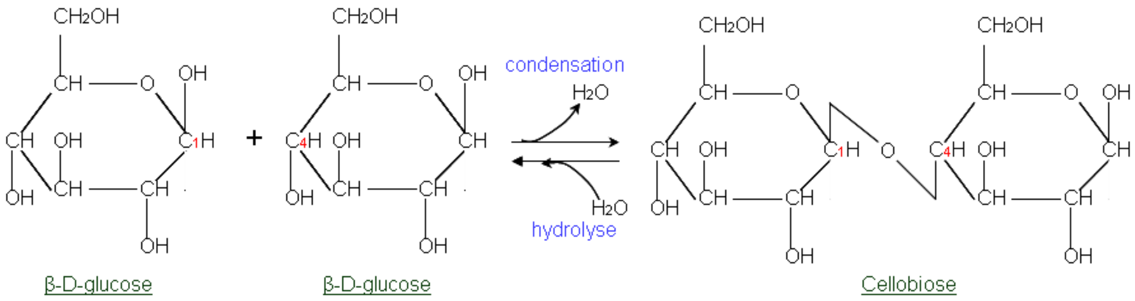
-consisting of 3,000 or more glucose units.

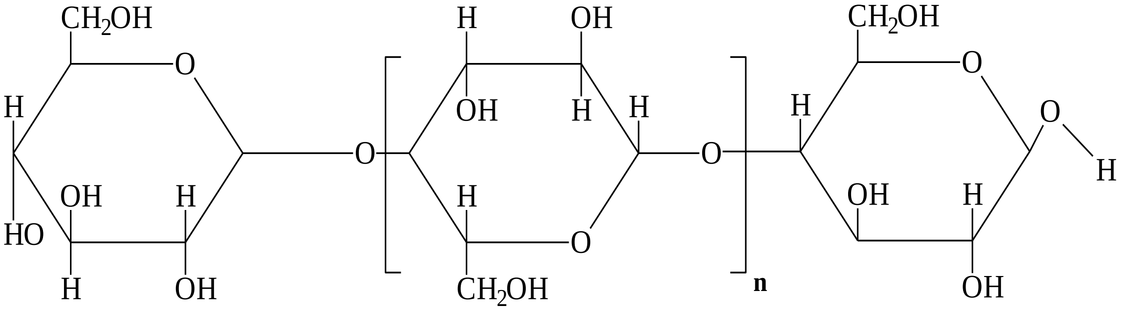
-Cellulose is an organic compound with the formula

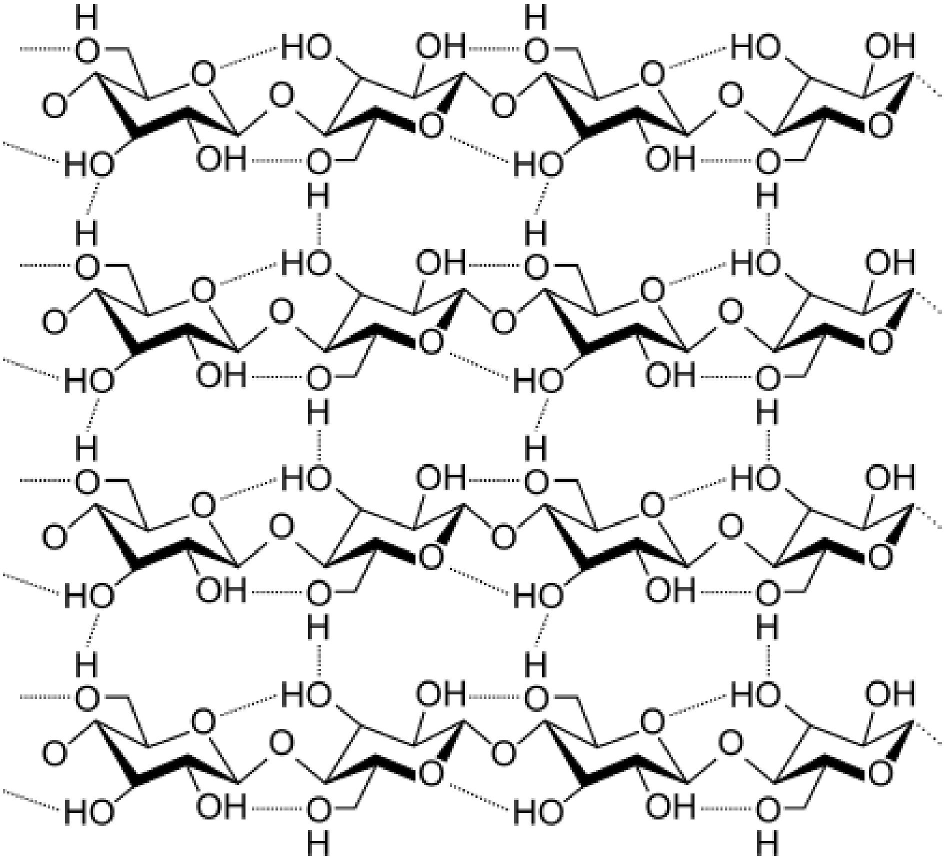
-$(C_6H_{10}O_5)_n$, a polysaccharide consisting of a linear chain of several hundred to many thousands of β(1→4) linked D-glucose units.

-Cellulose is a straight chain polymer.

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


β-D-glucose
+
β-D-glucose
condensation
H2O
hydrolyse
Cellobiose
CH2OH
OH
C1H
C4H
CH
O


CH2OH
O
H
OH
HO
n
CH2OH
OH



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.

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

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

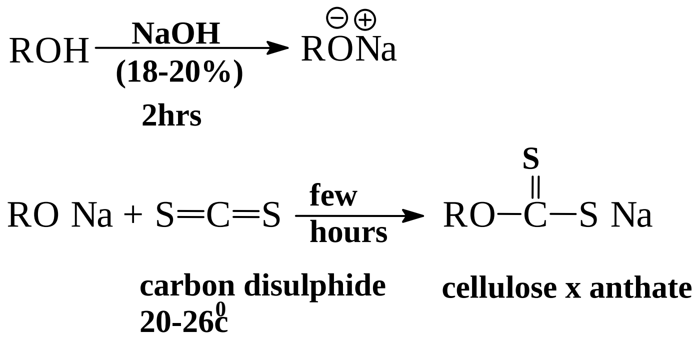
1- The fiber stronger.

