South Valley University

Faculty of Education

Chemistry Department

Organic Chemistry III

2nd year students – Faculty of Education

Biology group

Second Term 2022/2023

Dr/ Ibrahim Abdul-Motaleb Mousa

CHEMISRY OF NATURAL PRODUCTS

2nd Year Students Faculty of Education South Valley University

second term 2022/2023

Dr/ Ibrahim Abdul-Motaleb Mousa

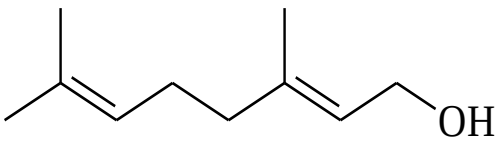
Contents

Introduction:

- **Natural products are organic compounds produced by**
- **living organisms, such as human organs, plants,**
- **animal organs, sea organisms and micro-organisms,**
- **as a result of the metabolism. These compounds**
- **comprise, the so called, primary metabolites and**
- **secondary metabolites.**

Classification of Natural Products:

- **Classes of Natural Products**
- **Classification based on chemical structure**



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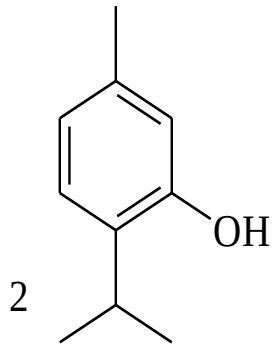
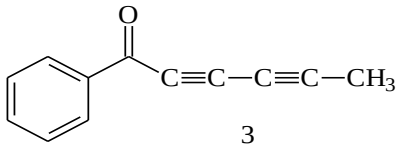


2

- ***Classification based on physiological activity***
- **as exemplified by hormones, antibiotics,..**
- ***Classification based on taxonomy***
- **xanthanolides from *Xanthium*, iridoids from *Iridomyrnex*, ergot alkaloids, alkaloid class of the ergot, iboga alkaloids, alkaloid of iboga, meinspermaceae alkaloids**



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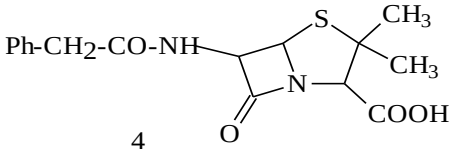

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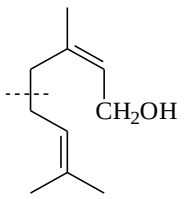
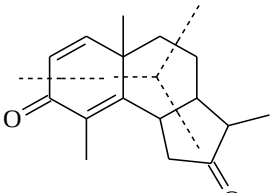
Classification based on biogenesis

Biogenesis : hypothesis

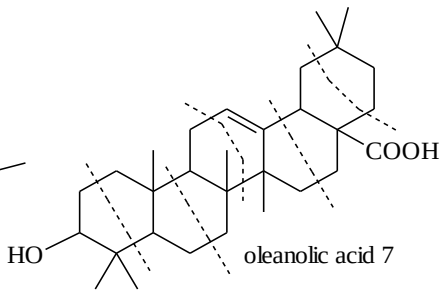
Biosynthesis : experimentally proven route



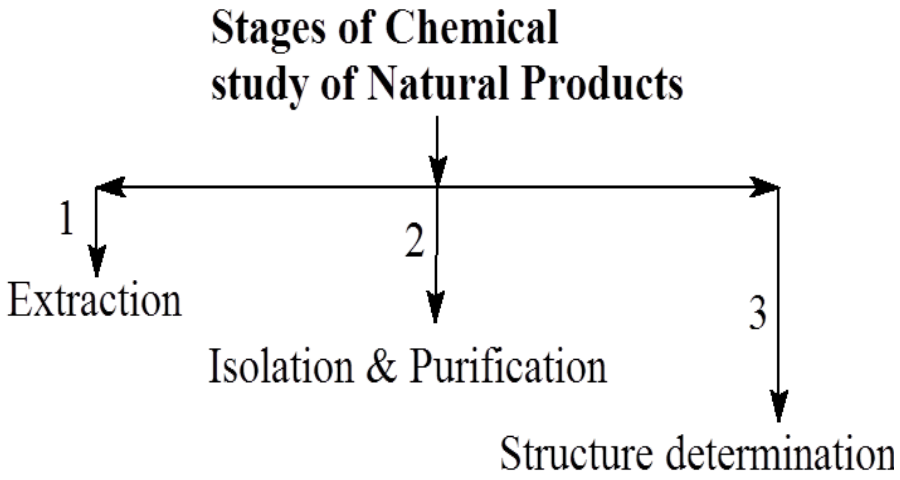
nerol 5



santonin 6

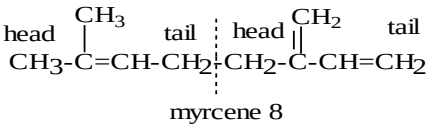


oleanolic acid 7

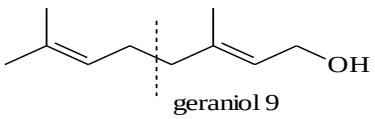


Terpenoids:

- **Terpenes are compounds, when heated in the absence of air (oxygen) give isoprene.**
- **Isoprene Rule, Wallach, 1887**
- **the skeleton structures of all naturally occurring terpenes can be built up of isoprene units**
- **Special Isoprene Rule, Ingold, 1925**
- **the isoprene units in natural terpenes were jointed "head-to-tail".**



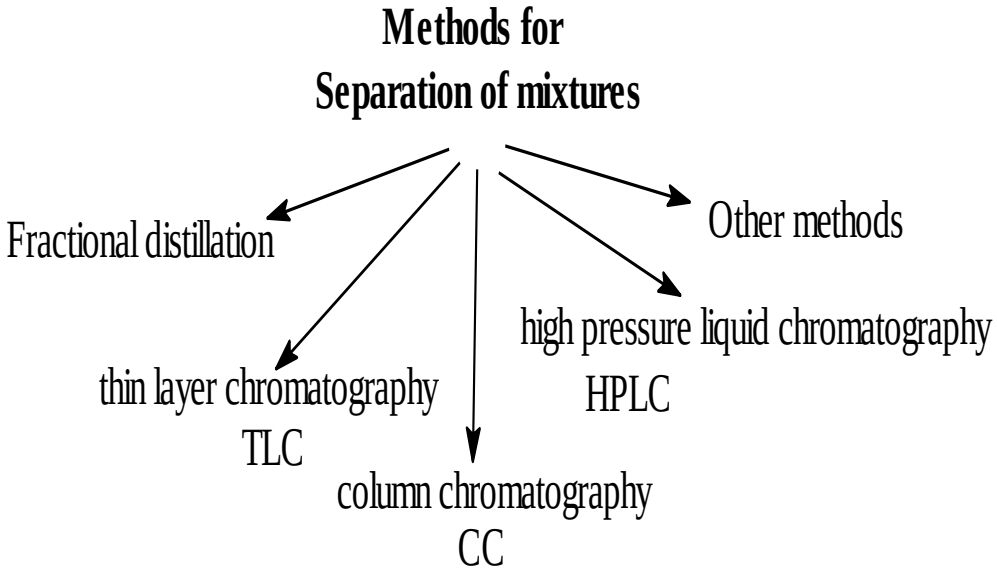
myrcene 8



geraniol 9

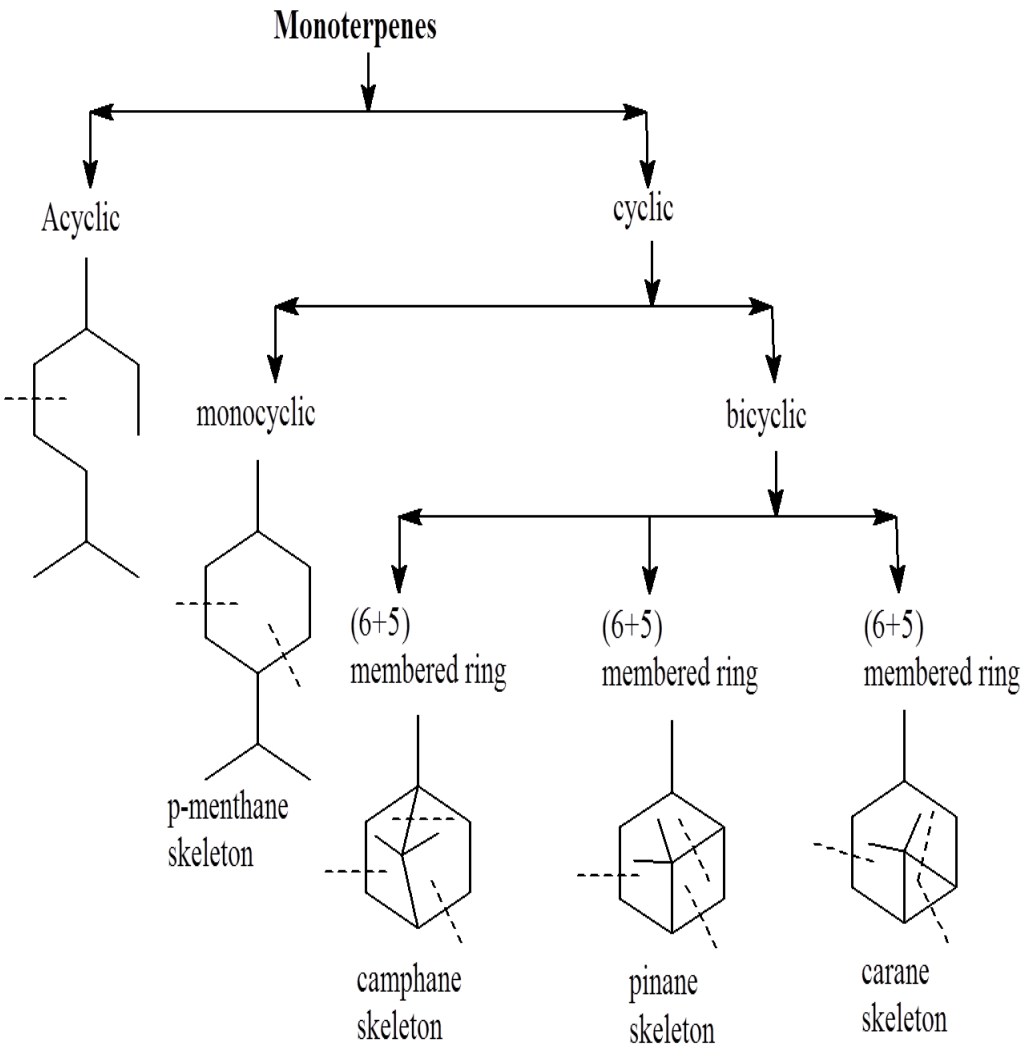
Isolation of Mono- and Sesequeterpenes (essential oils)

- **(i) Expression**
- · **(ii) Steam distillation**
- · **(iii) Extraction by means of volatile organic solvents**
- · **(iv) Adsorption on fats.**

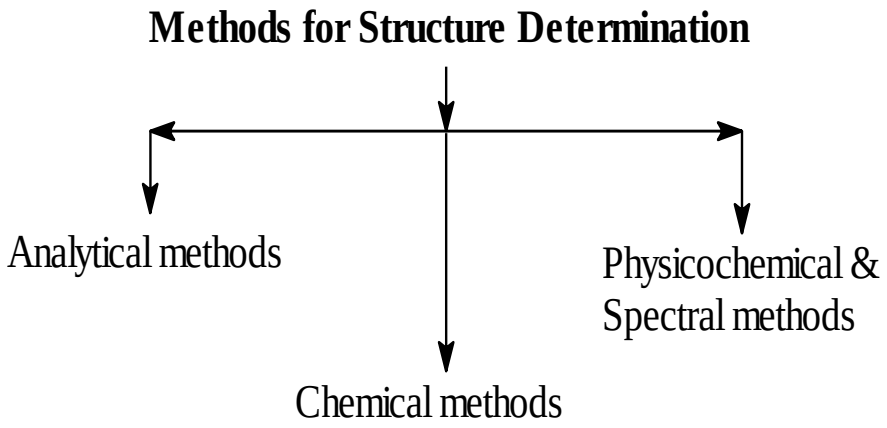


Classification of terpenes

No. of isoprene units	No. of carbon atoms	Class	Remarks
1	5	Hemi terpenes	Ester and ether groups
2	10	Mono terpenes	Volatile oils
3	15	Sesque terpenes	Volatile oils
4	20	Di-terpenes	Gums and resins
5	25	Sester terpenes	Gums and resins
6	30	Tri terpenes	Gums and resins
8	40	Tetra terpenes	Carotenoids
> 8	> 40	Poly terpenes	Natural rubber

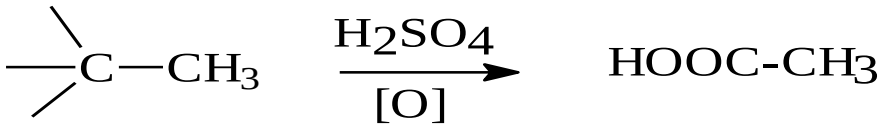

Monoterpenes
Acyclic
cyclic
monocyclic
bicyclic
(6+5)
membered ring
(6+5)
membered ring
(6+5)
membered ring
p-menthane
skeleton
camphane
skeleton
pinane
skeleton
carane
skeleton

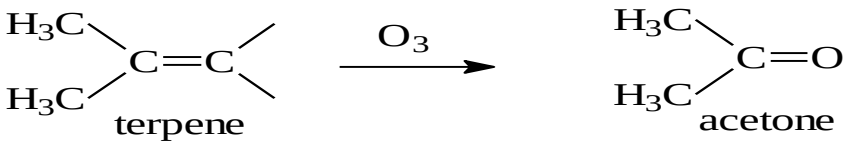
General methods for structure determination of terpenoids:



Analytical methods:

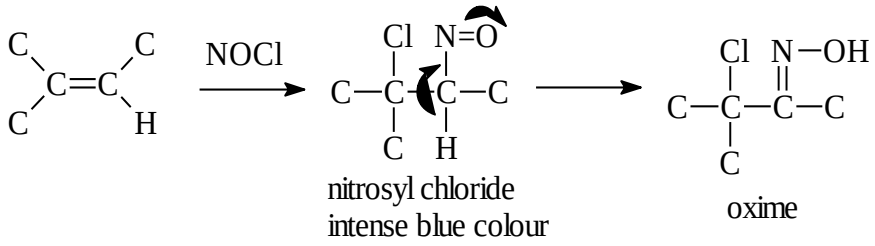
- **Analytical methods**
- **· Determination of % of C,H and O by combustion → empirical formula → molecular formula**
- **Degrees of unsaturation**
- **Estimation of groups**
- **· Active hydrogen**
- **Terpene + $LiA1H_4 \rightarrow H_2$ ----- estimated**





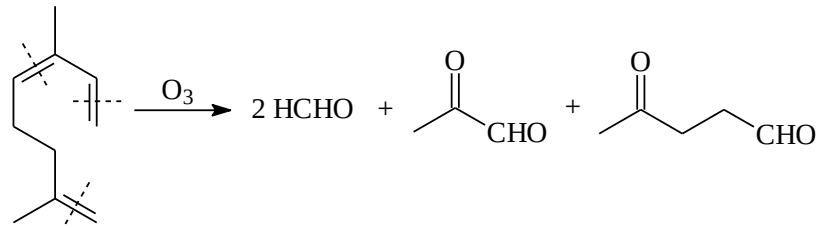
Chemical methods:

- **Functional groups**
- **Unsaturation**
- · **by bromination (Br_2)**
- · **by nitrosyl chloride NOCl**

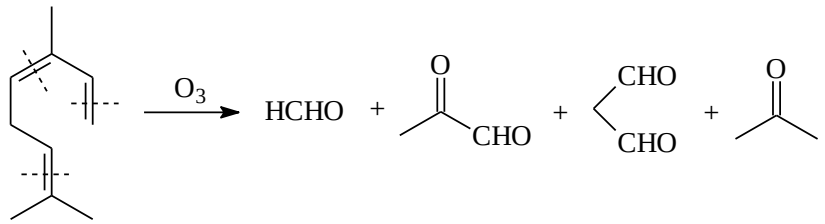


- **Ozonolysis is an example of oxidative degradation methods (O_3, $KMnO_4$, CrO_3 & OsO_4).**

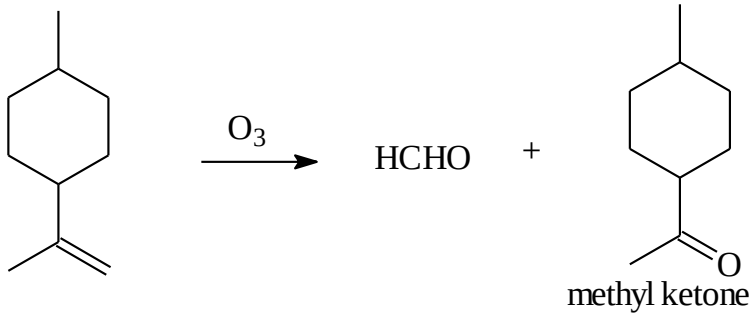
(i)



(ii)

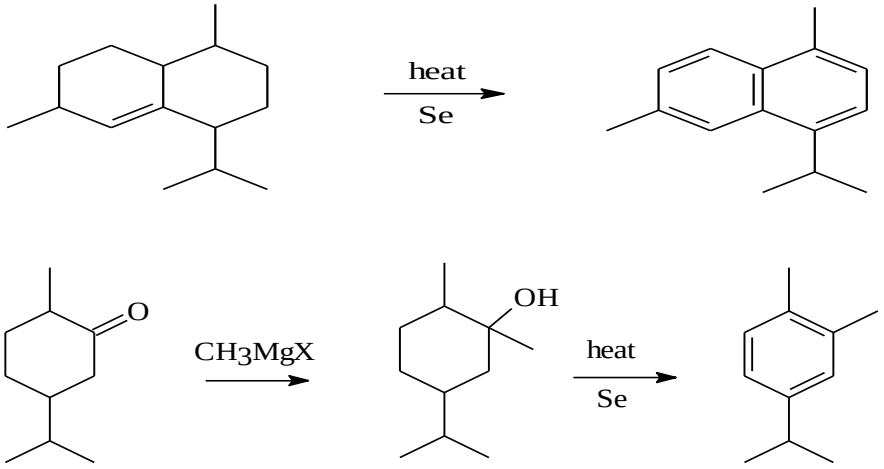


(iii)

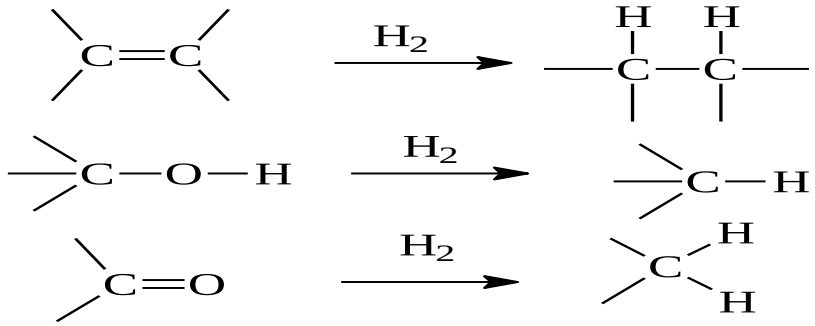


- **Conjugated and isolated double bonds are differentiated by Diel's Alder reaction.**

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



- **Hydrogenation of the substance to the parent hydrocarbon leads to the cyclic nature of the terpene (acyclic, monocyclic, bicyclic, ... etc).**

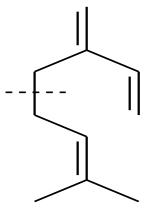


- saturated hydrocarbones

- Hydrocarbon C_nH_{2n+2} ---------- Acyclic
- C_nH_{2n} ---------- Monocyclic
- C_nH_{2n-2} ---------- Bicyclic
- C_nH_{2n-4} ---------- Tricyclic
- C_nH_{2n-6} ---------- Tetracycl
-

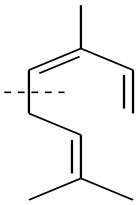
- **Physical and spectral methods:**
- **a) Molecular refraction (refractive index, refractometer).**
- **b) Optical rotation α_D (polarimeter)**
- **c) IR absorption**
- **d) NMR (^{1}H-NMR & ^{13}C-NMR)**
- **e) X-Ray analysis**
- **f) UV (ultraviolet absorption)**
- **· A final confirmation of the proposed structure is usually achieved by synthesizing the compound and comparing the spectral data with those of an authentic sample.**

- **Examples for different terpenes:**
- **Monoterpenes**
- **Acyclic**



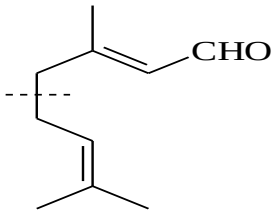
Myrcene

- occurs in verbena and bay oil



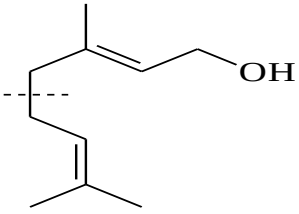
Ocimene

occurs in *Ocimum basilicum*



Citral

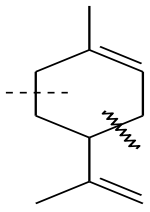
- occurs in lemon grass oil



Geraniol

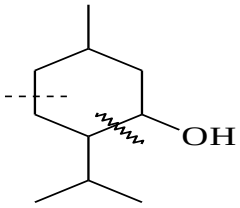
occurs in rose oil

- **Cyclic:**

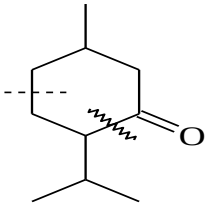


Limonene

occurs in lemon and orange oils

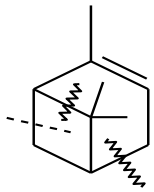


Menthol

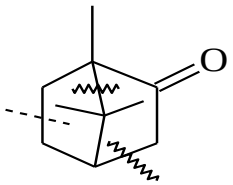


Menthone

both occur in pepermint oil

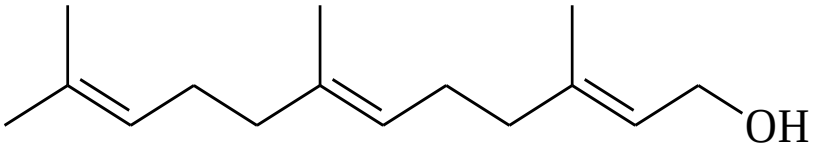


α-Pinene
occurs in turpentine oil

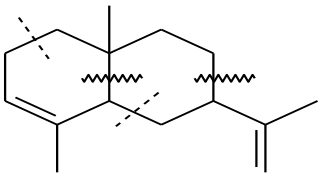


Camphor
occurs in camphor tree

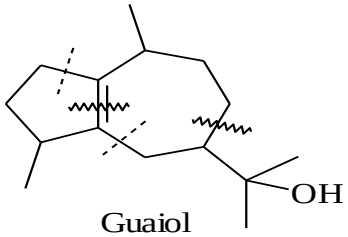
Sesquiterpenes:



Farnesol
occurs in oil of ambrette seeds

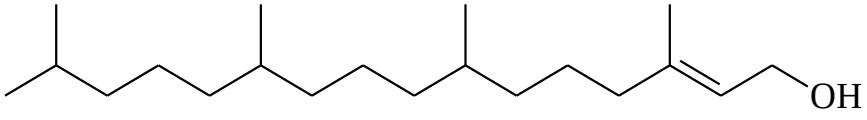


α-Selinene
occurs in celery oil

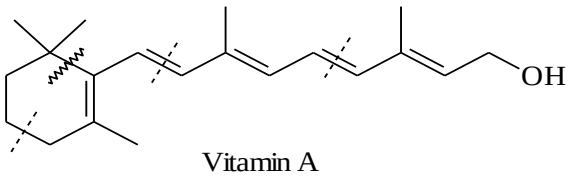


Guaiol
occurs in guaicum wood oil

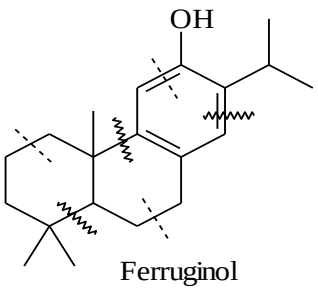
Diterpenes:



Phytol
is produced from hydrolysis of chlorophyll

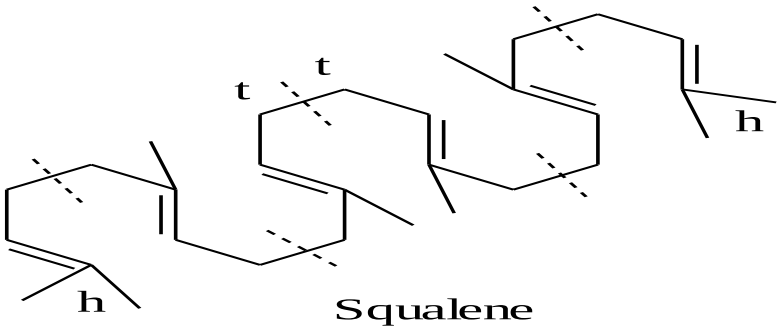


Vitamin A
occurs in carrot

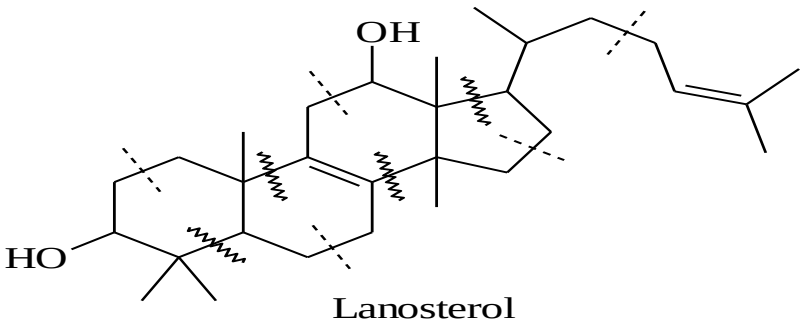


Ferruginol
occurs in *Podocarpus ferrugineus*

Triterpenes:

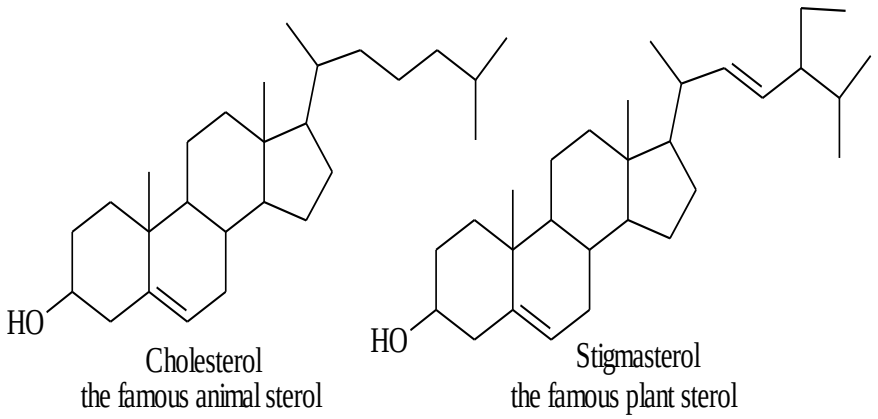


Squalene
occurs in olive oil



Lanosterol

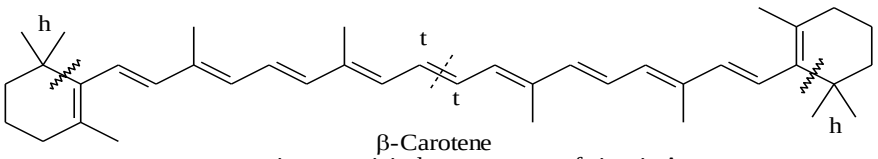
- **Sterols**



Cholesterol
the famous animal sterol

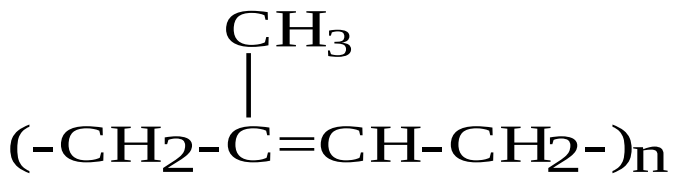
Stigmasterol
the famous plant sterol

Tetraterpenes:



β-Carotene
occurs in carrot, it is the precoursor of vitamin A

- **Polyterpenes**

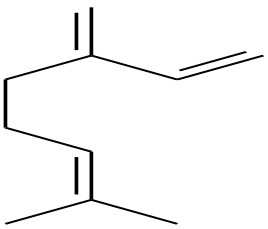


Polyisoprene, natural rubber

Structure-elucidation and Synthesis of selected terpenoids

Acyclic monoterpenes

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



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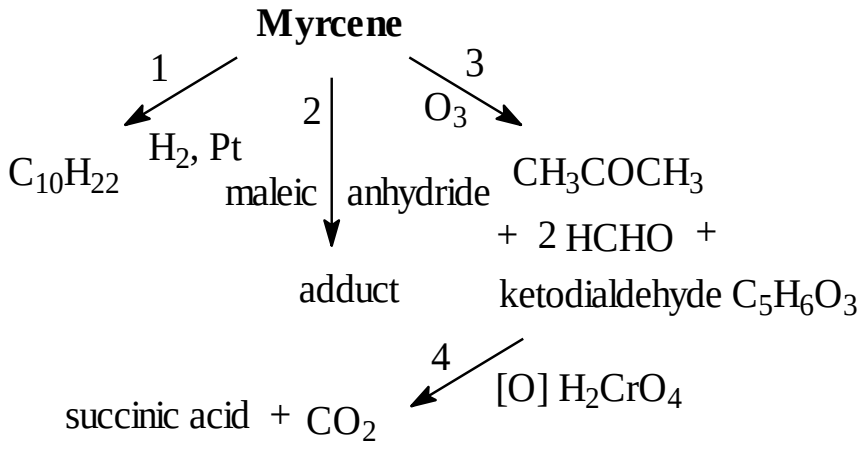

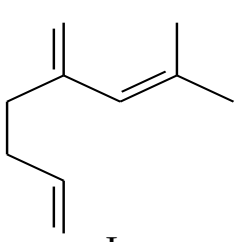

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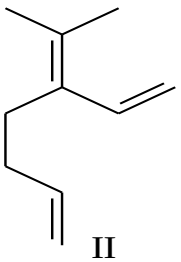

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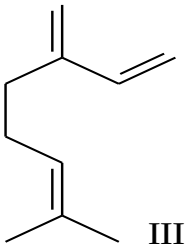
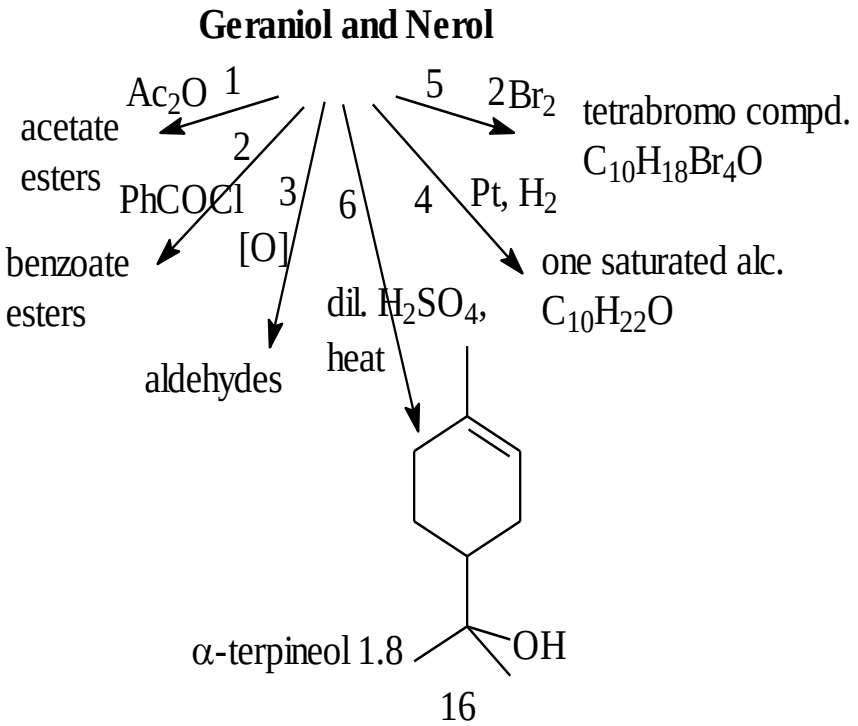
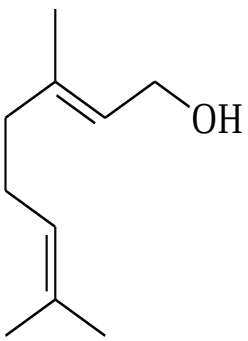


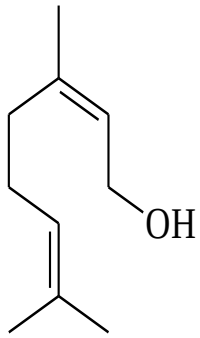
III

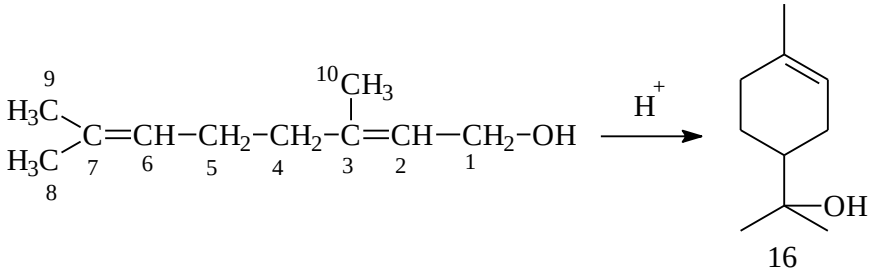
Geraniol and Nerol

$C_{10}H_{18}O$









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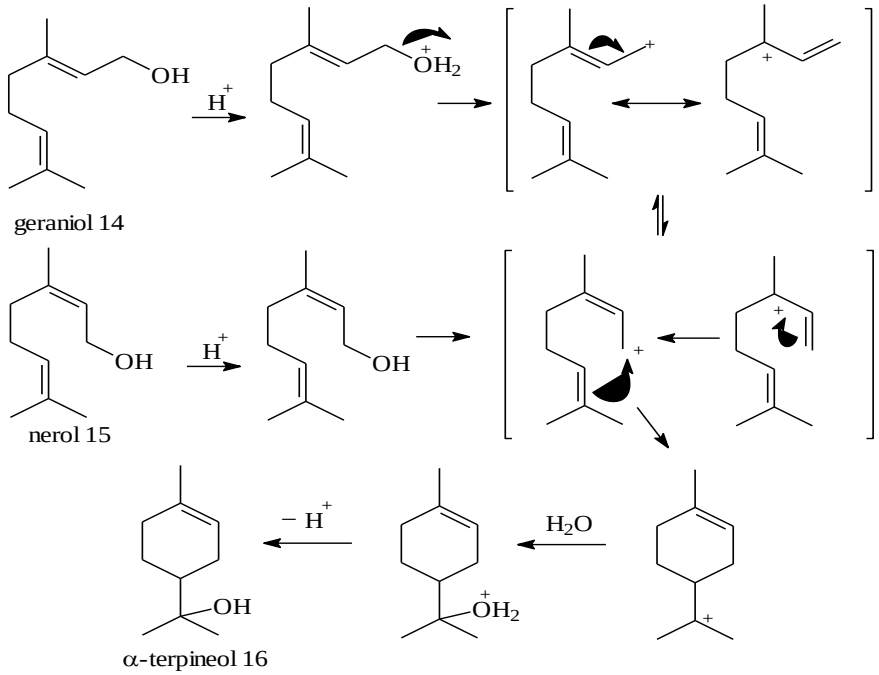
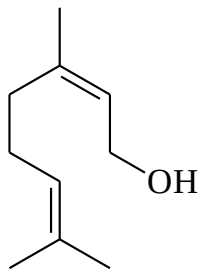
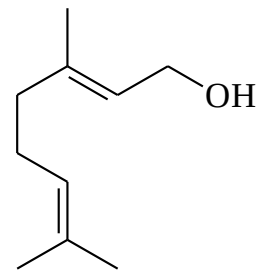




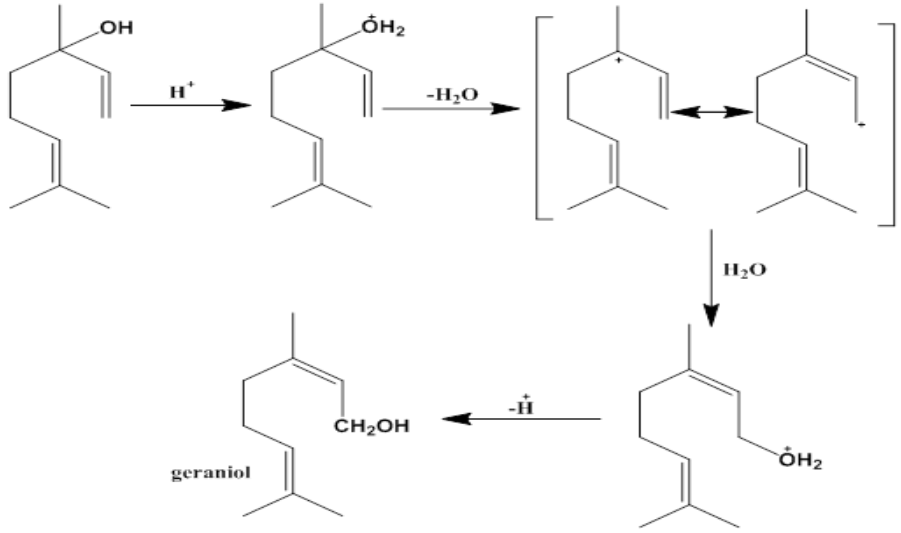
cis or Z



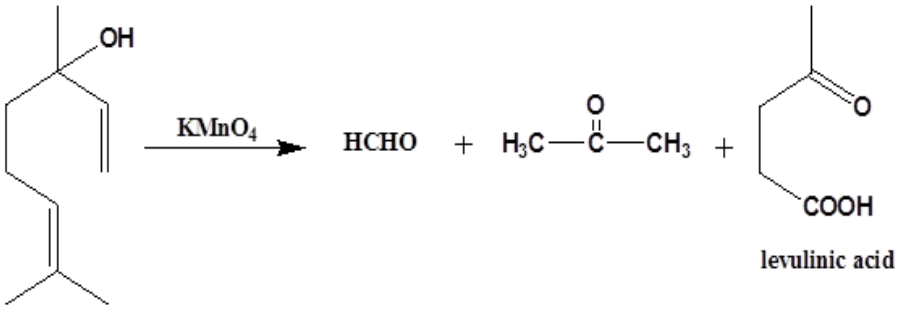
trans or E

Linalool ($C_{10}H_{18}O$)

1. **Elemental analysis shows that the molecular formula of linalool is $C_{10}H_{18}O$.**
2. **Catalytic hydrogenation of linalool give $C_{10}H_{22}O$,indicates the presence of two π–bonds.**
3. **Bromination of linalool give $C_{10}H_{18}Br_4O$, indicates the presence of two π–bonds.**
4. **Reaction of linalool with maleic anhydride give no adduct, this indicates the presence of isolated π-bonds.**
5. **Reaction of linalool with acetic anhydride give acetate, and with benzoyl chloride give benzoate, this indicates the presence of (OH) group.**
6. **Oxidation of linalool give no reaction, this indicates that (OH) is tertiary alcohol.**
7. **It is optically active. (-) form occurs in rose oil, and (+) form in orange oil.**
8. **Linalool reacts with acids and converted to geraniol.**

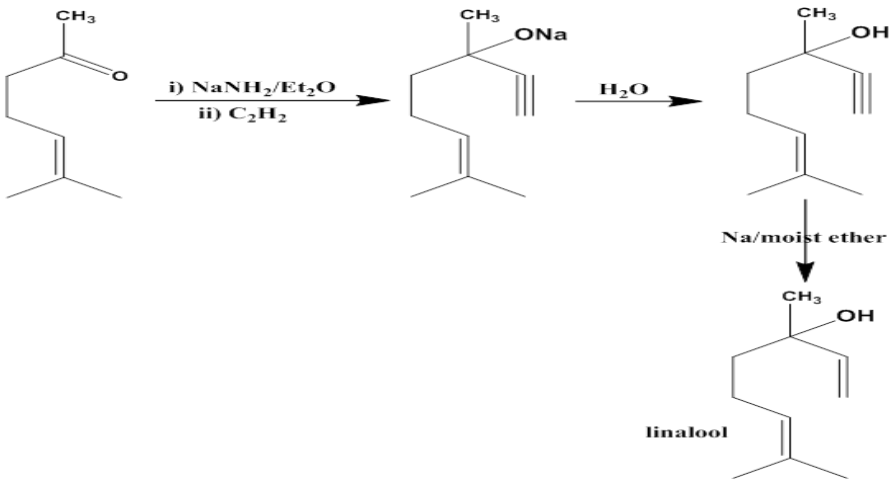


1. **Ozonolysis:**

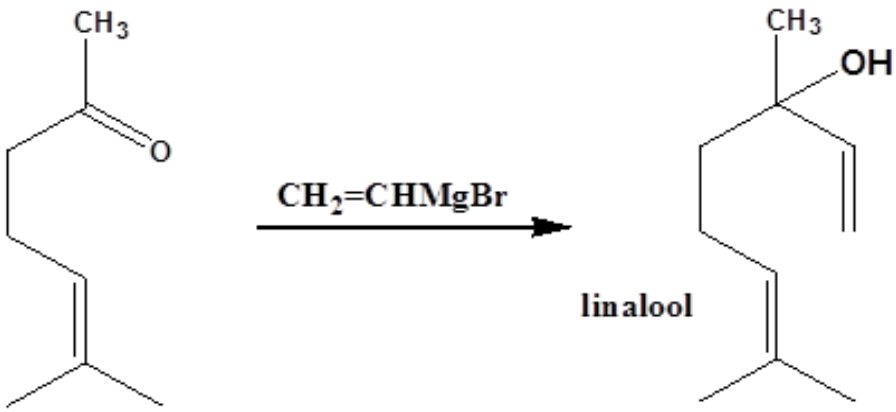


1. **Synthesis of linalool:**

a. **From methyl heptanone with acetylene followed by partial reduction of the triple bond to give linalool.**