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

artificial fibers

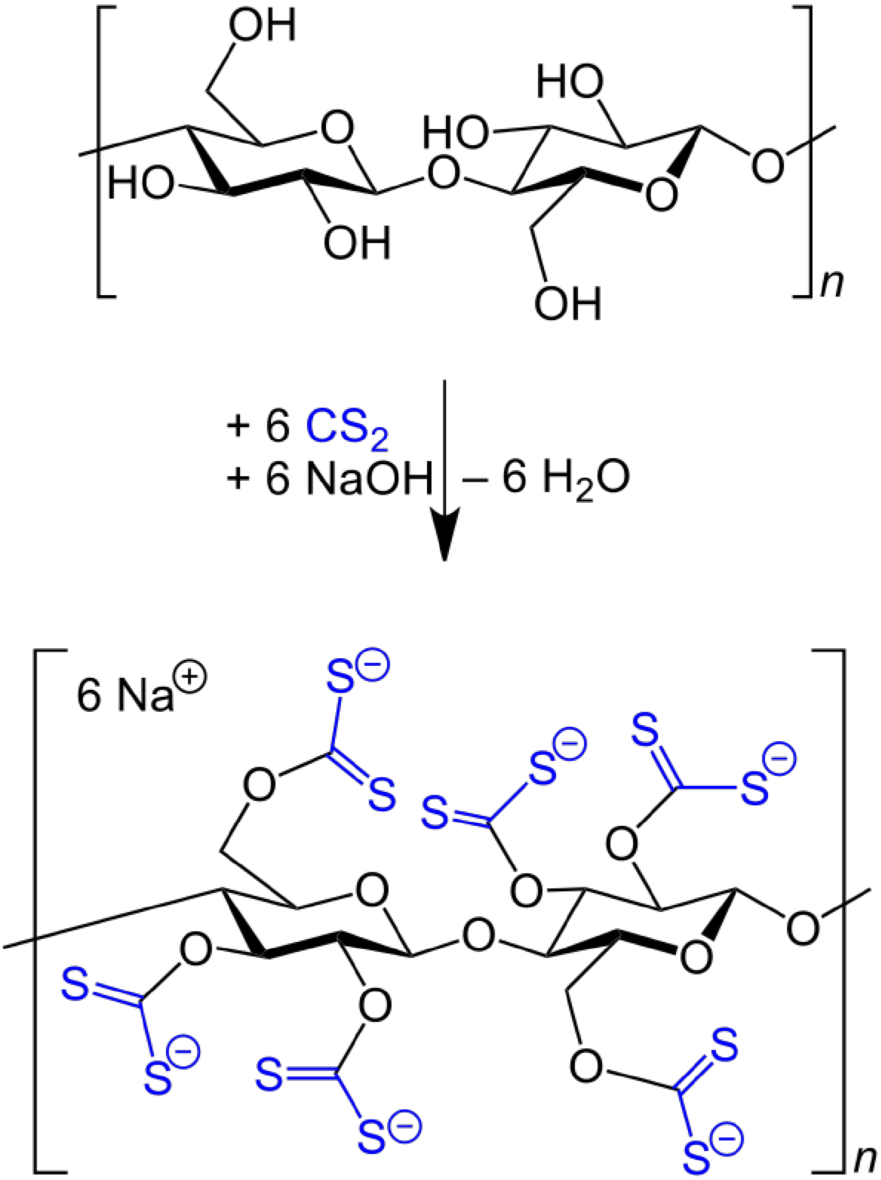
(1) viscose

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**



$$\mathrm{ROH} \xrightarrow[\text{(18-20\%)}\ \text{2hrs}]{\text{NaOH}} \mathrm{R}\overset{\ominus}{\mathrm{O}}\overset{\oplus}{\mathrm{Na}}$$

$$\mathrm{RO\ Na} + \underset{\text{carbon disulphide}\ 20\text{-}26^{0}\mathrm{c}}{\mathrm{S{=}C{=}S}} \xrightarrow[\text{hours}]{\text{few}} \underset{\text{cellulose x anthate}}{\mathrm{RO{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}S\ Na}}$$



(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

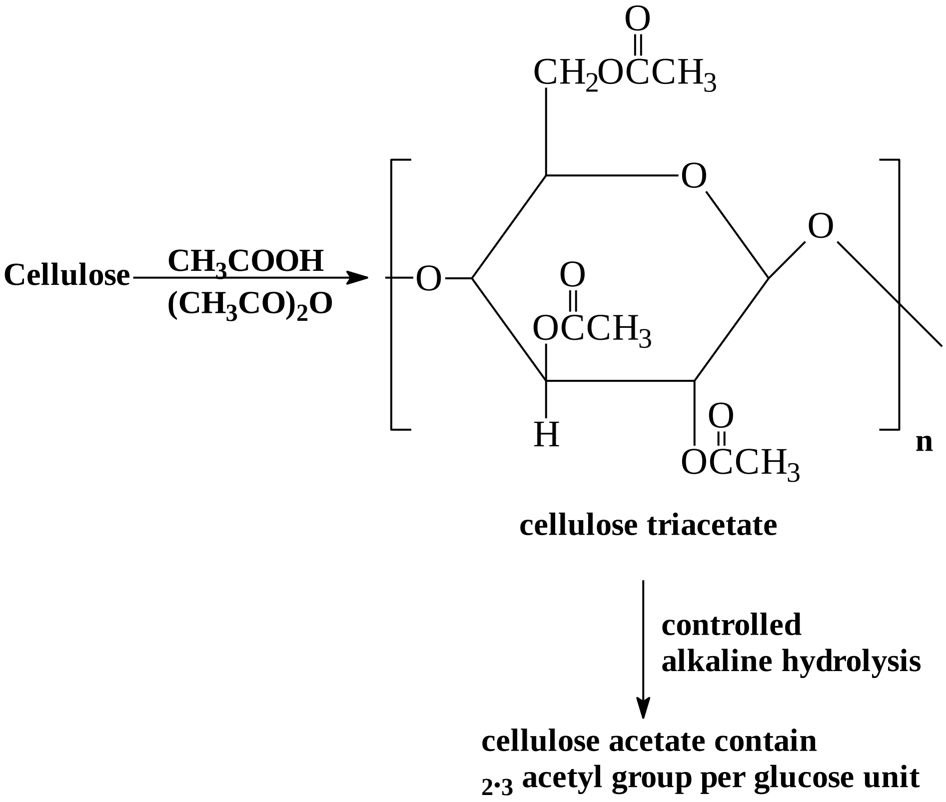
(A) Pretreatment:

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

cellulose acetate contain $_{2\cdot3}$ 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 H_2O. 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.