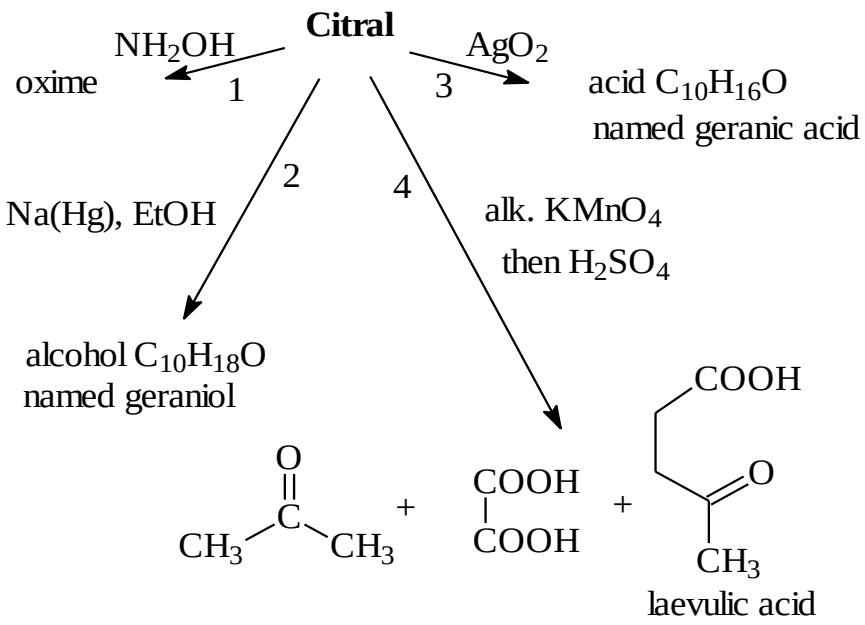


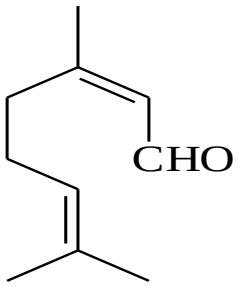
b- **Normant (1955): from methyl heptanone with vinyl magnesium bromide.**

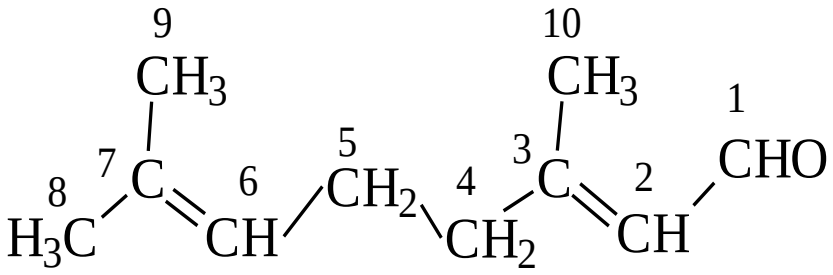


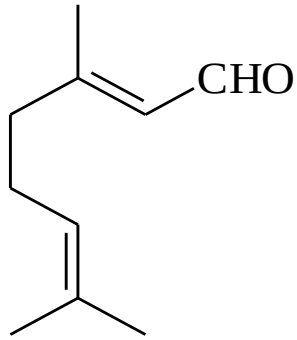
Citral

$C_{10}H_{16}O$

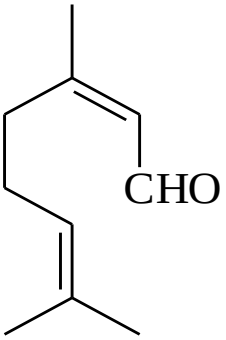








citral-a or geranial

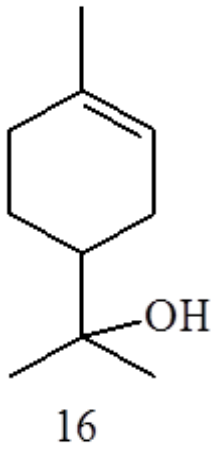


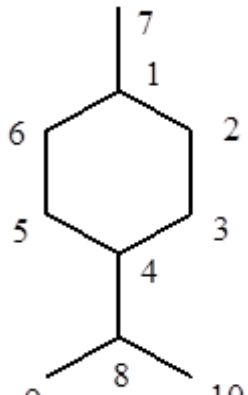
citral-b or neral

Monocyclic monoterpenes

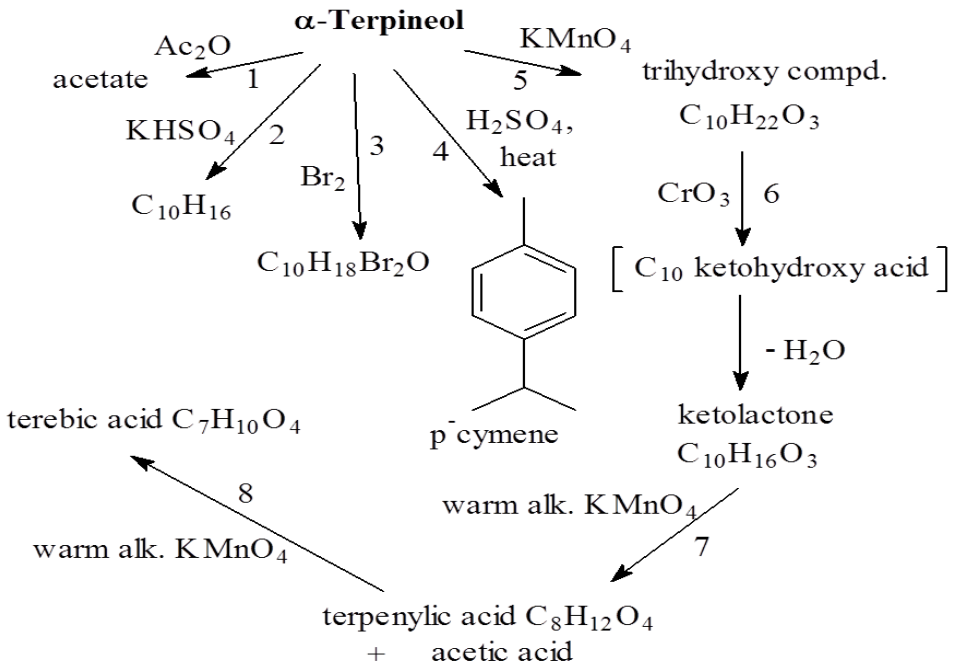
α-Terpineol

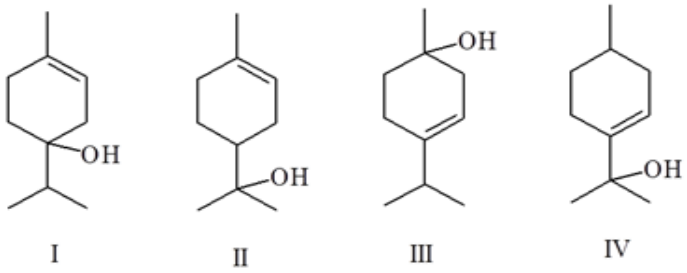
$C_{10}H_{18}O$

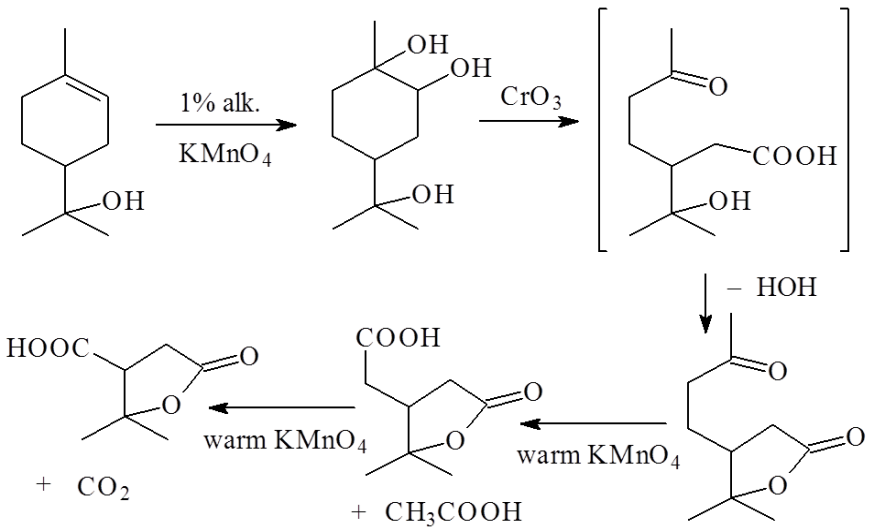




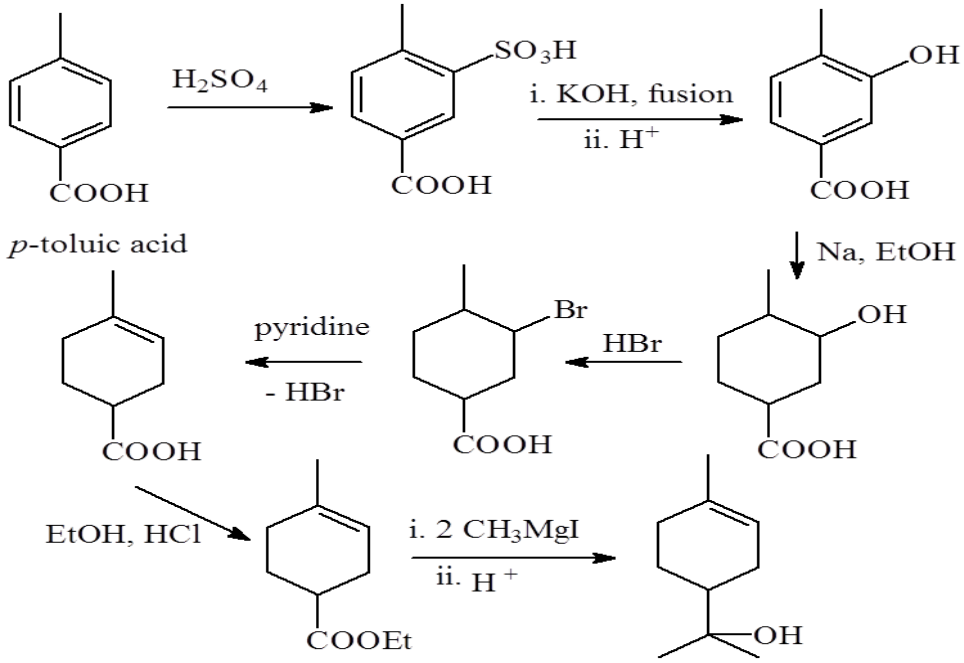
p-menthane or
hexahydro- *p*-cymene

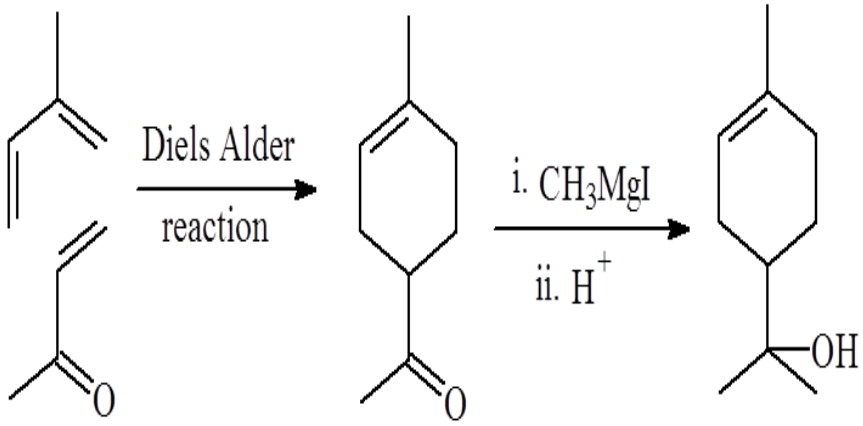



OH
OH
OH
OH
I
II
III
IV


OH
1% alk.
KMnO4
OH
OH
OH
CrO3
O
COOH
OH
– HOH
O
O
O
warm KMnO4
COOH
O
O
O
warm KMnO4
HOOC
O
O
+ CO2
+ CH3COOH

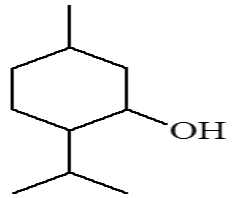
Synthesis of α-terpineol





Carvone

$C_{10}H_{14}O$



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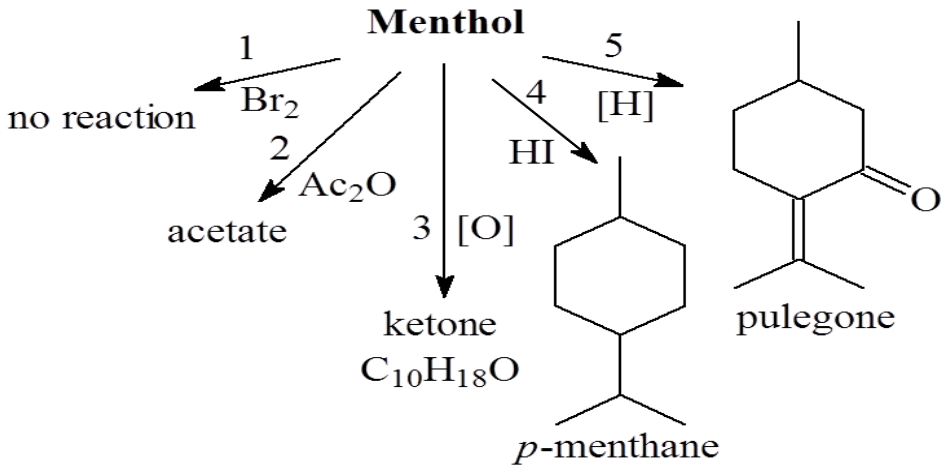
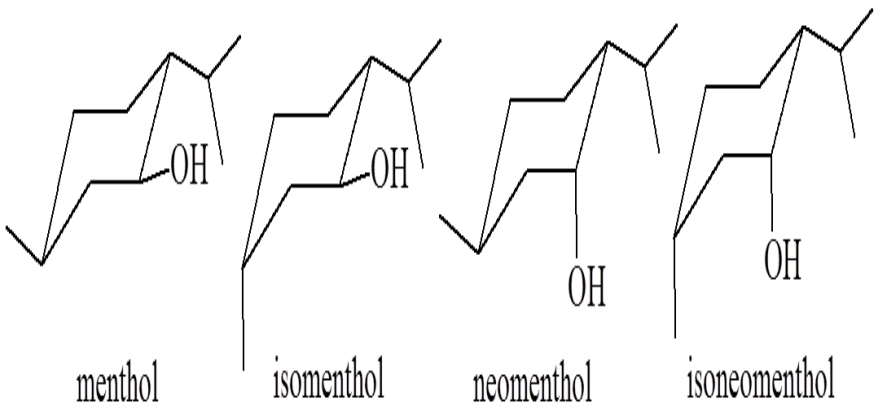
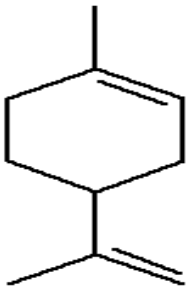


Stereochemistry of menthol



Limonene

$C_{10}H_{16}$



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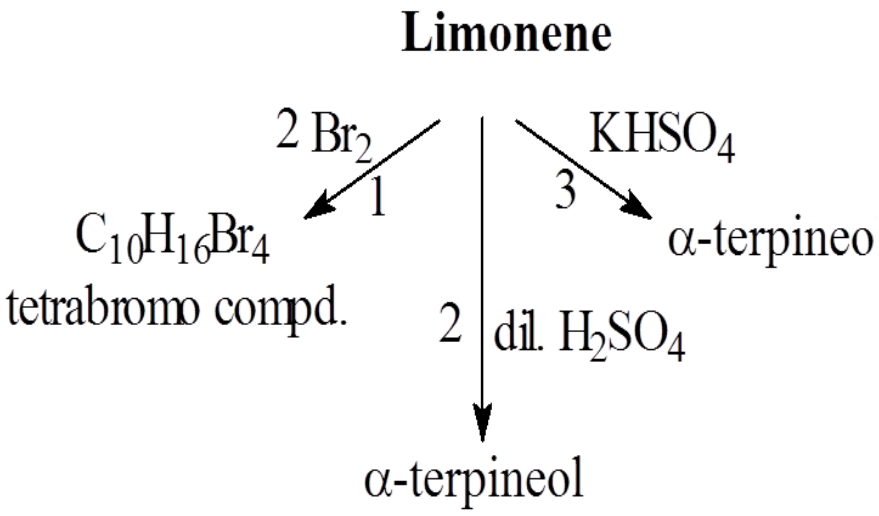
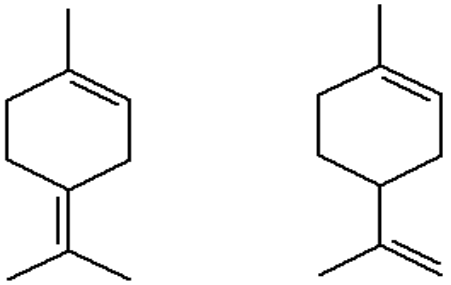




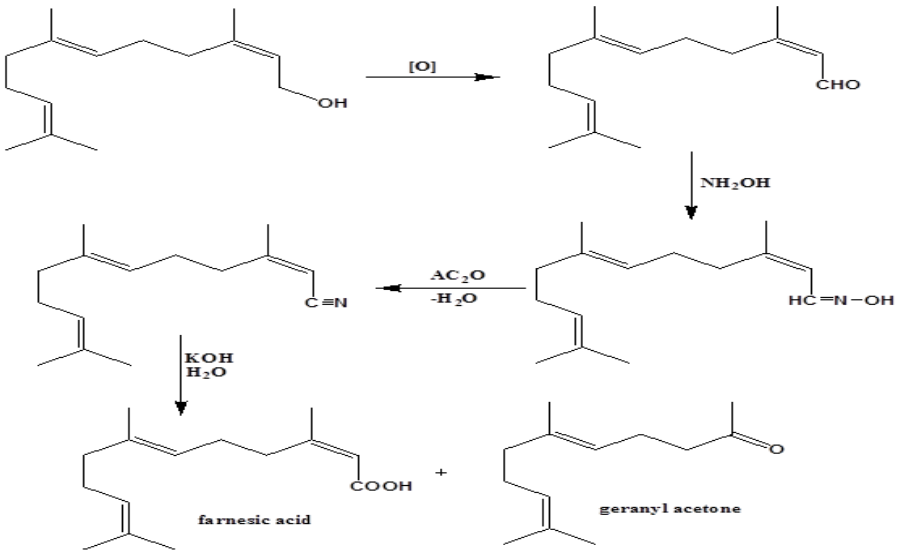
I II

Sesqueterpenes and Diterpenes

Sesqueterpenes

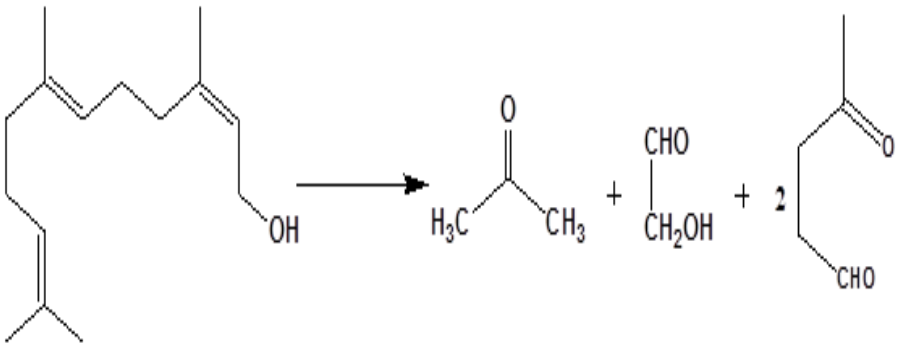
Farnesol ($C_{15}H_{26}O$)