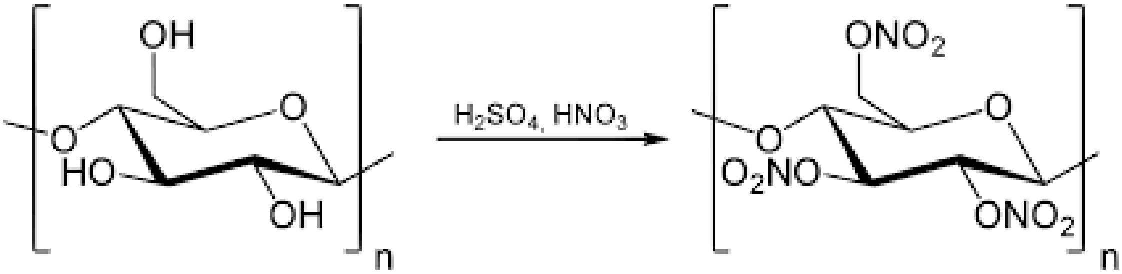
Good heat resistance

(3) cellulose nitrate silk :-

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

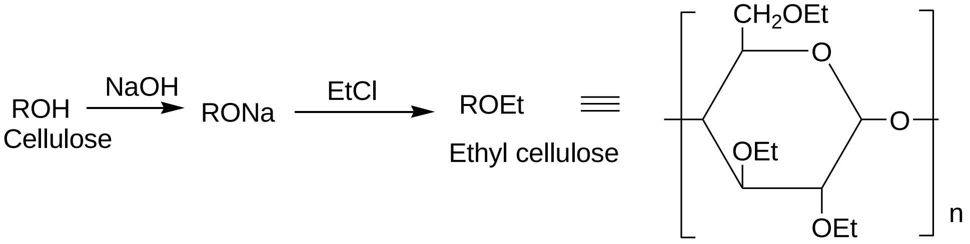
by nitrating cellulose through reaction of mixture of nitric acid and sulfuric acid.

-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:

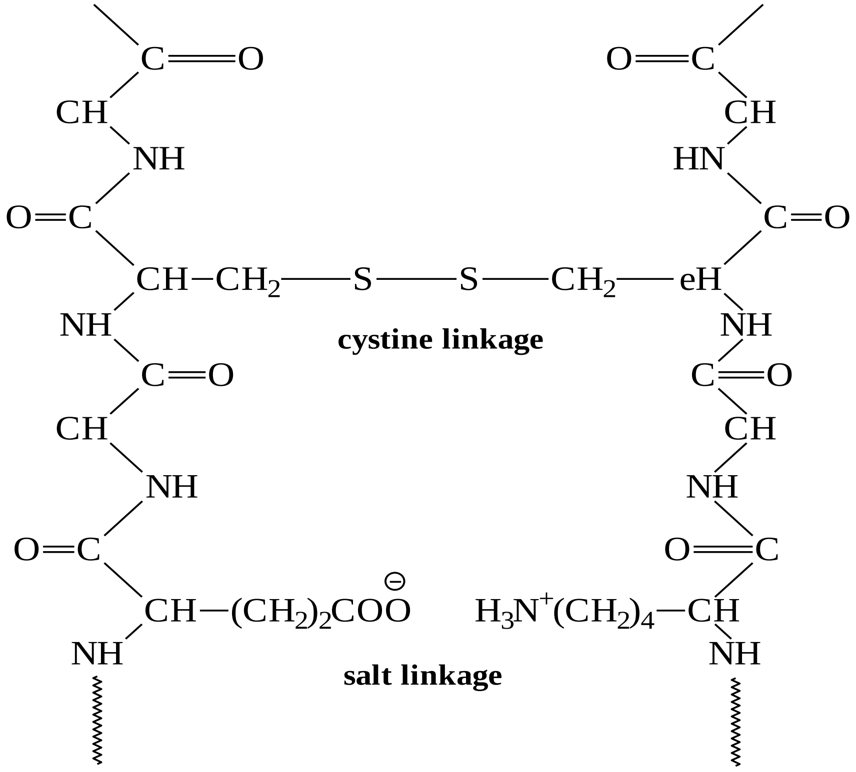
(1) Wool

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.

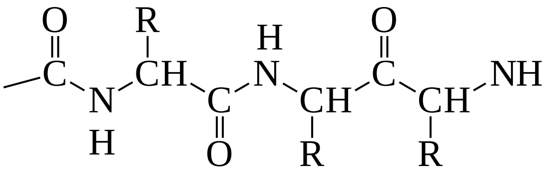
5-They have poor resistance to alkalis but good resistance to acids.

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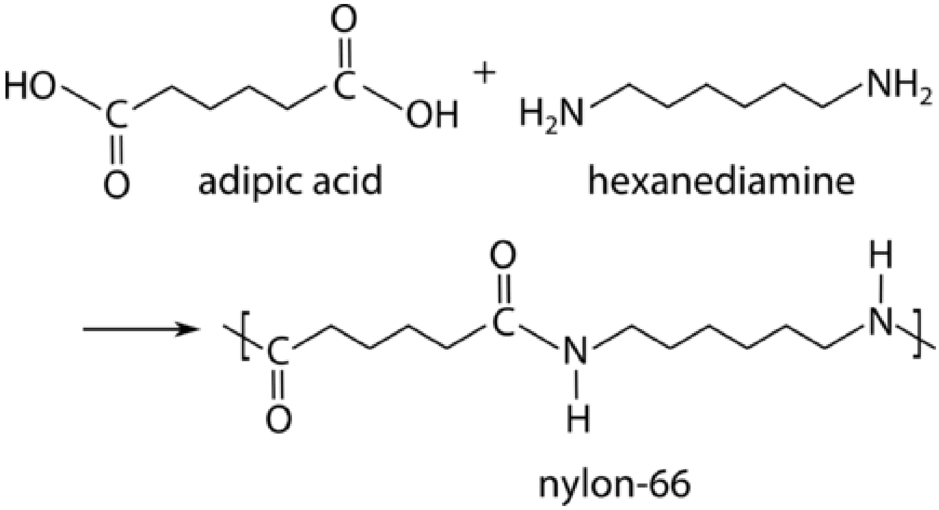
Nylon -6,6 is synthesized by polycondensation of hexamethylenediamine and adipic acid.



Used of nylone 66 :-

1-airbags, tires, ropes.