- **Elemental analysis shows that the molecular formula of farnesol is $C_{15}H_{26}O$.**
- **Catalytic hydrogenation of farnesol give $C_{15}H_{32}O$, indicates the presence of three π–bonds.**
- **Bromination of farnesol give $C_{15}H_{26}Br_6O$, indicates the presence of three π–bonds.**
- **Reaction of farnesol with maleic anhydride give no adduct, this indicates the presence of isolated π-bonds.**
- **Reaction of farnesol with acetic anhydride gives acetate, and with benzoyl chloride gives benzoate, this indicates the presence of (OH) alcoholic group.**
- **Oxidation of farnesol give an aldehyde farnesal ($C_{15}H_{24}O$), this indicates that (OH) is primary alcohol.**



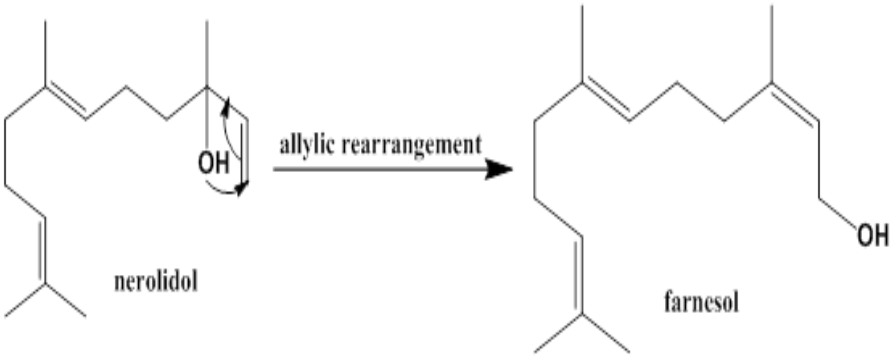
1. **Ozonolysis:**

- **Ozonolysis of farnesol give acetone & acryledehyde & two livunaldehyde.**

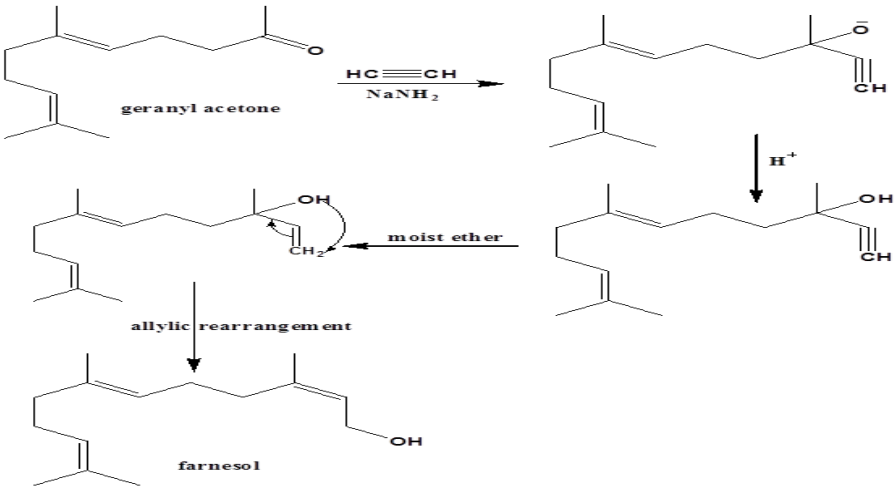


Synthesis of farnesol

- **From nerolidol:**



- **From geranyl acetone:**



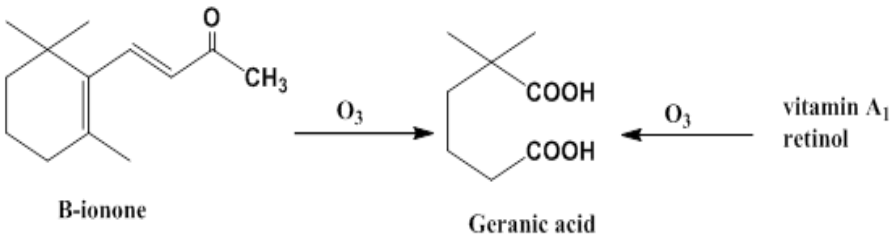
Diterpenes

Retinol (vitamin A_1) $C_{20}H_{30}O$

1. **Elemental analysis shows that the molecular formula of retinol is $C_{20}H_{30}O$.**
2. **Catalytic hydrogenation of retinol give $C_{20}H_{40}O$, indicates the presence of five π–bonds and it is monocyclic.**
3. **Bromination of retinol give $C_{20}H_{30}Br_{10}O$, indicates the presence of five π–bonds and it is monocyclic.**
4. **Reaction of retinol with maleic anhydride give adduct and consumed more than one molecule of maleic anhydride, this indicates the presence of multiple conjugated π-bonds.**
5. **U.V. absorption give λmax = 328, this indicates the presence of conjugated polyene.**
6. **Reaction of retinol with acetic anhydride gives acetate, and with benzoyl chloride gives benzoate, this indicates the presence of (OH) alcoholic group.**

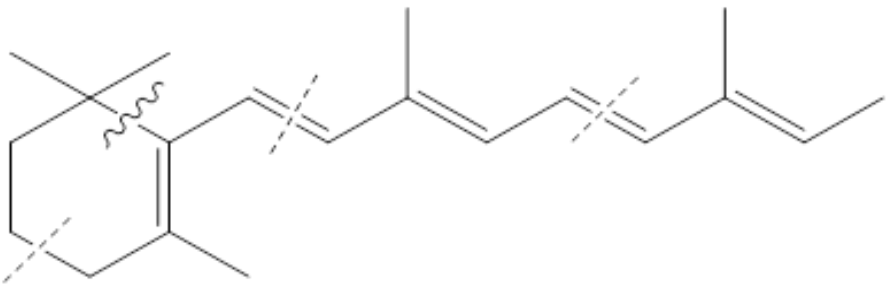
7. **Oxidation of retinol give an aldehyde retinal ($C_{20}H_{28}O$), this indicates that (OH) is primary alcohol.**

8. **Ozonolysis of retinol give geranic acid, also, ozonolysis of β-ionone give geranic acid, this indicates that retinol contains β-ionone.**

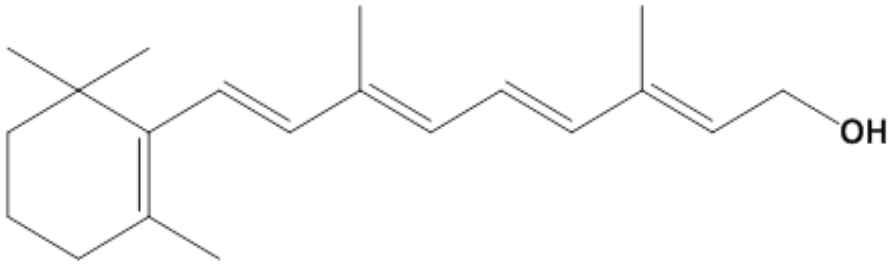


9- **Oxidation of retinol with $KMnO_4$ give acetic acid, this indicates that retinol contains some (-C-CH_3).**

10- **from the isoprene rule the hydrocarbon skeleton of retinol is:**

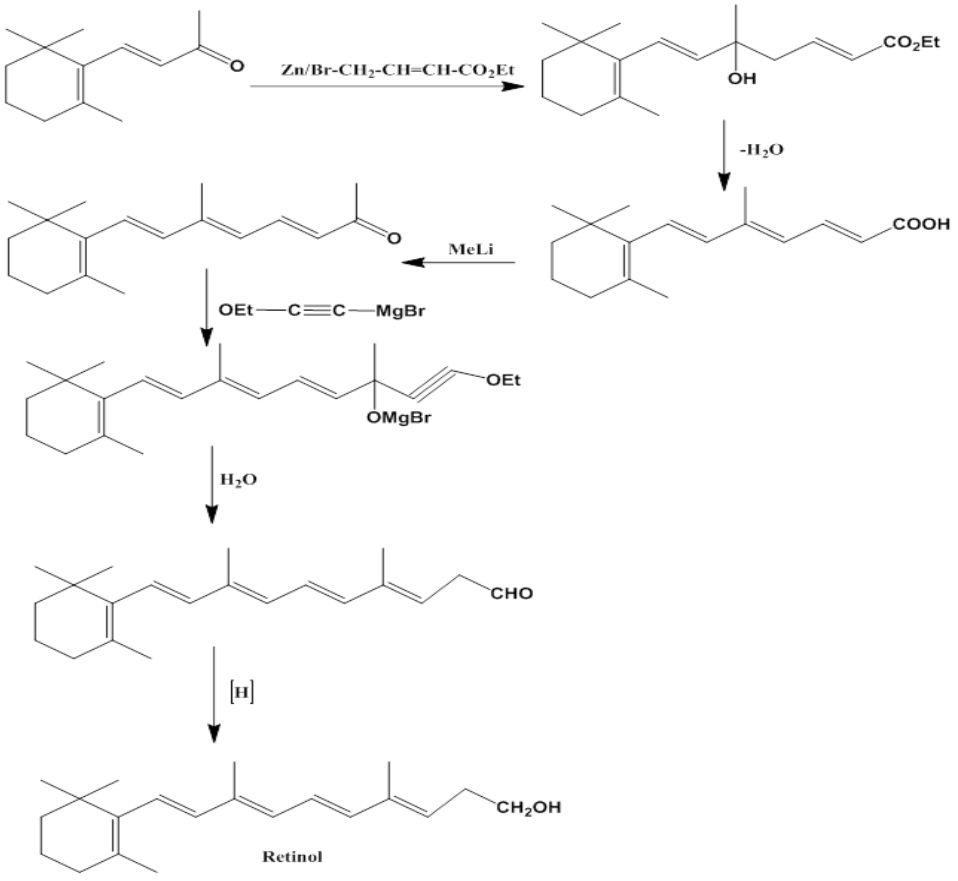


- **Structure of retinol is:**



- **The structure of retinol is half of β-carotene.**

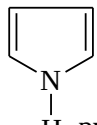
- **Synthesis of retinol:**



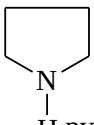
Alkaloids

- **Structure and 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**
- **(10) Tropolone alkaloids**

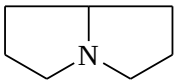
Basic nuclei of alkaloids



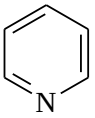
pyrrole



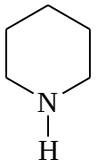
pyrrolidine



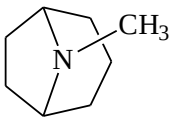
pyrrolizidine



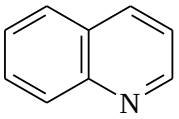
pyridine



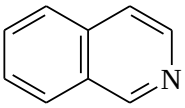
piperidine



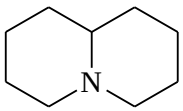
tropane
(piperidine-pyrrolidine)



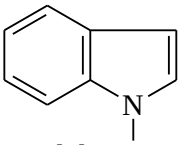
quinoline



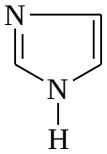
isoquinoline



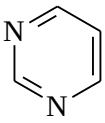
nor-hipinane



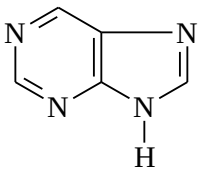
indole
(benzopyrrole)



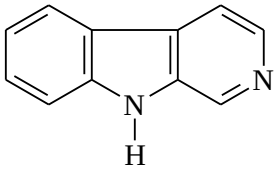
imidazole



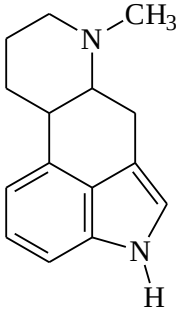
pyrimidine



purine

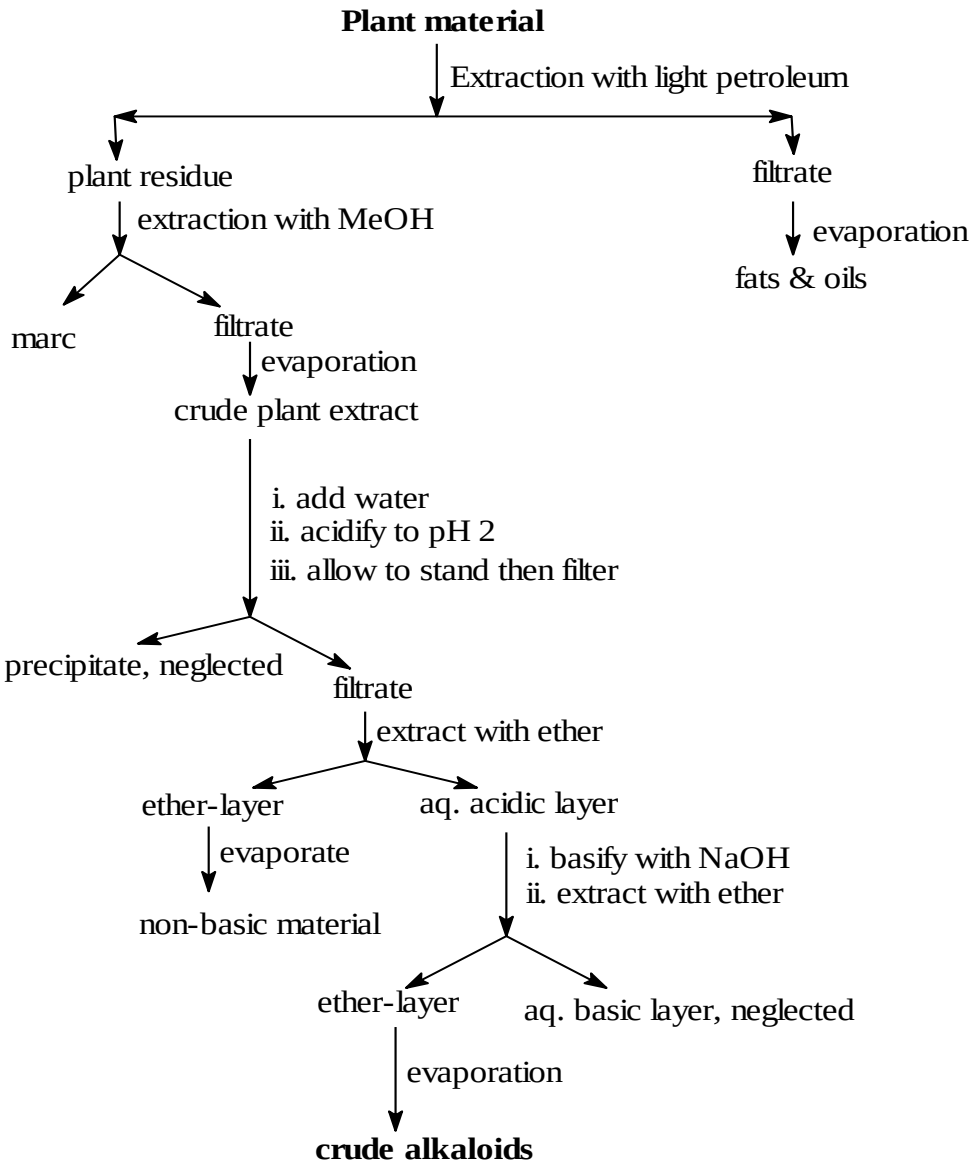


carboline



indole + hydroquinoline

Isolation of alkaloids



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- The presence of unsaturation in an alkaloid may ascertained by the addition of bromine or halogen acids or by hydroxylation with dilute alkaline permanganate.**

- **3- Frequently an alkaloid is cleaved into simple fragments by hydrolysis with water, acid or alkali and the fragments so obtained are examined separately since the structure of the fragment may easily be established than that of the whole molecule.**

- **4- The next step involves in ascertaining the functional nature of oxygen and nitrogen atoms either in the molecule itself or in its fragments obtained by hydrolysis as in step 2.**

- **5- Functional nature of oxygen: The oxygen atom may be present in the form of alcoholic or phenolic hydroxyl (-OH), methoxyl ($-OCH_3$),**

acetoxyl reOCOCH$_3$), benzoxyl (- COC$_6$H$_5$), carboxyl (-COOH) or carbonyl (C=O) group, various oxygen functional groups can be characterized according to the following characteristics

- **(i) 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.**

- **(i) 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.**

- **(iii) 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.

- **(IV) 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 hydriodic 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.

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

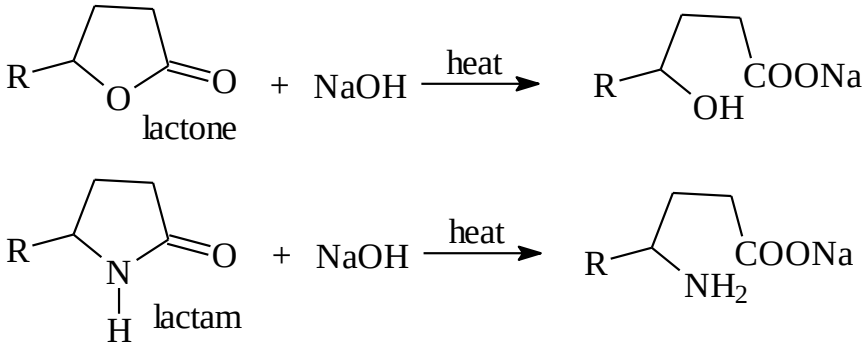
The related group, methylenedioxy (-O-CH_2-O-) is estimated on the basis that it librates formaldehyde

when treated with hydrochloric or sulphuric acid; thus the quantitative estimation of formaldehyde will give the number of methylenedioxy groups.

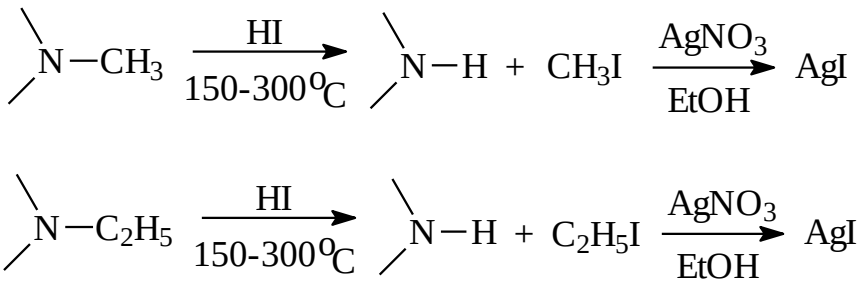
- **The number of moles of silver iodide is equivalent to the number of alkoxyl groups in the alkaloid.**
- **The related group, methylenedioxy (-O-CH_2-O-) is estimated on the basis that it librates formaldehyde when treated with hydrochloric or sulphuric acid; thus the quantitative estimation of formaldehyde will give the number of methylenedioxy groups.**
- **(vi) Ester groups (-OCOR) : Esters (such as -$OCOCH_3$, -$OCOC_6H_5$) and related groups like amide, lactone, and lactam are detected by their hydrolysis with water, dilute acids, alkali to hydroxyl and acidic compounds. The nature is established by knowing the nature of the acid.**

$$—CONH_2 + NaOH \xrightarrow{heat} —COONa + NH_3$$

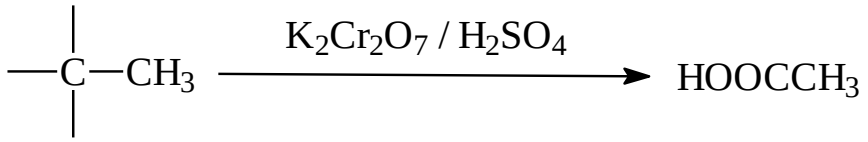
$$—COOR + NaOH \xrightarrow{heat} —COONa + ROH$$



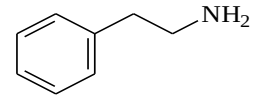
- **functional nature of nitrogen**
- **The N-alkyl groups are frequently estimated by Herzig Meyer method**