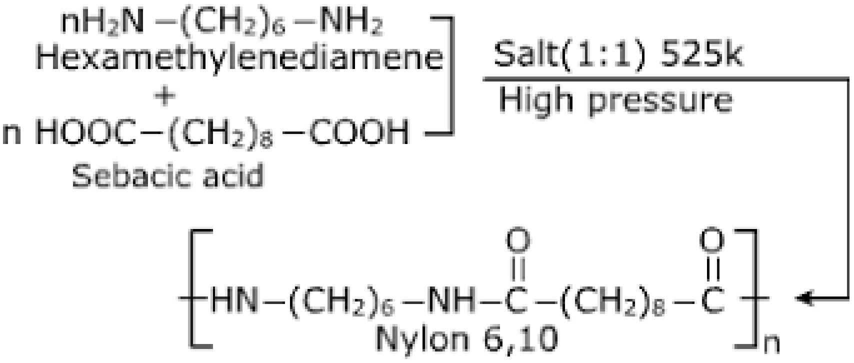
2-It is light material so it suitable to be used for parachutes

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

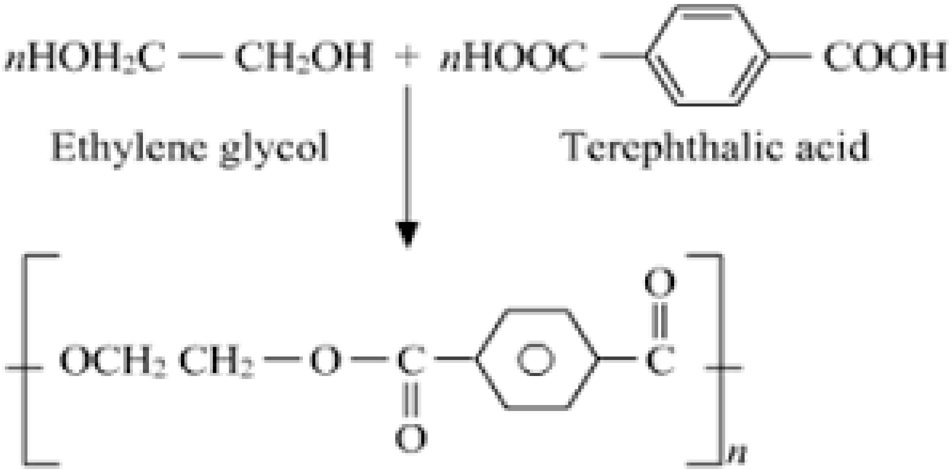
Nylon -6,10

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

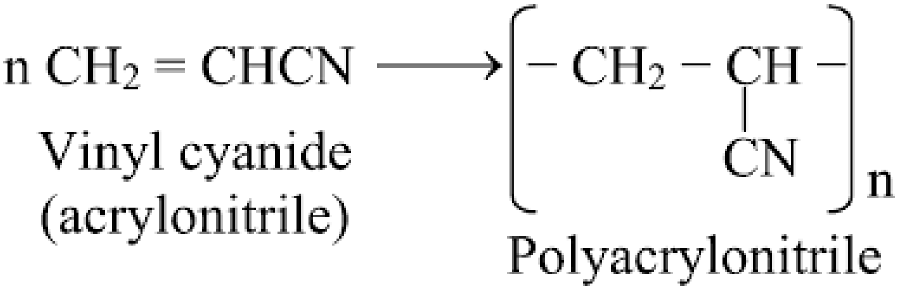
Polyethylene terephthalate commonly PETP common thermoplastic polymer resin of the polyester family and is used in fibers for clothing, containers for liquids and foods.



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.



$$n\,CH_2=CHCN \longrightarrow \left[-CH_2-\underset{\displaystyle CN}{\underset{|}{CH}}-\right]_n$$