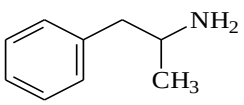
- **Estimation of C-methyl groups**



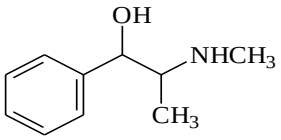
Phenylethyl amine Alkaloids



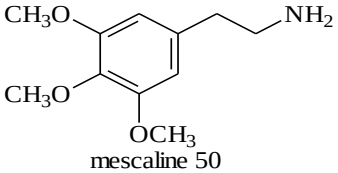
β-phenylethyl amine 47



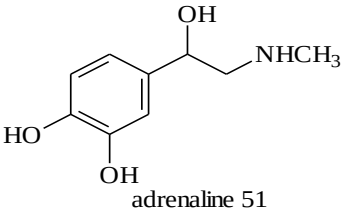
amphetamine 48



ephedrine 49

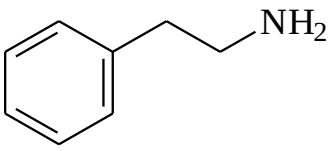


mescaline 50



adrenaline 51

β-Phenylethyl amine



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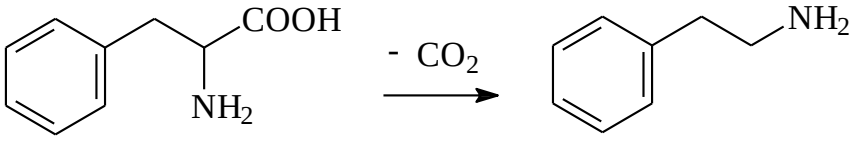
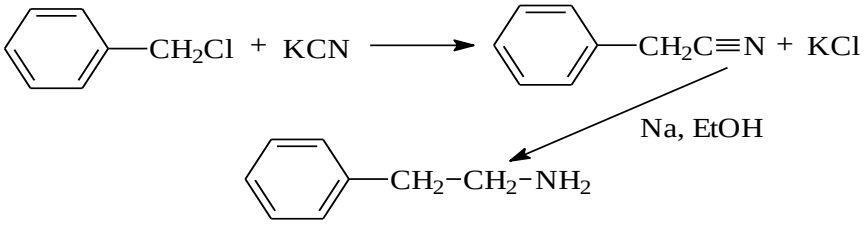
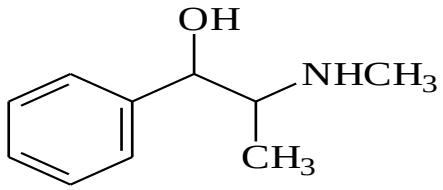


phenylalanine β-phenylethyl amine



(-)- Ephedrine



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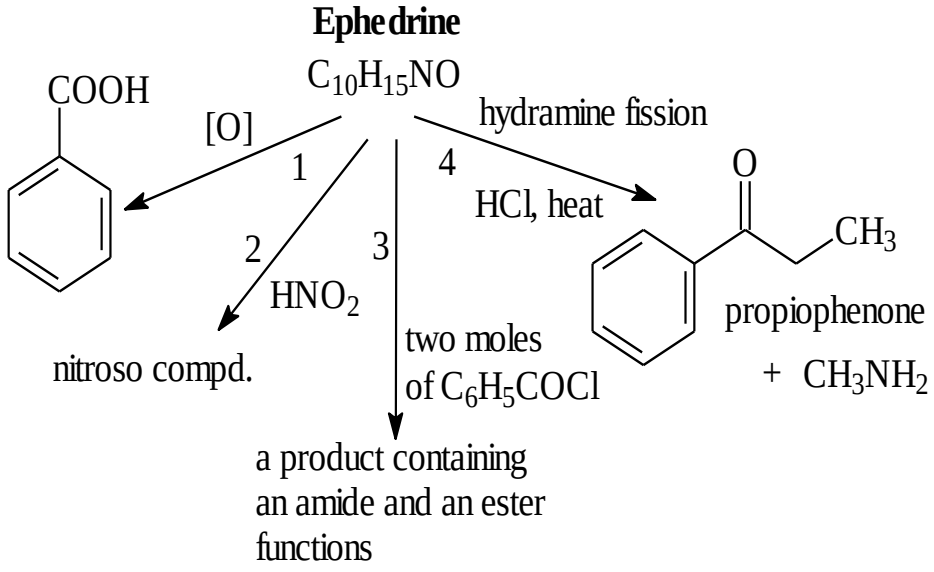
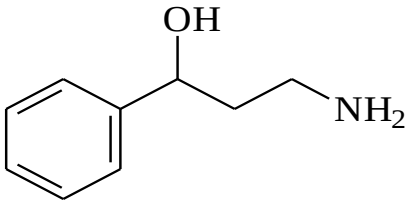
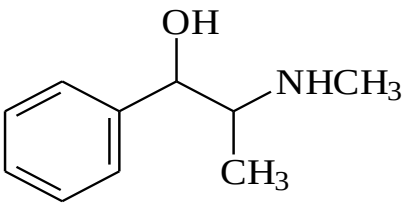
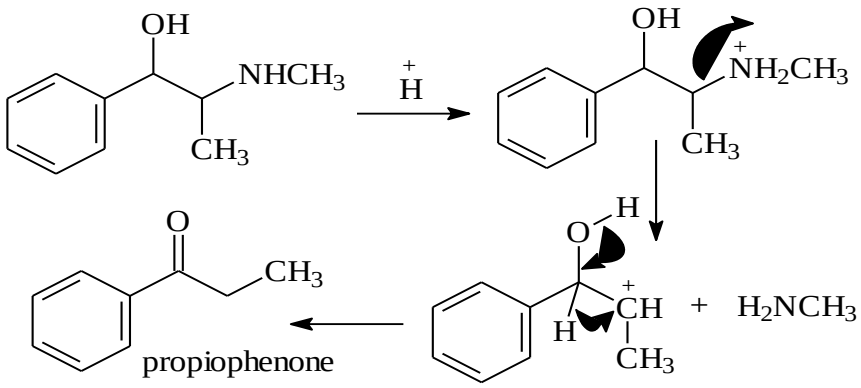


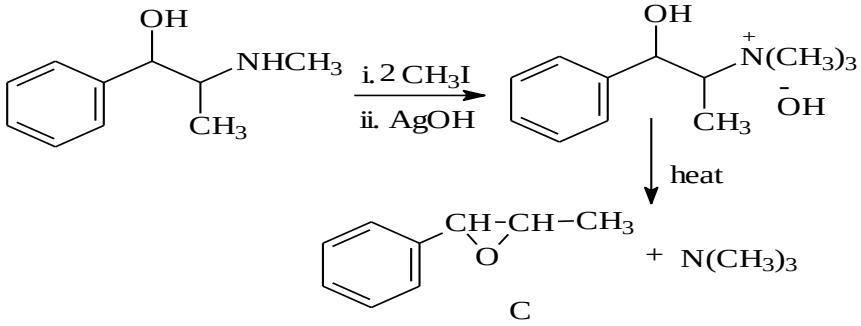


A

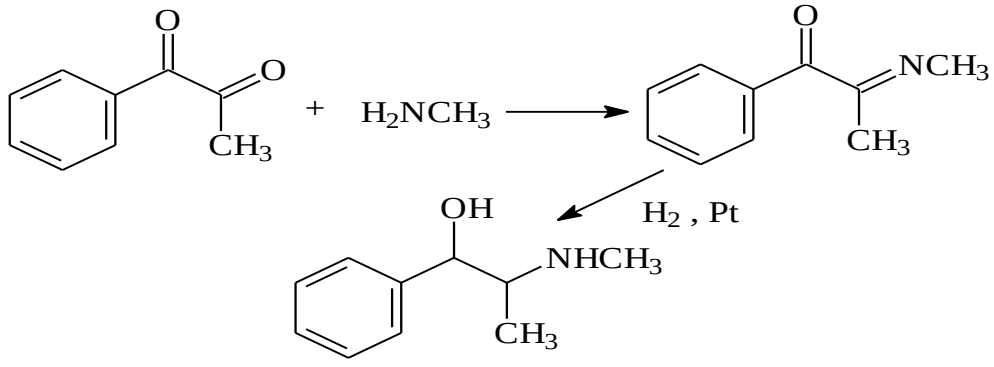


B





Synthesis of ephedrine

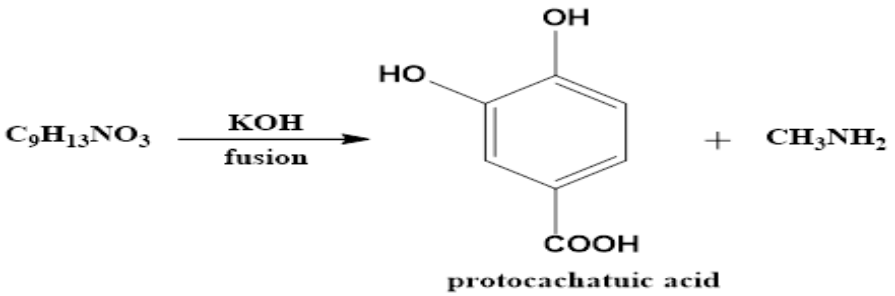


Adrenaline

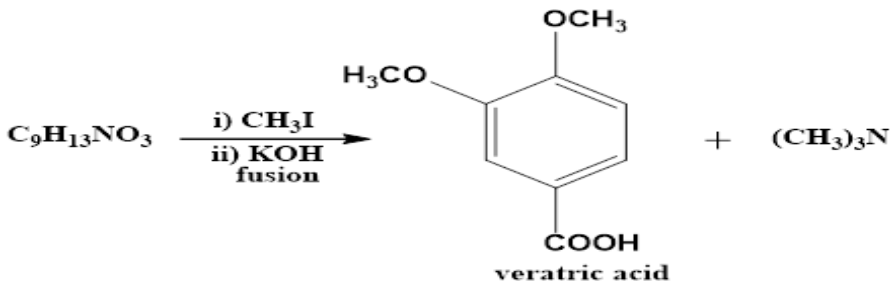
$C_9H_{13}NO_3$

- **Adrenaline is colorless crystals.**
- **Reaction of adrenaline with three moles of benzoyl chloride give benzoate, this indicates the presence of three (OH) groups.**
- **Adrenaline is soluble in NaOH and reprecipitated by carbon dioxide, so adrenaline has phenolic character.**
- **Reaction of adrenaline with $FeCl_3$ give green color, so adrenaline is catechol having a side-chain, so adrenaline must contain two phenolic hydroxyl groups, and the third must be an alcoholic hydroxyl group and present in the side-chain.**
- **Oxidation of adrenaline give ketone, so the alcoholic hydroxyl group is secondary (CHOH).**
- **Boiling of adrenaline with aqueous KOH, methyl amine (CH_3NH_2) is involved, thus a methylamine group is present.**
- **Fusion of adrenaline with KOH, the product is protocatechuic acid and methylamine. On the other hand, methylation of adrenaline followed by fusion with KOH gives veratric acid and trimethylamine, so, the formation of**

trimethylamine indicates that the nitrogen atom must occur at the end of the side-chain.

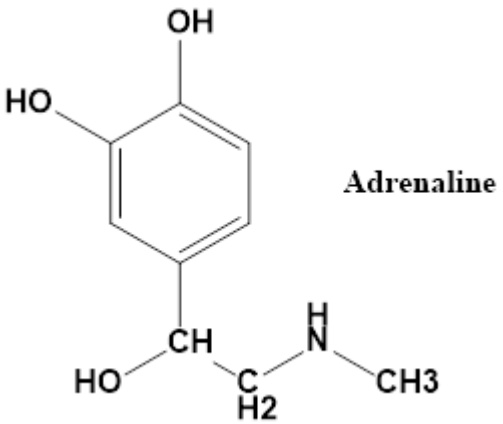


protocachatuic acid



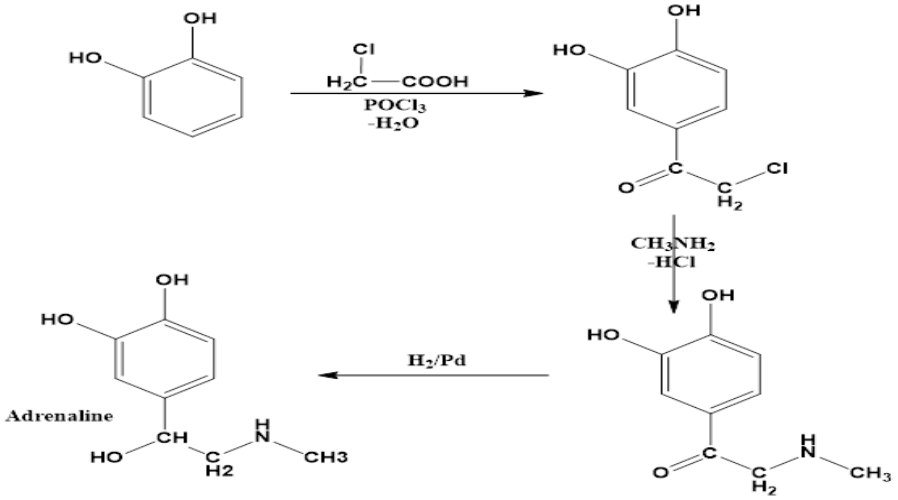
veratric acid

- **<u>Adrenaline is optically active, it contain at least one chiral center.</u>**
- **So, the structure of adrenaline is:**



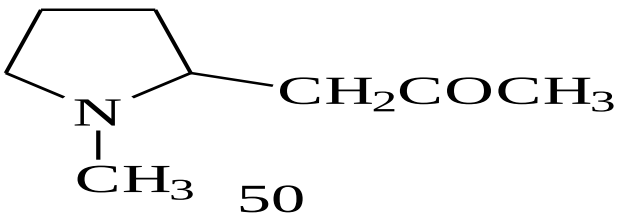
Adrenaline

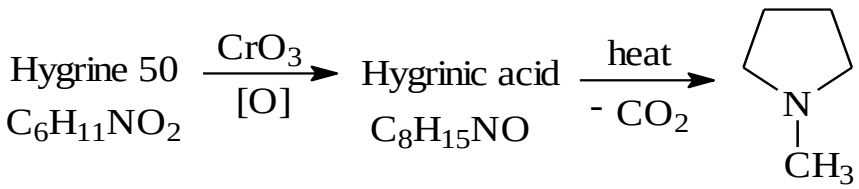
- **Synthesis of adrenaline from catechol:**



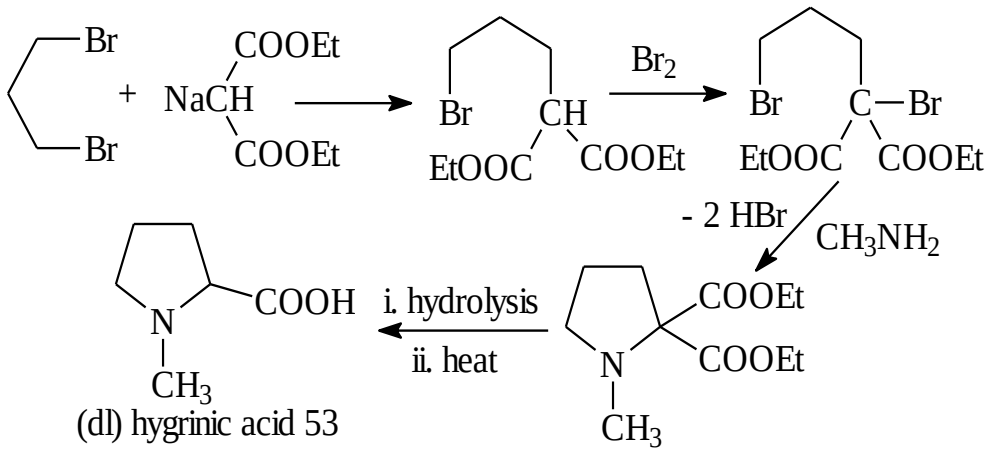
Pyrrolidine Alkaloids

Hygrine



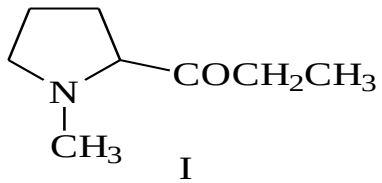


Synthesis of hygrinic acid

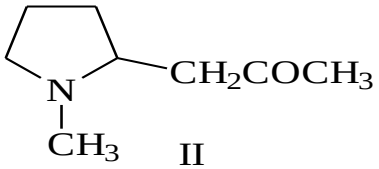


(dl) hygrinic acid 53

Based on the above results, hygrine 50 may be formulated either I or II.

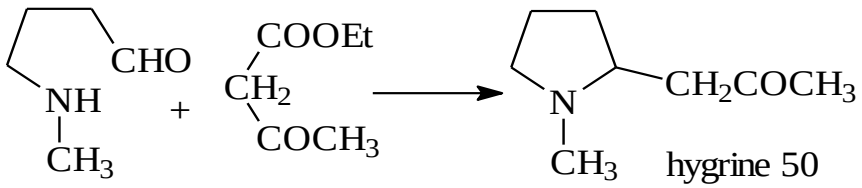


I



II

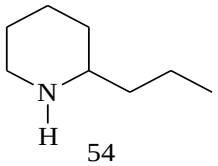
Synthesis of hygrine



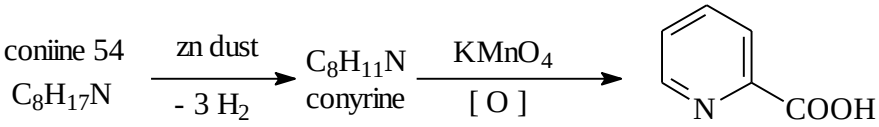
hygrine 50

Pyridine or Piperidine alkaloids

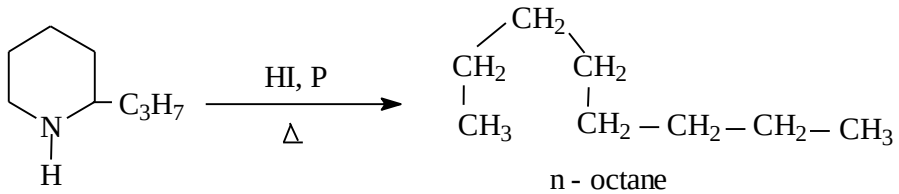
Coniine



54

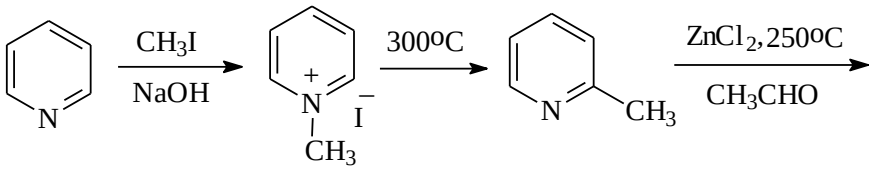


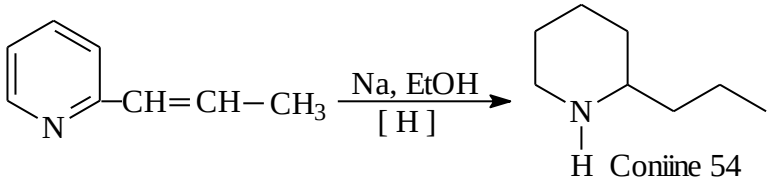
pyridine-2-carboxylic acid



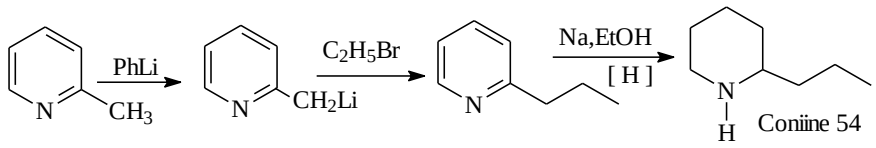
n - octane

Synthesis of Coniine



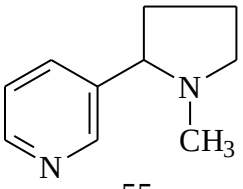


Coniine 54



Pyridine, pyrrolidine alkaloids

Nicotine



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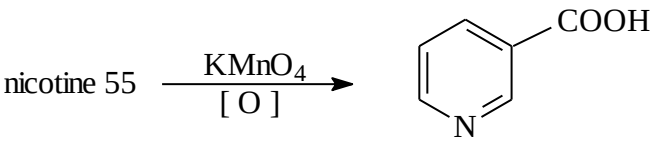
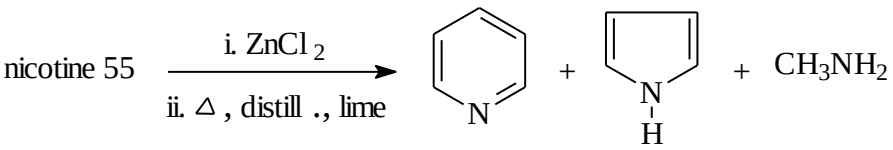
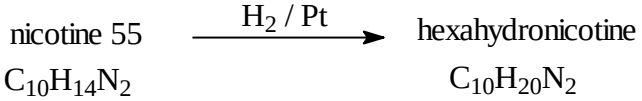
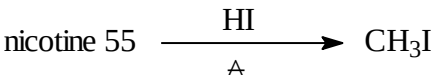
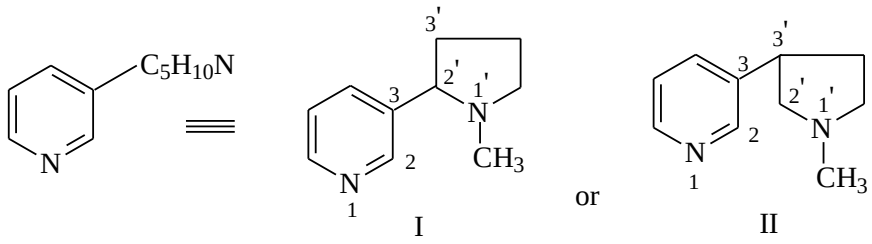
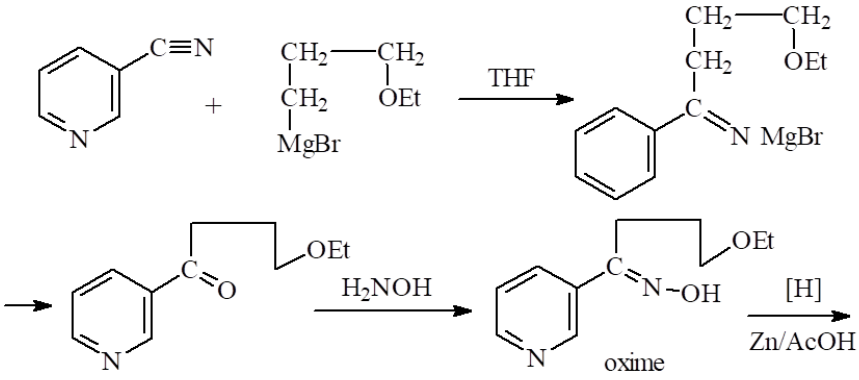


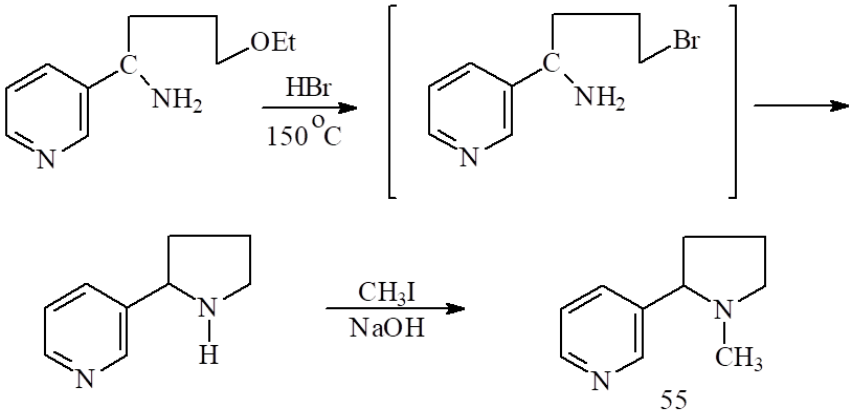







C5H10N
I
or
II


THF
MgBr
H2NOH
oxime
[H]
Zn/AcOH


HBr
150 °C
CH3I
NaOH

55

Quinoline Alkaloids

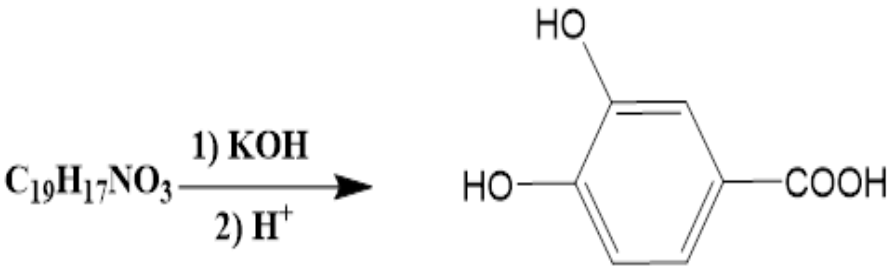
Cusparine

$C_{19}H_{17}NO_3$

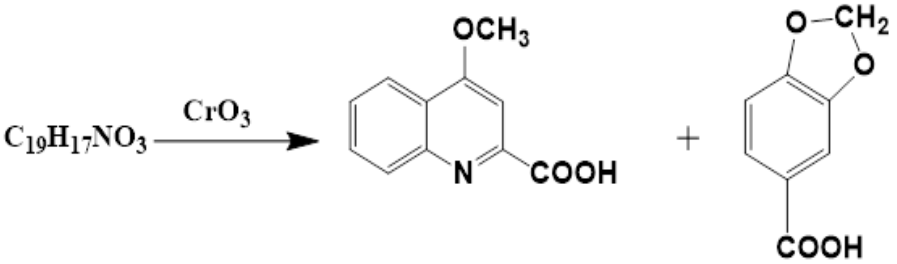
1. **Cusparine has been to contain one methoxy group by Zeisel method.**

- **$C_{19}H_{17}NO_3$ + HI ---------- CH_3I ---- $AgNO_3$ --- AgI**

- **Fusion of cusparine with potassium hydroxide, protochtechuic acid was obtained.**

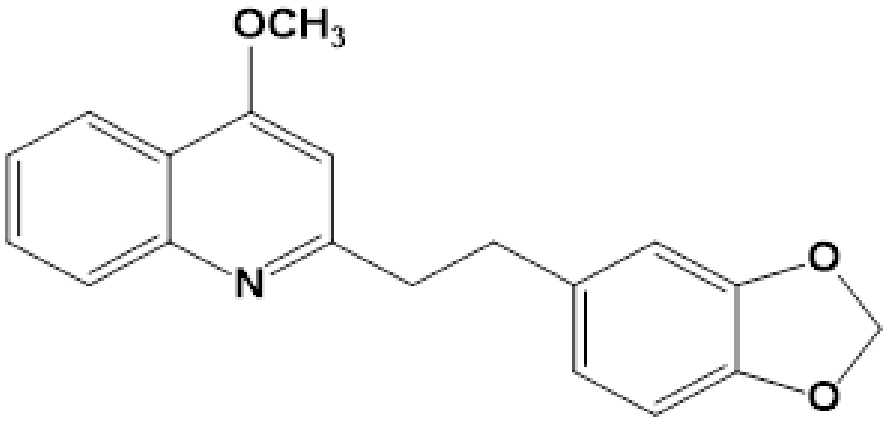


- **Oxidation of cusparine gives piperonylic acid and 4-methoxyquinoline-2-carboxylic acid.**

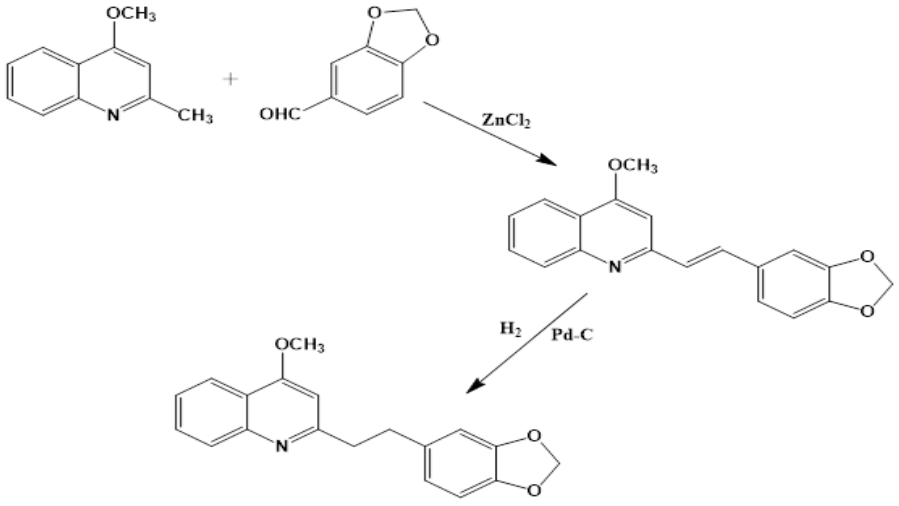


-

- **Consideration of this information led to the suggestion of the following structure of cusparine.**



- **The considered structure for cusparine has been confirmed also by synthesis of it, as follow:**



Isoquinoline alkaloids

Papaverine ($C_{20}H_{21}NO_4$)

- **Papaverine is one of the optically inactive alkaloids.**
- **Papaverine reacts with one molecule of methyl iodide to form a quaternary iodide salt,**
- **$C_{20}H_{21}NO_4$ ------ CH_3I -------- quaternary iodide salt**
- **Thus, the nitrogen atom in papaverine is in the tertiary state.**
- **Application of Zeisel method on papaverine, afforded the presence of four methoxy groups, and the demethylated product is known as papaveroline ($C_{16}H_{13}NO_4$).**
-
- **$C_{20}H_{21}NO_4$ + 4HI ---------- $4CH_3I$ + $C_{16}H_{13}NO_4$**
-

Papaveroline

- **Oxidation of papaverine by using cold dilute permanganate, an alcohol papaverinol ($C_{20}H_{21}NO_5$) is obtained. Oxidation with hot permanganate give a ketone papaveraldine ($C_{20}H_{19}NO_5$) is obtained, thus this indicates that the structure of papaverine must be contain an methylene group ($-CH_2-$).**

- **$(C_{19}H_{19}NO_4)CH_2$ ---[O]--- $(C_{19}H_{19}NO_4)CHOH$ ---[O]-- $(C_{19}H_{19}NO_4)CO$**

- **Papaverine papaverinol papaveraldine**

- **Oxidation of papaverine by concentrated permanganate give:**

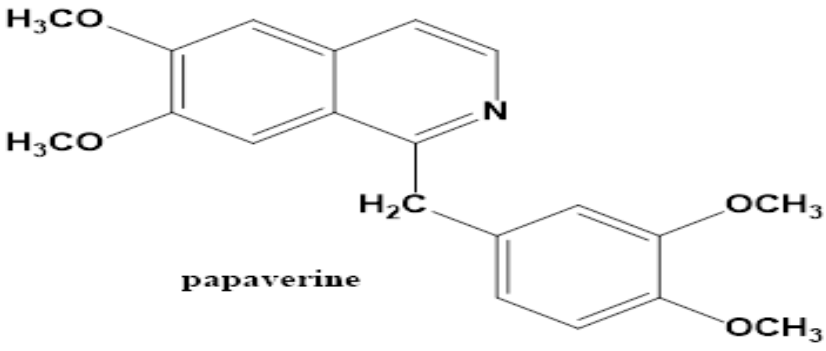
- **veratric acid.**

- **Metahemipinic acid.**

- **Pyridine-2,3,4-tricarboxylic acid.**

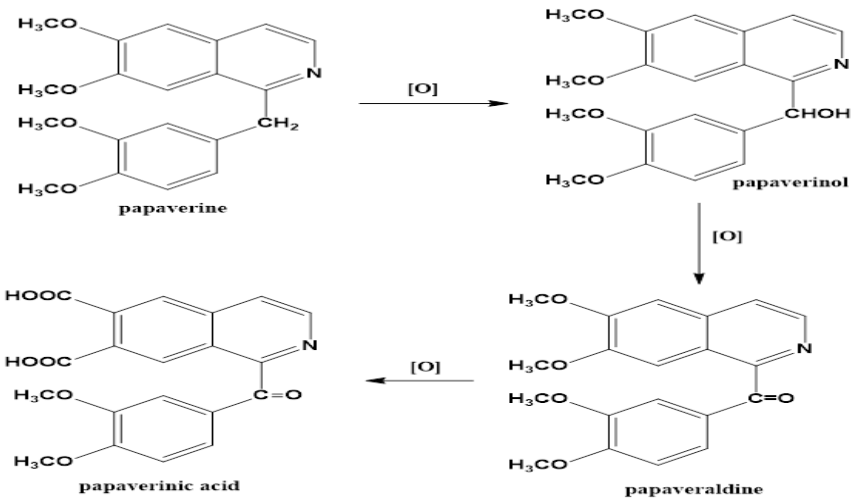
- **6,7-dimethoxyisoquinoline-1-carboxylic acid.**

- **Thus, the structure of papaverine is:**

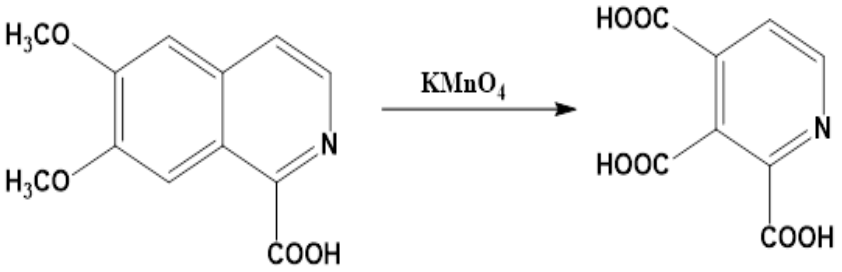


papaverine

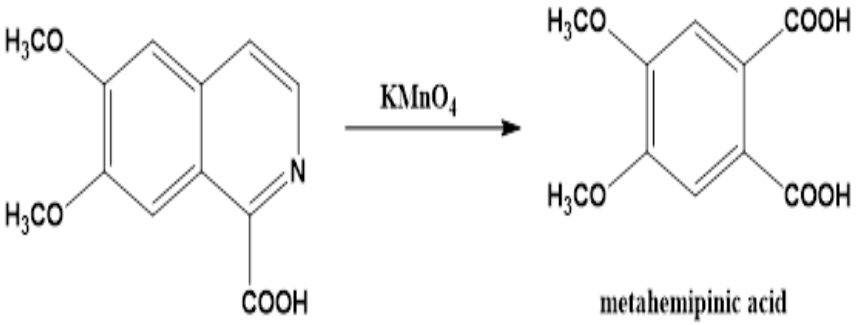
With this formula, we can formulate the oxidation of papaverine as follow:



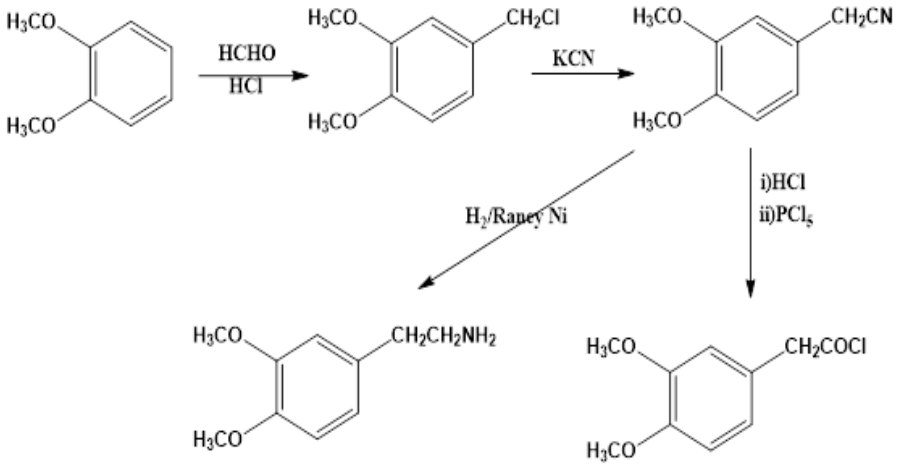
- Pyridine-2,3,4-tricarboxylic acid:

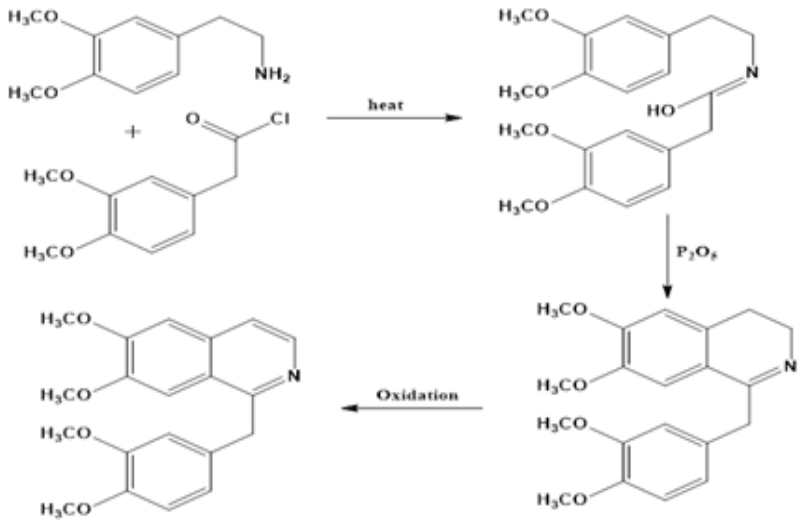


- Metahemipinic acid:



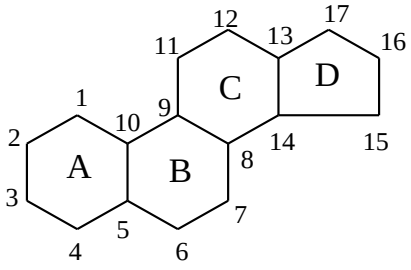
This structure for papaverine has been confirmed by synthesis as follow:



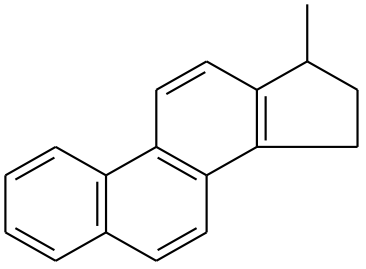


Steroids

- **Steroids (Gk., stereos = solid) are solid alcohols that are widely distributed in the animal and plant kingdoms. The basic skeleton consists of 17 carbon atoms arranged in the form of a perhydro-cyclopentenophenathrene 25. A steroid could be defined, in another way, as any compound which gives Diel's hydrocarbon 26 when distilled with selenium.**



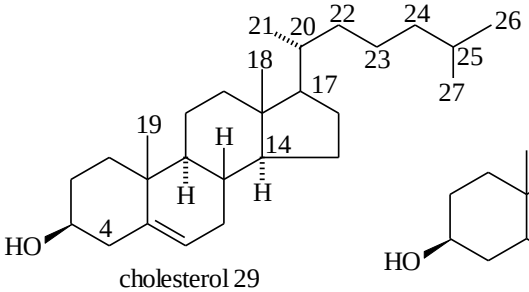
steroid nucleus 25



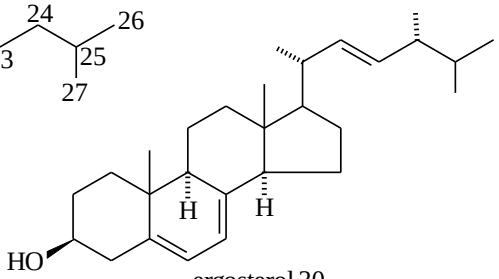
Diel's hydrocarbon 26

Classes of steroids

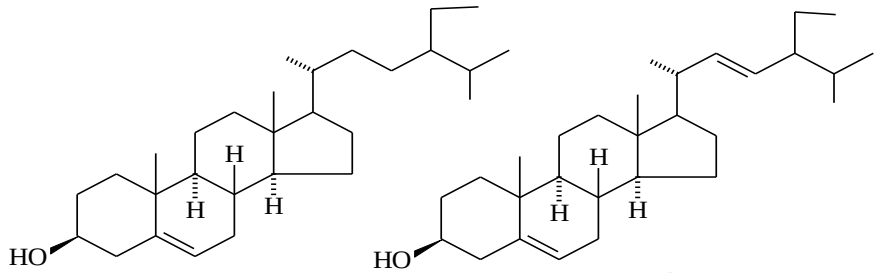
Sterols



cholesterol 29



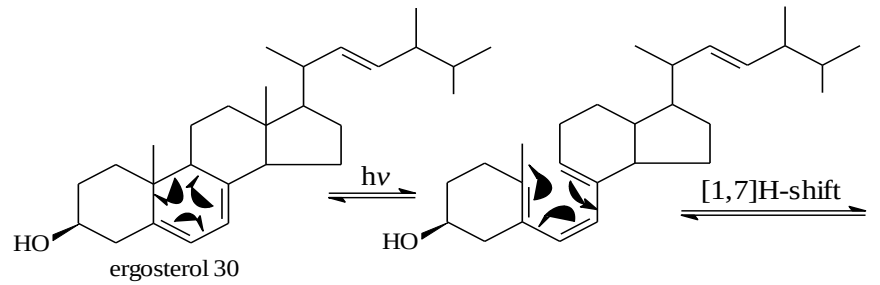
ergosterol 30



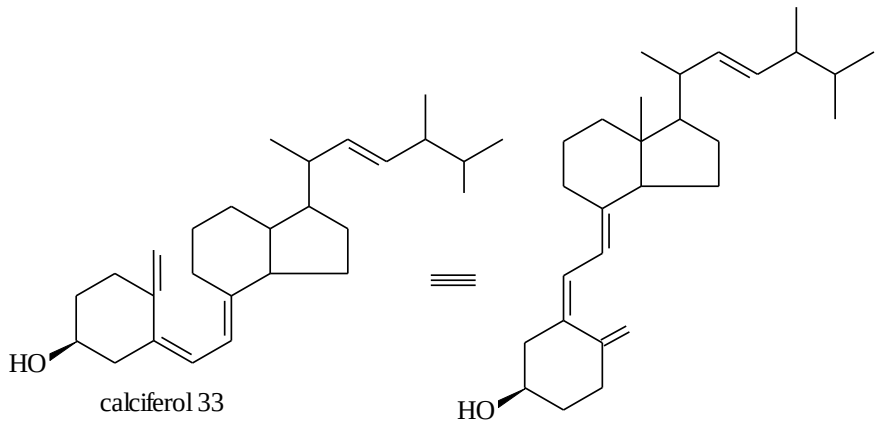
β-sitosterol 31 stigmasterol 32

Vitamine D group

- **they are about seven compounds (Vitamin D1 - D7) with the ring B being opened. Vitamin D2 33 (or calciferol) is formed from ergosterol 30 by the sunlight irradiation**