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

dyes

2) Basic dyes

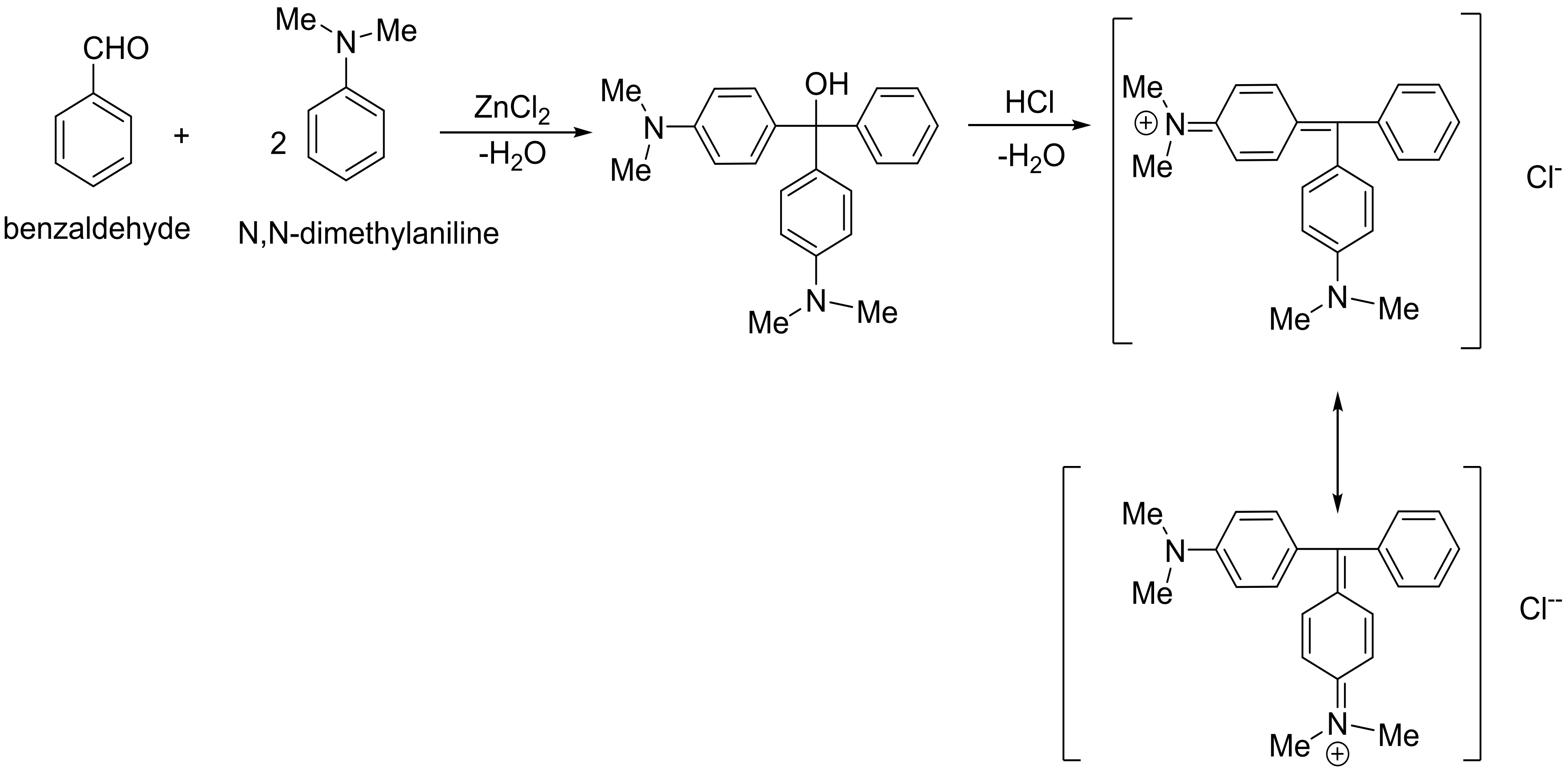
3)Vat dyes

4) Oxidative dyes

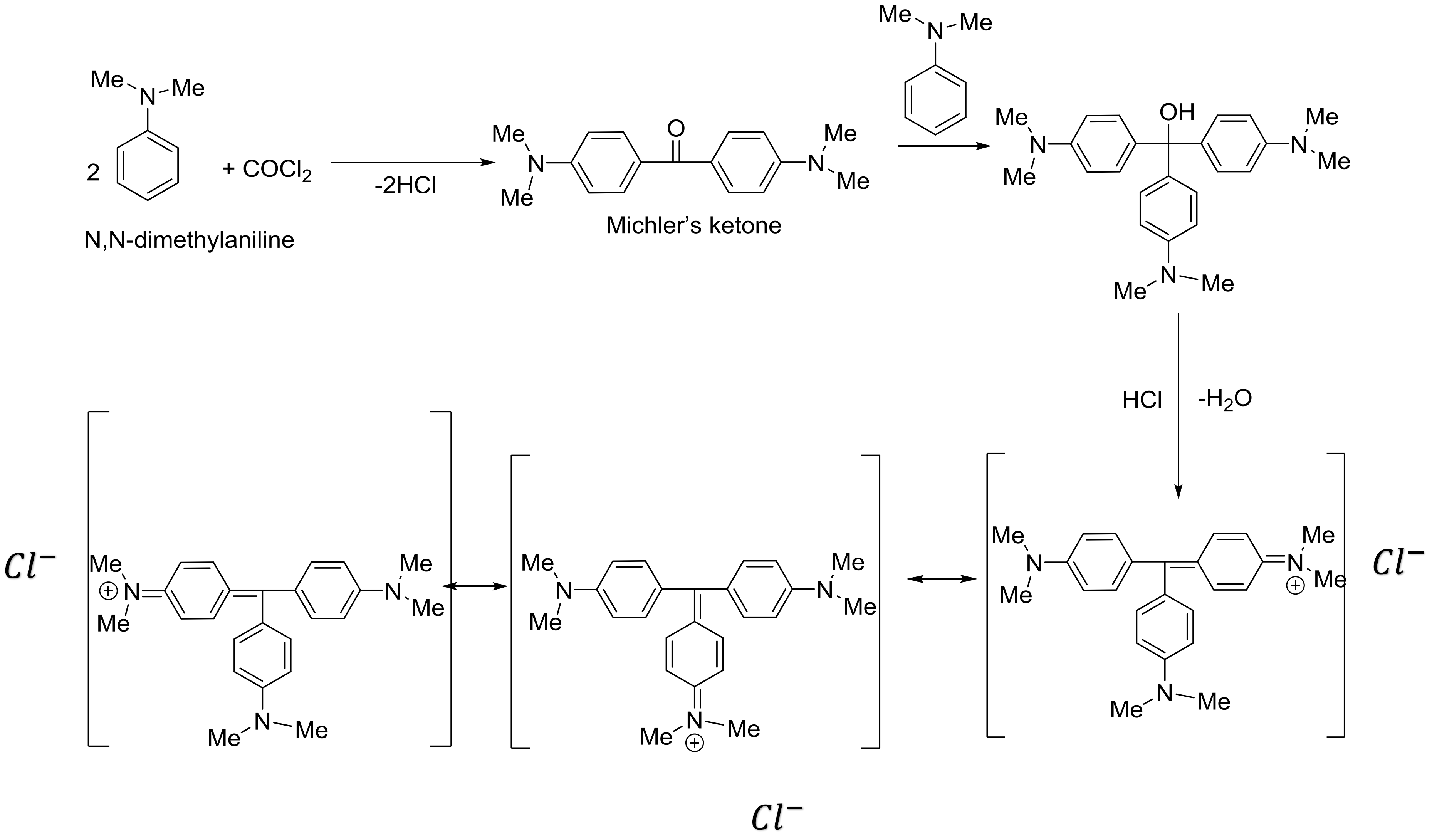
Basic dyes

- It is used to dye cotton and wool, and it is the most widely used dyes for its cheap price and bright color. **Acetic acid** used for
- improvement the leveling properties
- slow diffusion of dyes through the fiber
- increase the affinity of basic dyes to cellulosic fibers
- . **Malachite green and Crystal violet** are examples of basic dyes.

1- preparation of malachite green dye:-



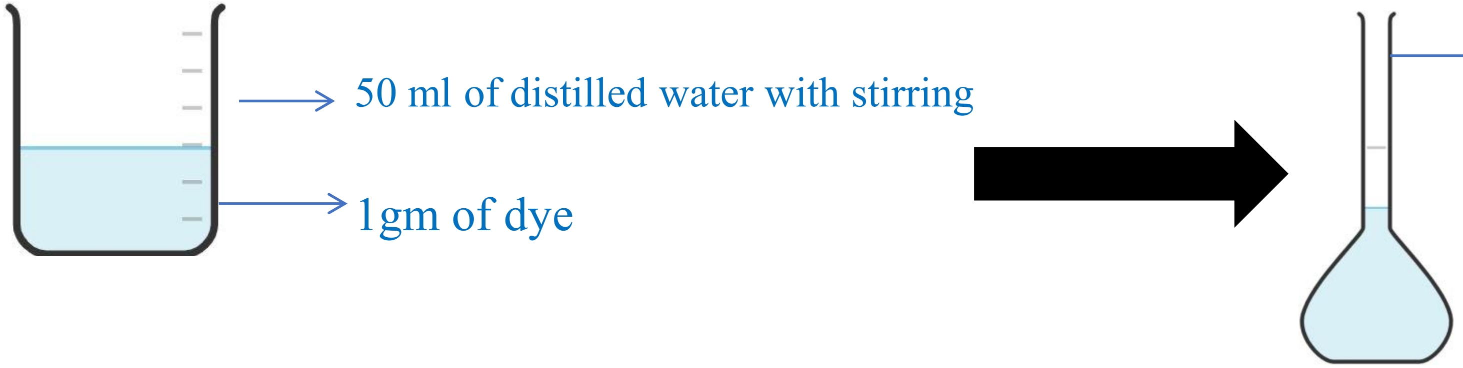
1-preparation of crystal violet:-



❖Practice:

Dye a 1gram of fibers with dyeing ratio 4% , and liquar ratio 1: 100 :-

(1) Preparation of dye solution:



50 ml of distilled water with stirring

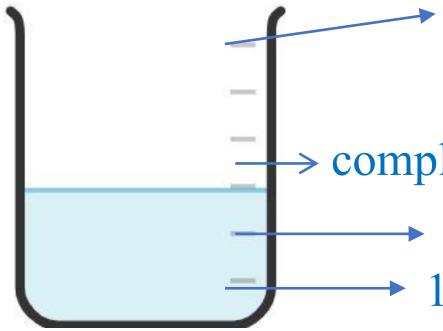
1gm of dye

Complete till 250 ml with distilled water

C= weight of dyeX100 / volume of dye

(2) Preparation the dyeing bath:

As
P=4% , w= 1gm,
C= weight of dyeX100 / volume of dye solution
W= 1X100/250 = 0.4%
and thus the volume required from stock solution
V=4%x1/ 0.4% = 10 ml



add 1gm of fibers with stirring for 1hr at 40-50 ° C then take out it, wash with cold water and dry

complete to 100 ml by distilled water

5ml of acetic acid

10 ml of dye solution (stock solution)

Vat dyes

Vat dyes are in soluble in water so it is reduced by sodium hydrosulphate($NaHSO_4$) in basic medium to it’s colorless reduced form which has affinity to fiber and soluble in water

And after dyeing process the dye is oxidized by air or by using oxidizing agent

After dyeing process the fiber is treatment with in hot soap bath to remove the excess un fixed dye on fiber and appearing the color of dye

Azo dyes

Azo dyes:- dyes that contain azo group (N=N) as an chromophores group

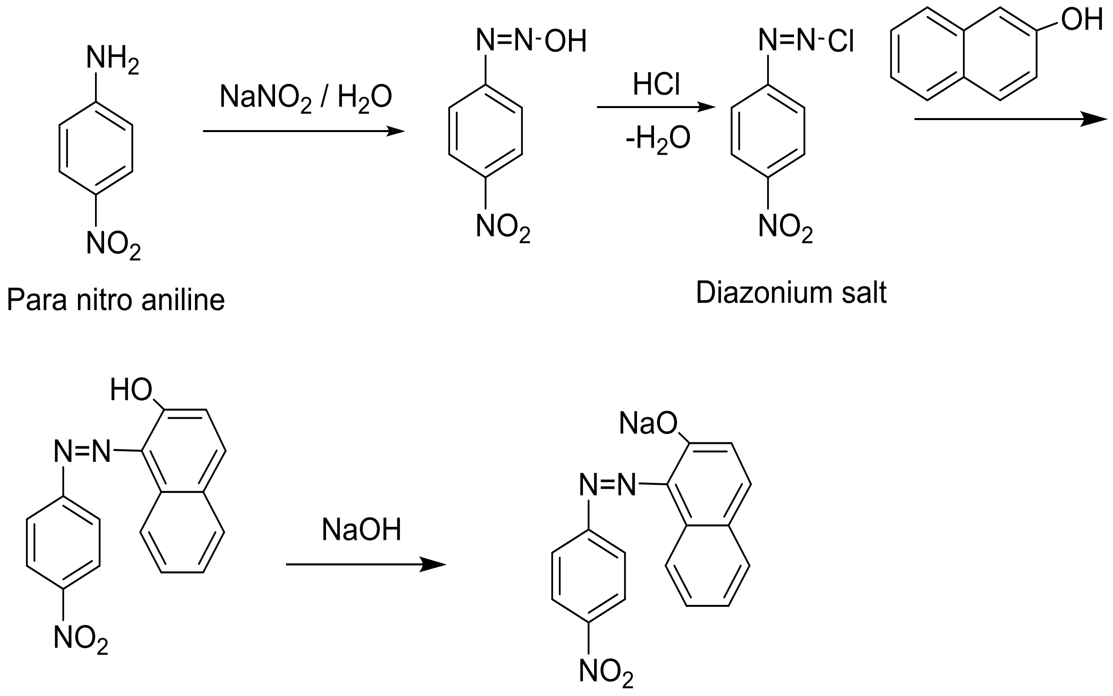
It is formed inside the fiber by two steps . The first is formation the diazonium salt and the second is coupling step