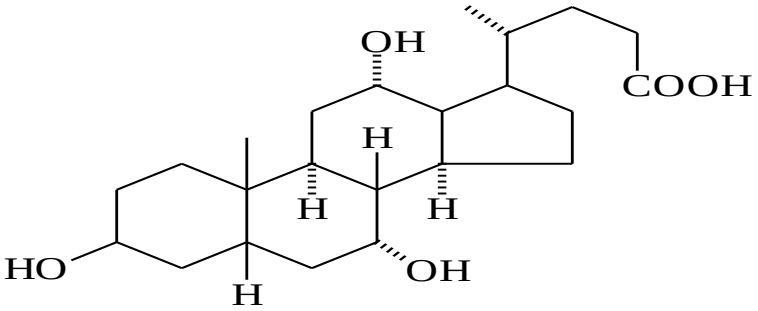
ergosterol 30



calciferol 33

Bile acids

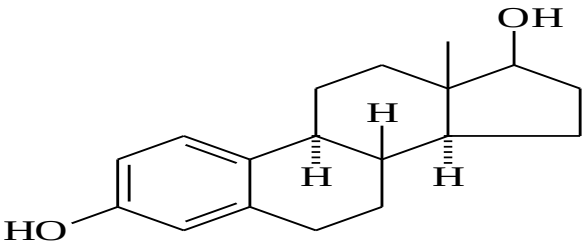
are isolated from the bile of various animals



cholic acid 34

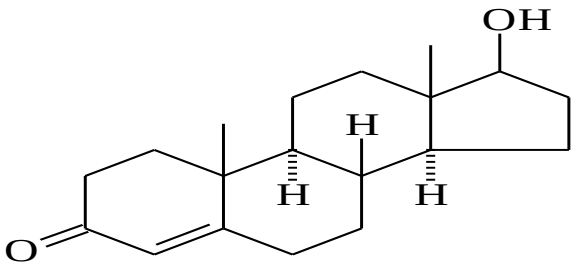
Sex hormones

- ***Estrogens*** **(female sex hormones)**



α-oestradiol 35

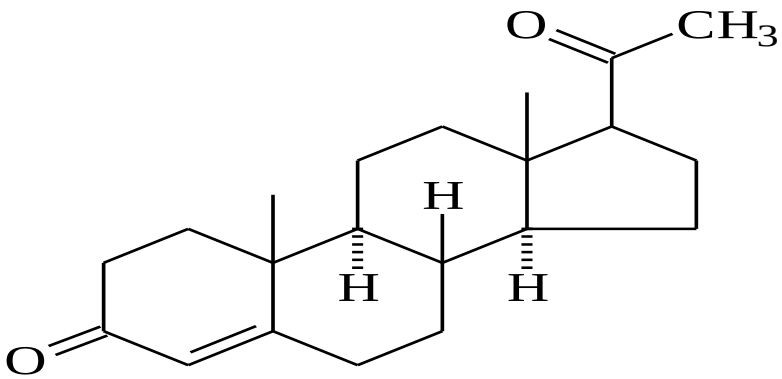
Androgens **(male sex hormones**



testosterone 36

- ***Gestogens***

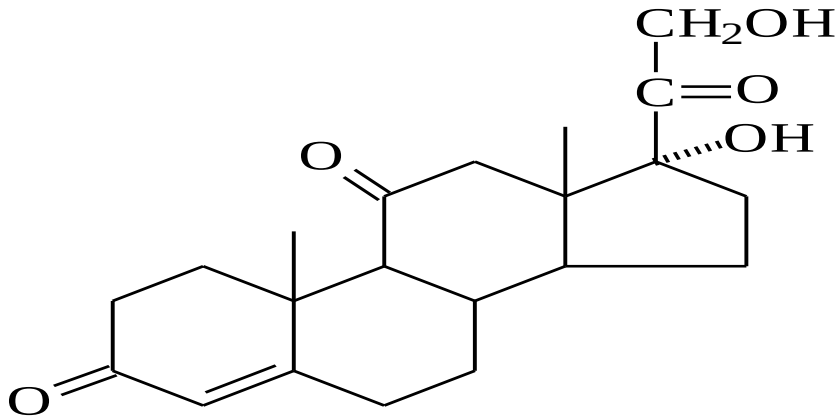
- **hormones which are responsible for the maintenance of pregnancy**



progestrone 37

- **Adrenocortical hormones**

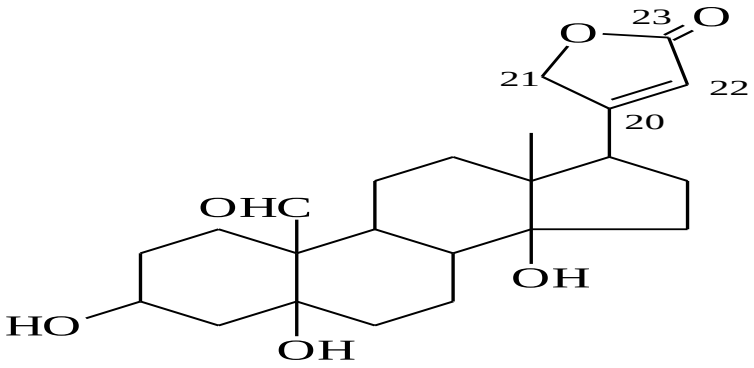
- **produced by the cortex of the adrenal glands**



cortisone 38

- **Cardenolides**

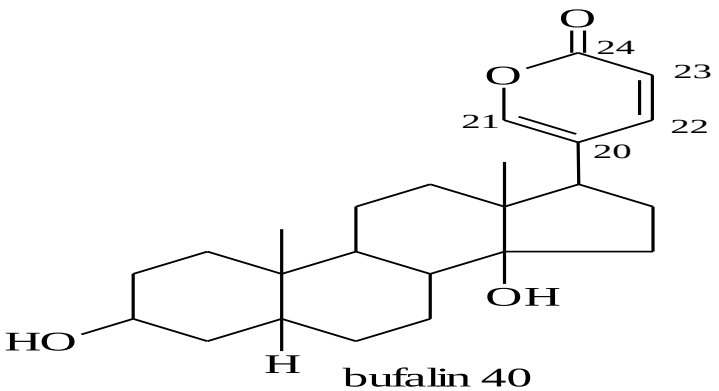
- **Cardiac glycosides have powerful cardiotonic activity and can be used for treatment of some heart diseases**



strophanthidin 39

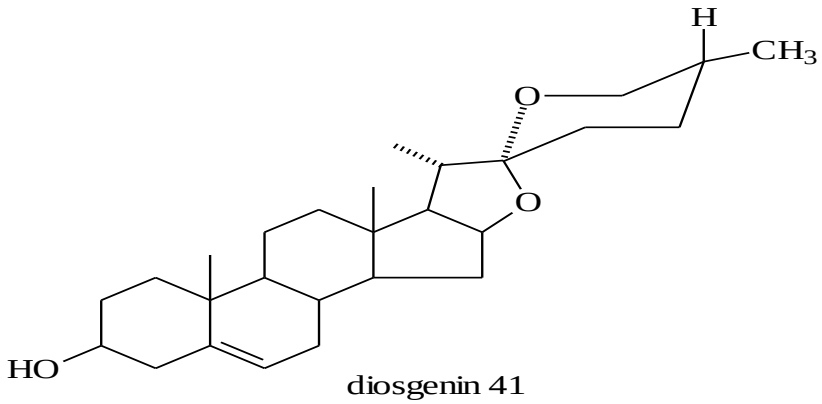
- **Bufadienolides**

- **present in the toad venoms secreted from the parotid glands and also some of these compounds were isolated from plants**



bufalin 40

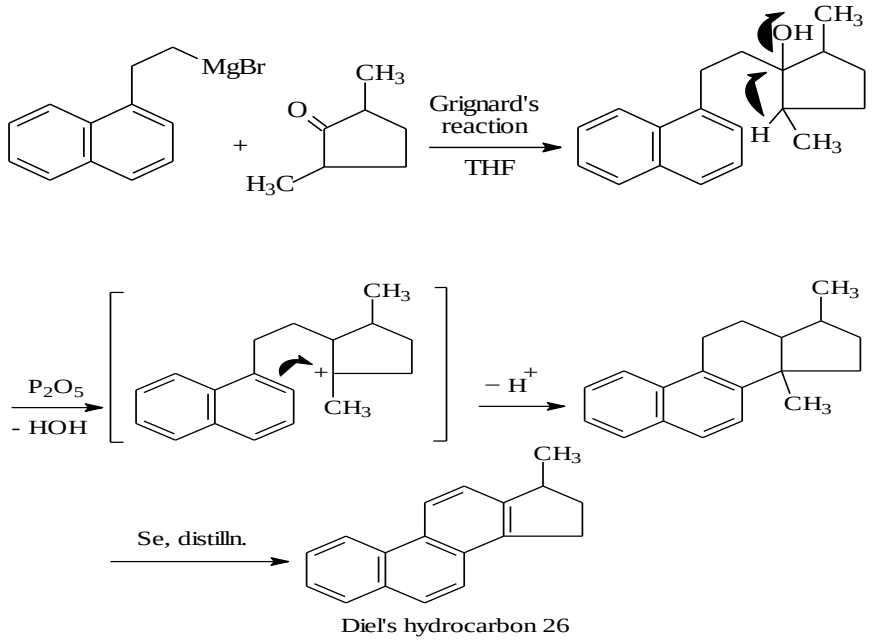
- **Sapogenins**
- **are the aglycones of saponins (named spirostane)**



diosgenin 41

Diel's hydrocarbon

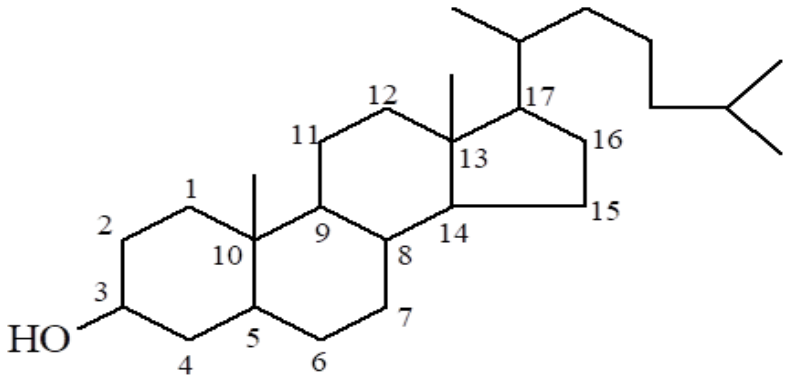
- **3'-methyl-1:2-cyclopentenophenanthrene**



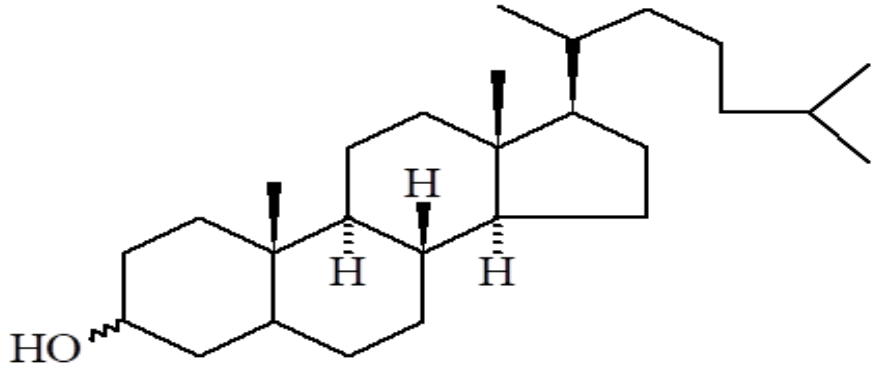
Diel's hydrocarbon 26

Stereochemistry of the steroid nucleus

- **there are eight dissimilar chiral centers in the nucleus (3,5,8,9,10,13,14 and 17). Thus there are 2^8 = 256 possible optical isomers**



- **In most naturally occuring sterols the configuration at C-8, C-9, C-10, C-13, C-14 and C-17 is definite, i.e. does not change from one molecule to the other**



Structure elucidation of some steroids by chemical methods

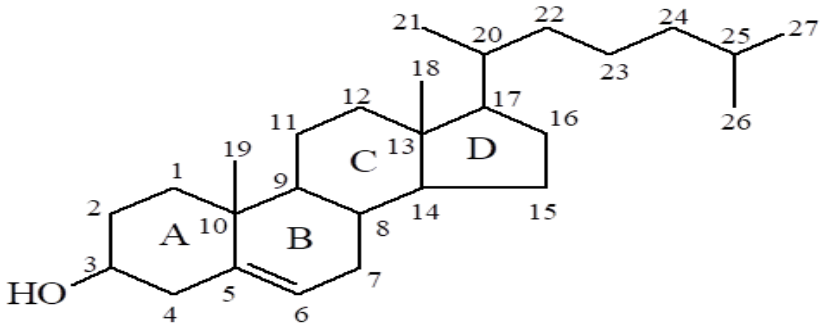
Cholesterol

characteristic features :-

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

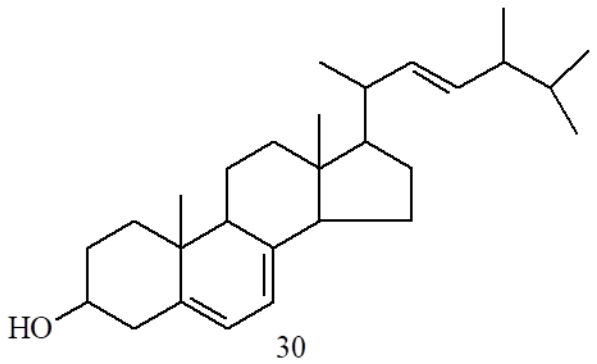
ii) There is a secondary OH group at C-3, and a double bond at C-5 (between C-5 and C-6).

iii) There are two angular methyl groups at C-10 and C-13, and a saturated side-chain C8H17 at C-17.

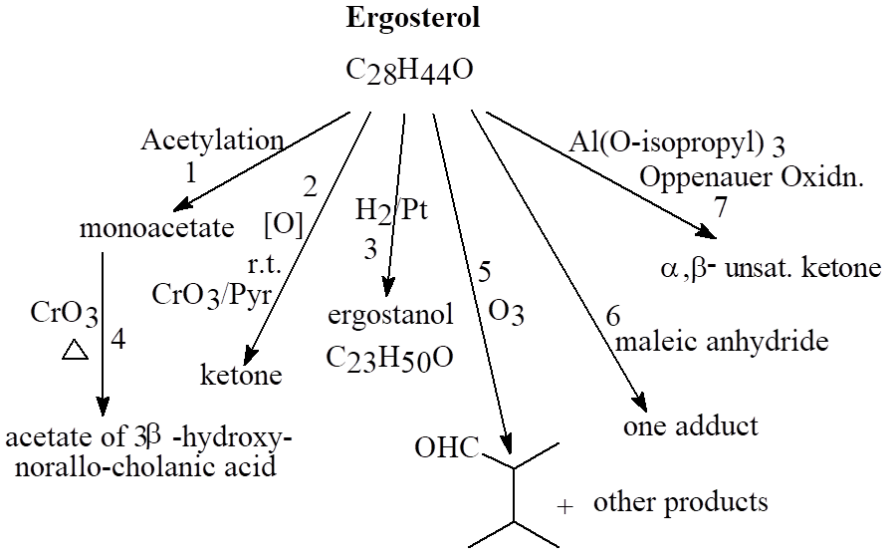


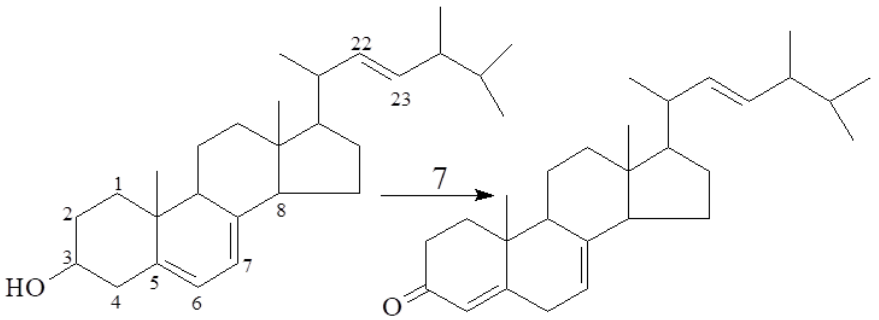
29

Ergosterol



30

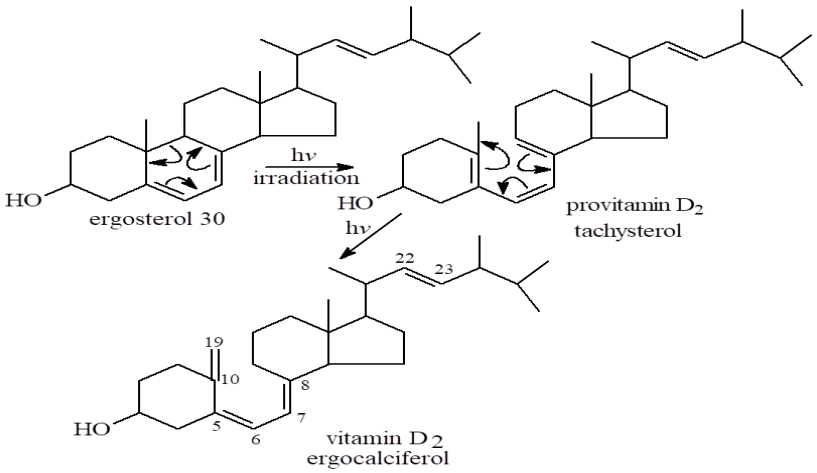




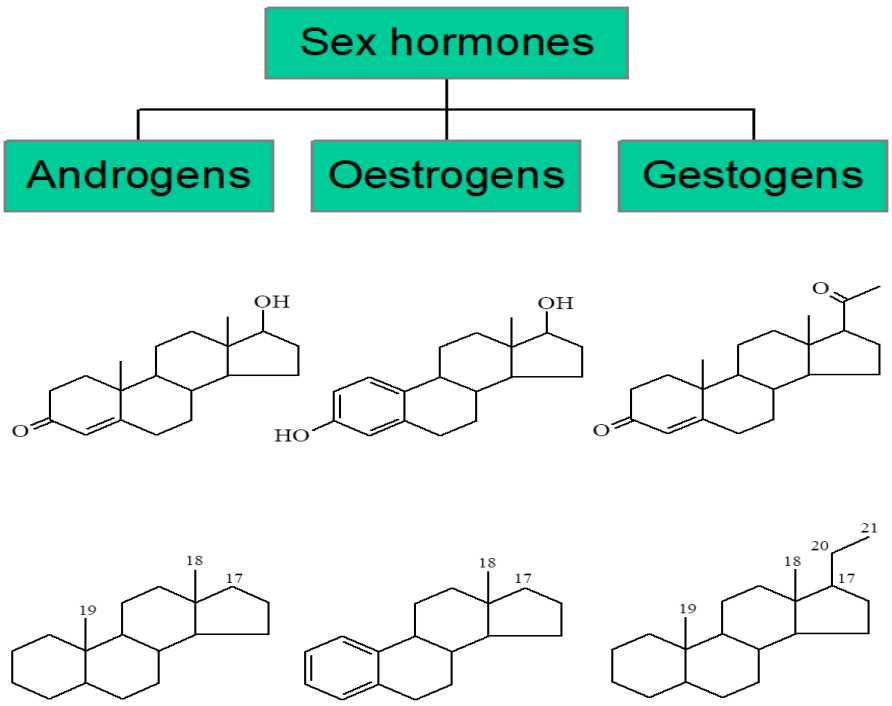
ergosterol 30

λ_{max} found 235 nm, calc. 239 nm

Formation of vitamin D_2 from ergosterol 30 by sunlight irradiation.