Example

Para red

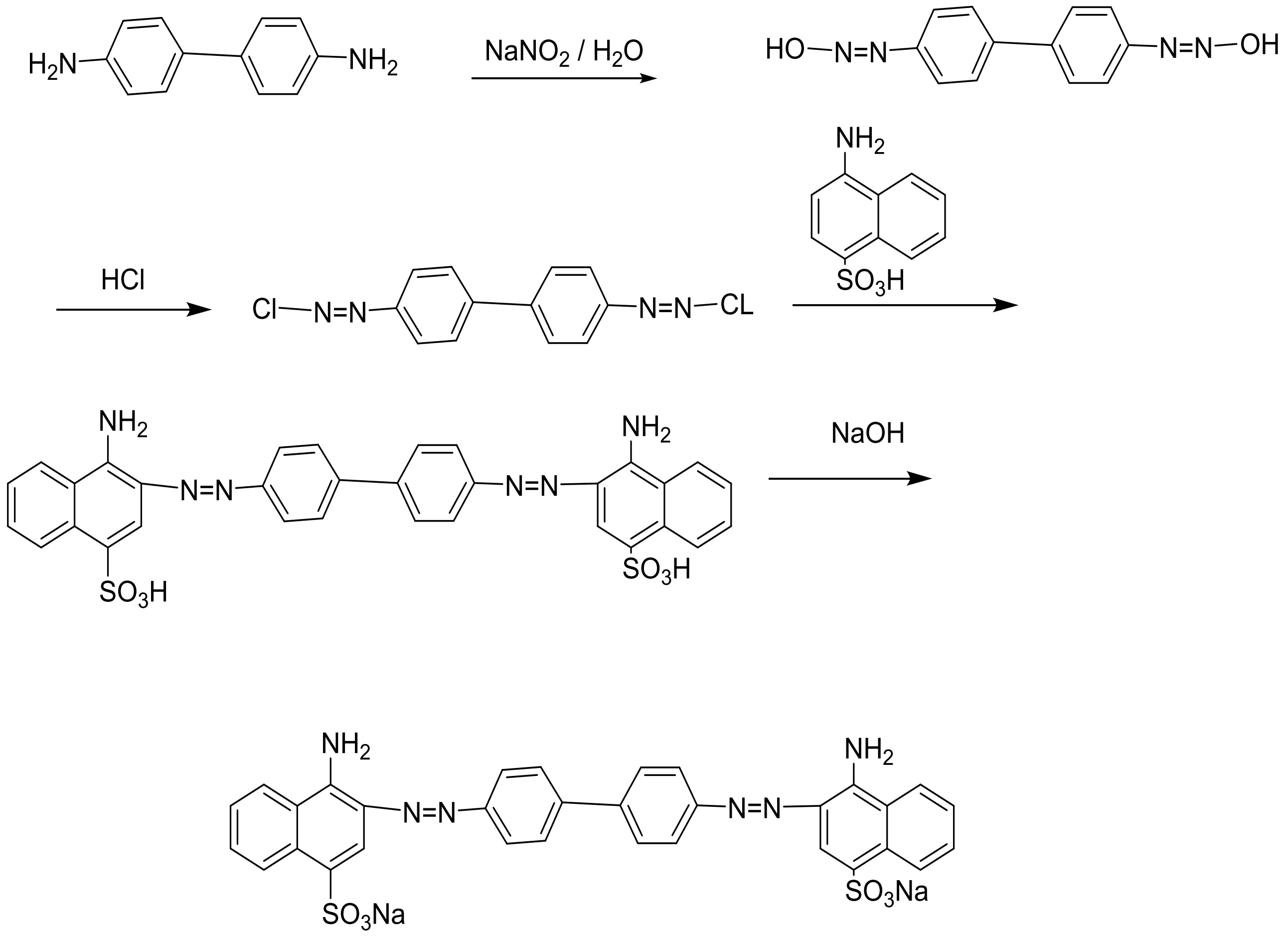
Congo red

Preparation of para red

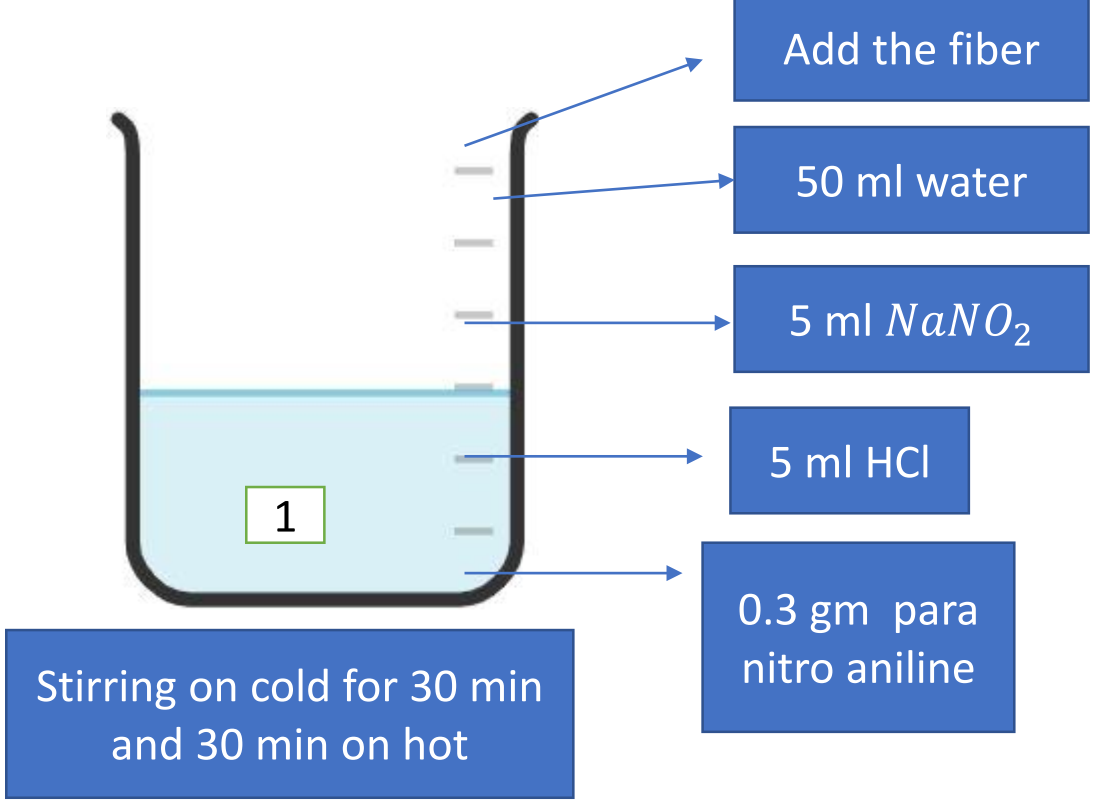


para red

Preparation of congo red



congo red



Add the fiber

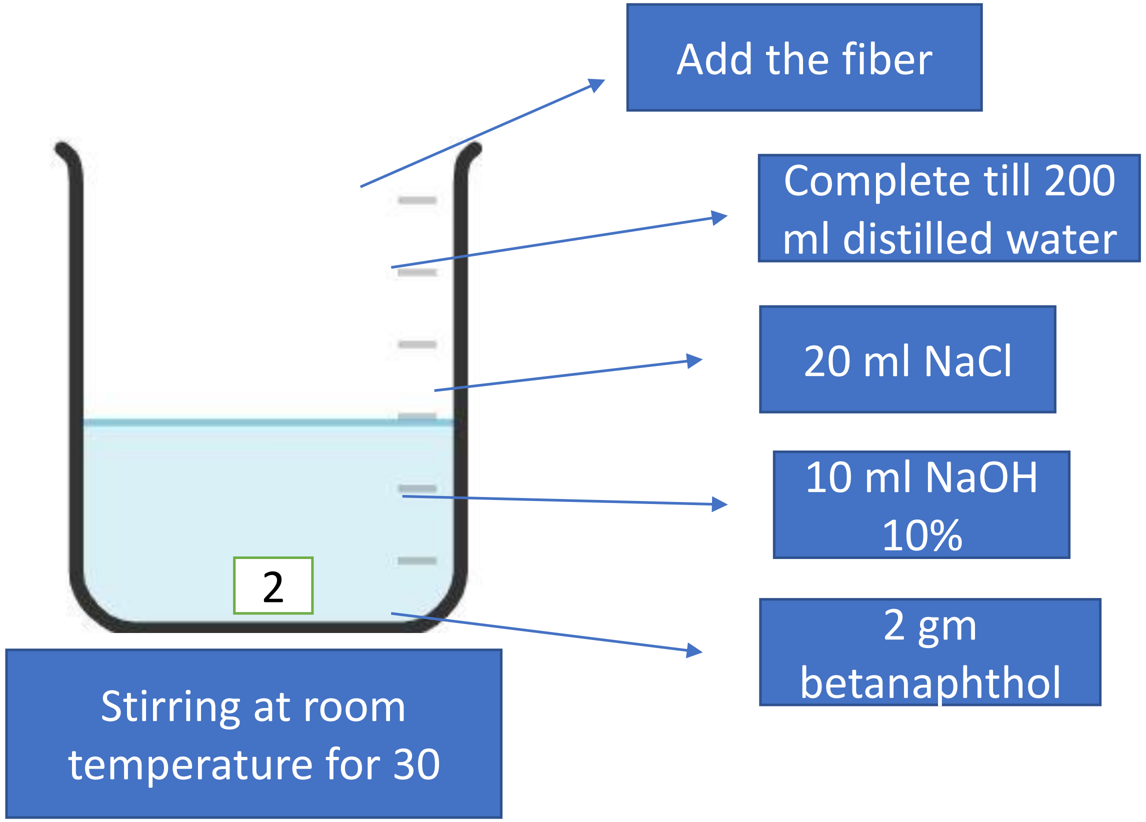
50 ml water

5 ml $NaNO_2$

5 ml HCl

0.3 gm para nitro aniline

Stirring on cold for 30 min and 30 min on hot



Add the fiber

Complete till 200 ml distilled water

20 ml NaCl

10 ml NaOH 10%

2 gm betanaphthol

Stirring at room temperature for 30

الخطوات

١) قم بتحضير محتويات الكاس (١) ثم قم باضافة ١ جم من الالياف مع التقليب لمدة نصف ساعة على البارد

٢) قم بتجفيف الالياف

٣) قم بتحضير الكاس (٢) ثم اضف الالياف التي تم تجفيفها اليه مع التقليب لمدة نصف ساعة عند درجة حرارة الغرفة

٤) قم باستخراج الالياف ووضعها فى حمام صابون ساخن

the role of HCl and NaOH during dyeing of fiber with azo dye

The role of HCl

1) Dissolving the amino compound
2) Formation of diazonium salt
3) Formation of NaCl during dyeing process which increase the exhaustion and increase the affinity of fiber to dye

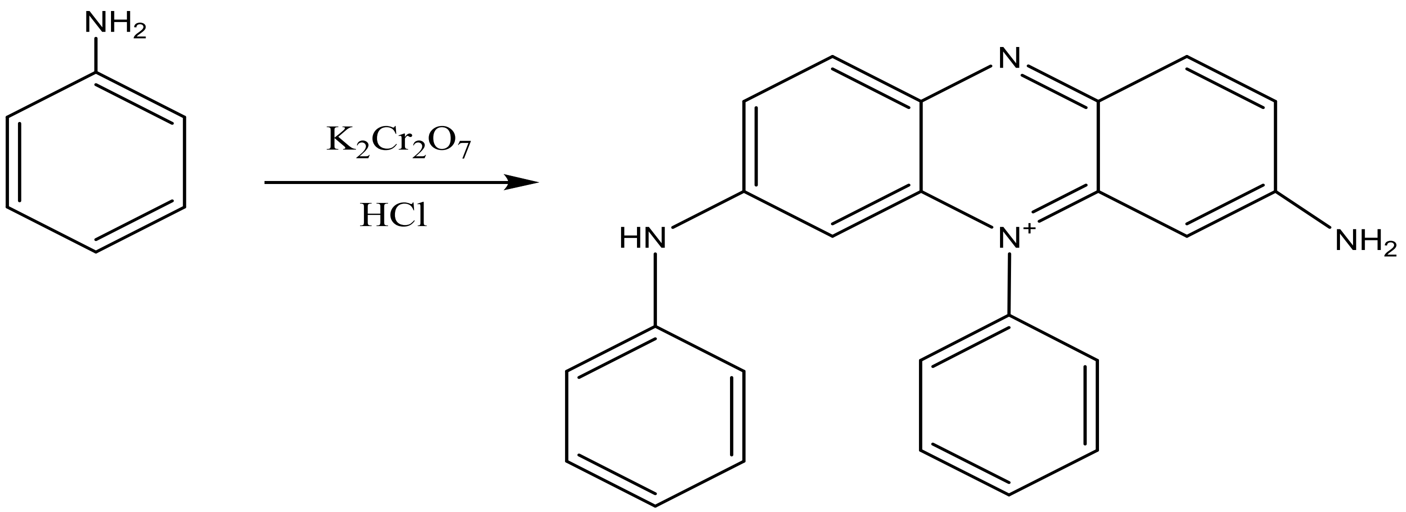
The role of NaOH

1)Dissolving the phenol
2) Neutralize the excess of HCl to form NaClwhich increase the exhaustion and increase the affinity of fiber to dye

Oxidative dyes

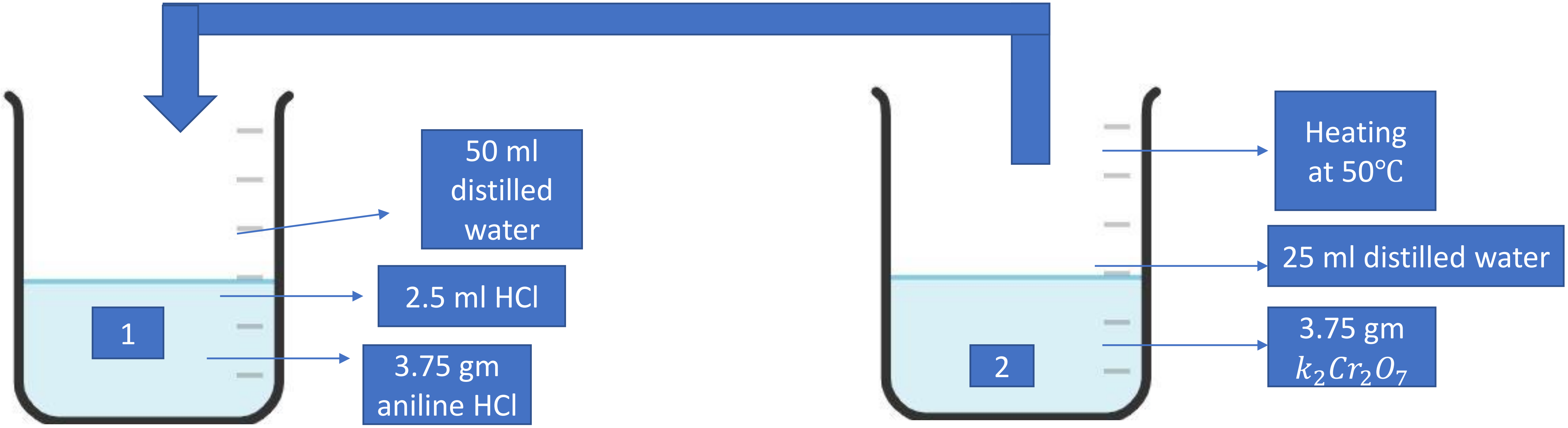
Dyes that is prepared by oxidizing agents ($k_2cr_2o_7$ in presence of strong acid)

Example of oxidative dyes :- (black aniline)



Aniline black

procedure



1

50 ml distilled water

2.5 ml HCl

3.75 gm aniline HCl

2

Heating at 50°C

25 ml distilled water

3.75 gm $k_2Cr_2O_7$

الخطوات

١) قم بتحضير الكاس (١)والكاس(٢) ثم قم بتسخين الكاس(٢)عند درجة حرارة منخفضه

٢)اضف الكاس (٢) الى الكاس(١) ثم اضف ١ جم من الالياف وقم بالتقليب ٣٠ دقيقه على البارد ثم ٣٠ دقيقه على الساخن

٣) قم بتجفيف الالياف ثم ضعها فى حمام من محلول الصابون السائل