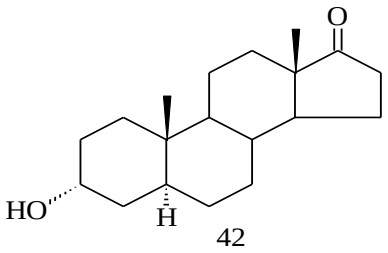


Sex hormones

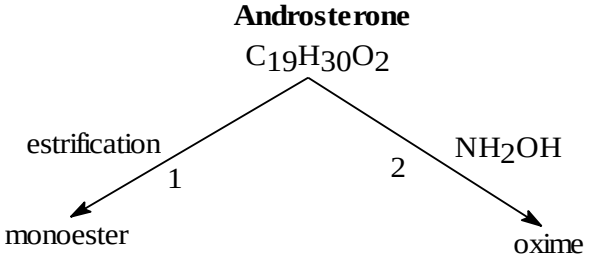


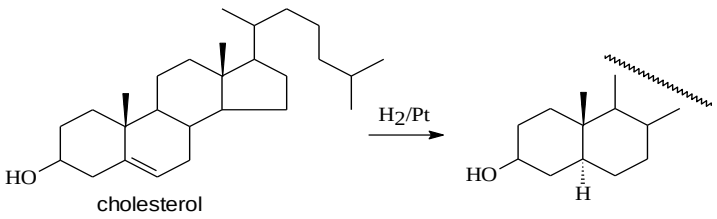
Androgens

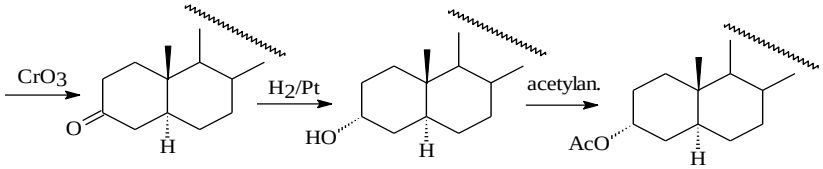
Androsterone

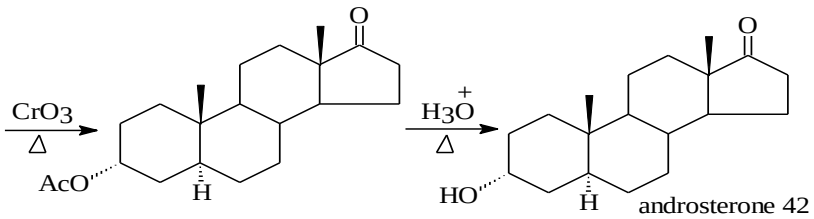


42



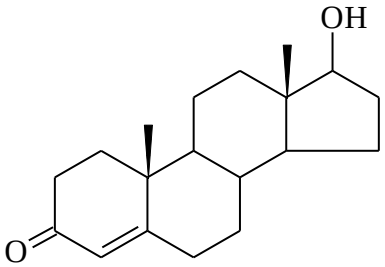




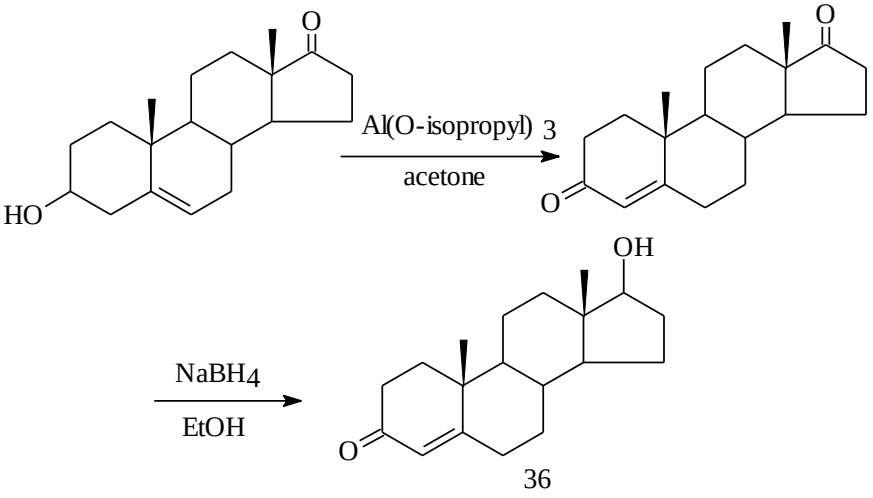


Testosterone

manufacture of testosterone



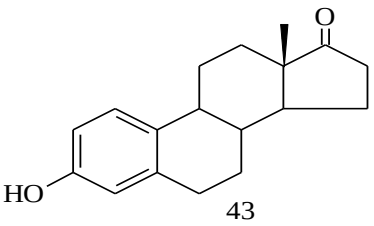
36



36

Oestrogens

Oestrone



43

Oestrone

$C_{18}H_{22}O_2$

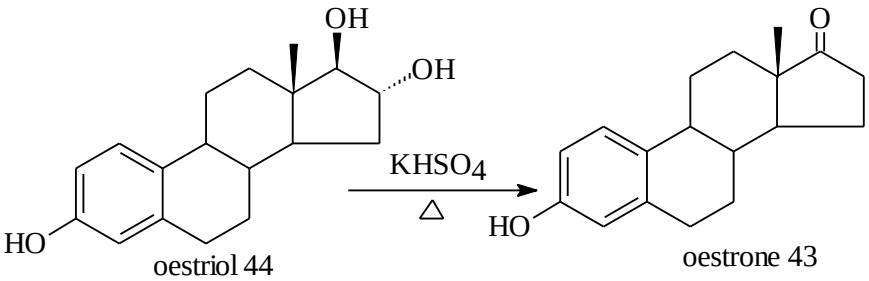
1 NH_2OH → oxime

2 $ArN_2^+Cl^-$ → couples with diazonium salts in alkaline solution

3 MeI → monomethyl ether

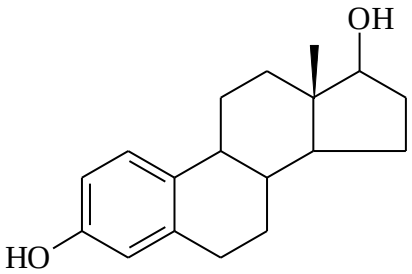
4 Ac_2O → monoacetate

5 catalytic reduction → octadhdro-oestrone $C_{18}H_{30}O_2$

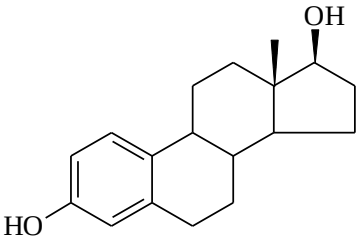


oestriol 44 → oestrone 43

Oestradiol

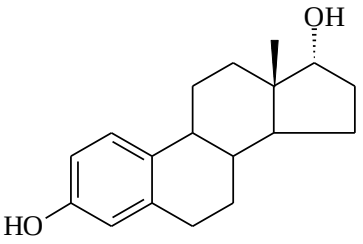


35



35a, α-oestradiol (oestraiol-17 β)

m.p 178°C

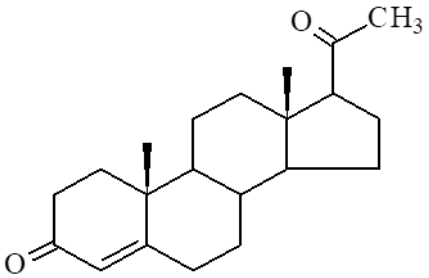


35b, β-oestradiol (oestradiol-17 α)

m.p 222°C

Gestogens

Progesterone



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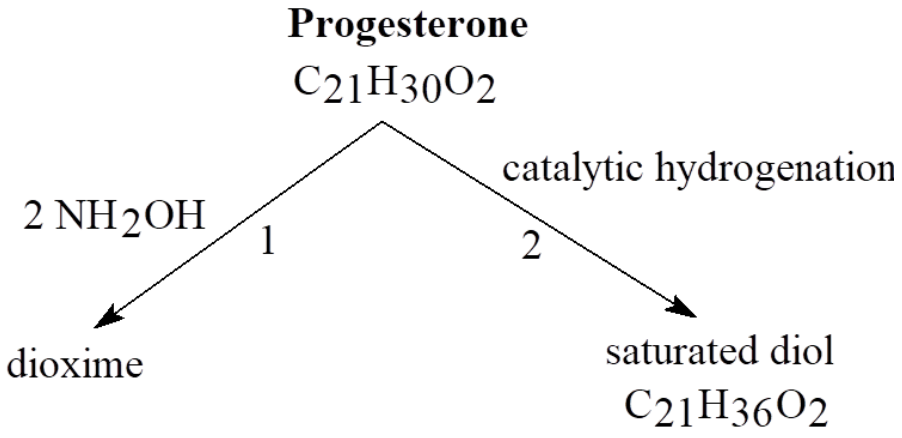
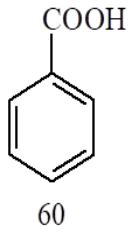
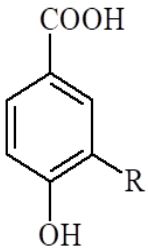


Shikimates

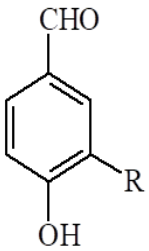
Benzoic acid and related compounds (C6-C1)



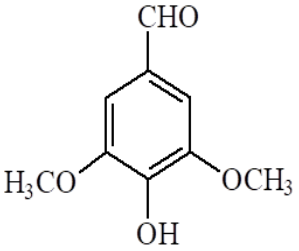
60



61; R = H
62; R = OH
63; R = OMe

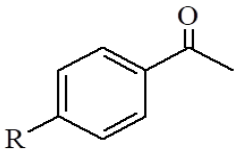


64; R = H
65; R = OMe

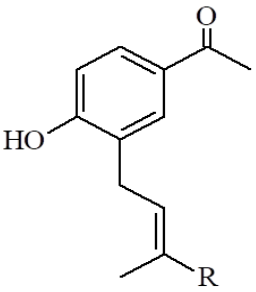


66

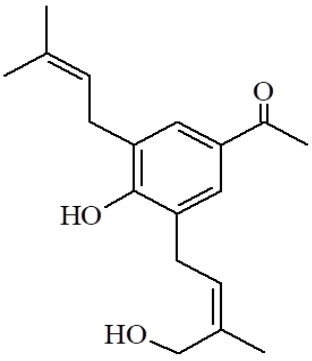
Acetophenones and related compounds (C6-C2)



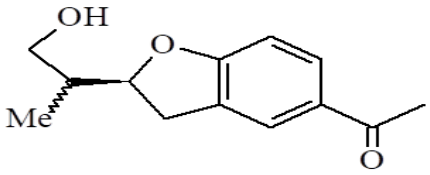
67; R = OH
68; R = OMe



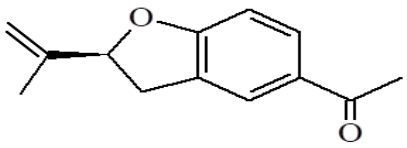
69; R = Me
70; R = CH_2OH



71



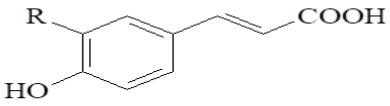
72; R = α-Me
73; R = β-Me



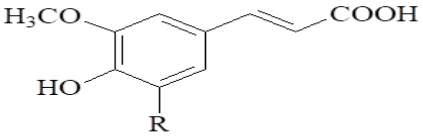
74

Phenylpropanoids (C6-C3)

Cinnamic acids

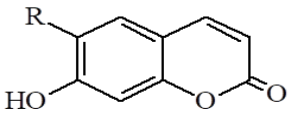


75; R = H
76; R = OH

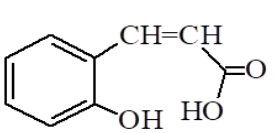


77; R = H
78; R = OMe

- **Coumarins**



81; R = H
82; R = OH
83; R = OMe



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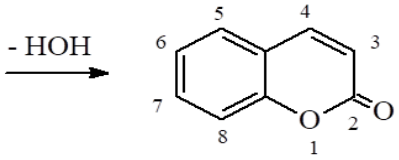
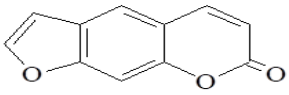


80



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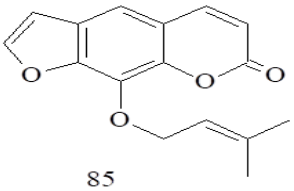

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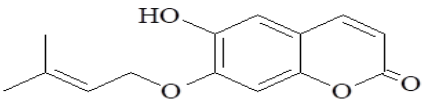

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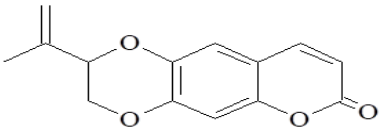
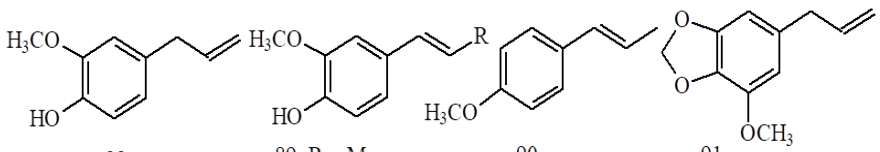
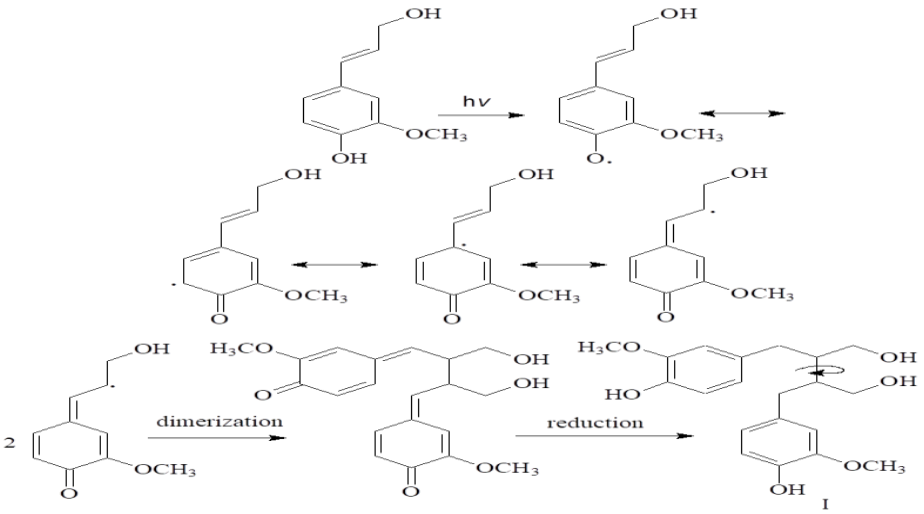


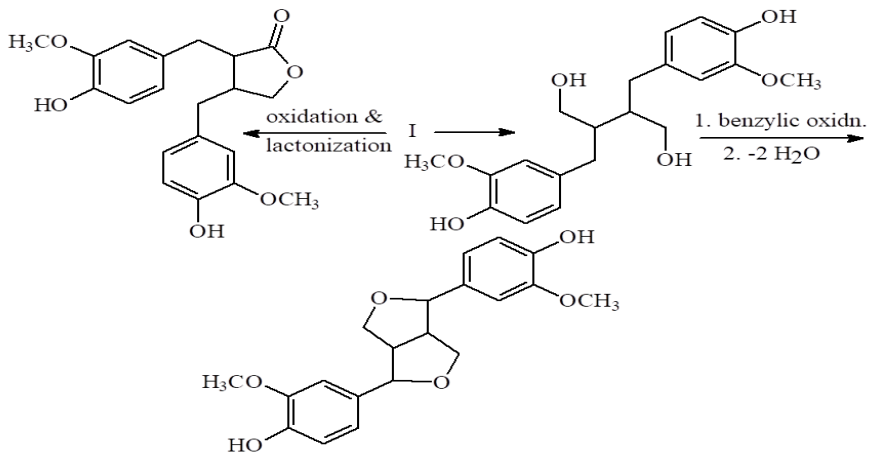
87

Phenyl propenes



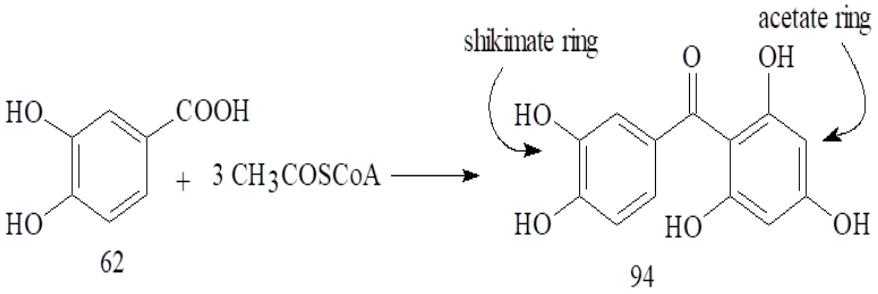
Lignans



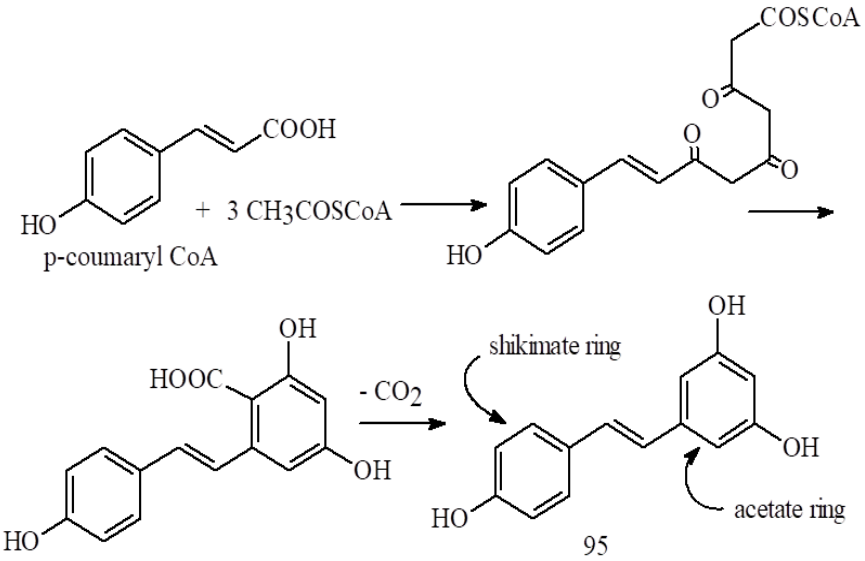


Compounds containing "shikimate" ring

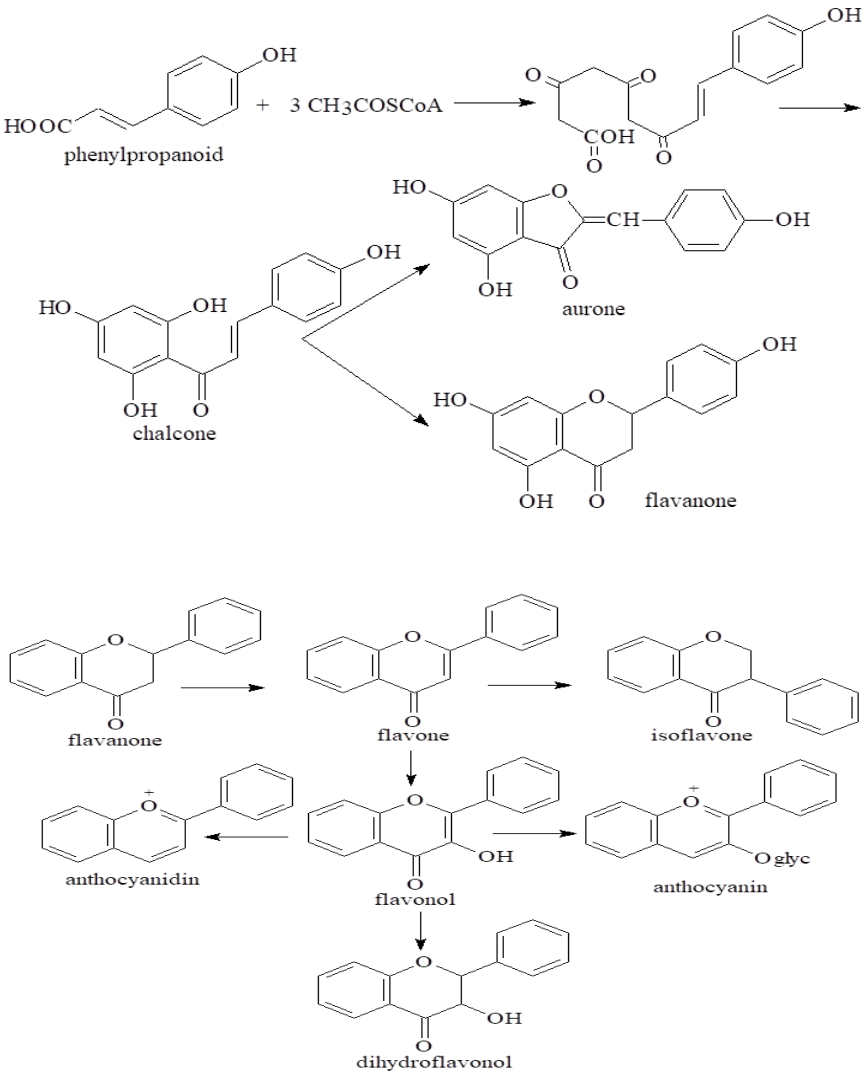
- **Benzophenones (C6-C1-C6)**



Stilbenes (C6-C2-C6)

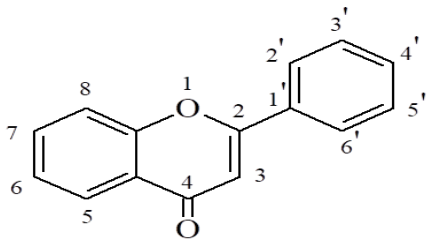


Flavonoids (C6-C3-C6)

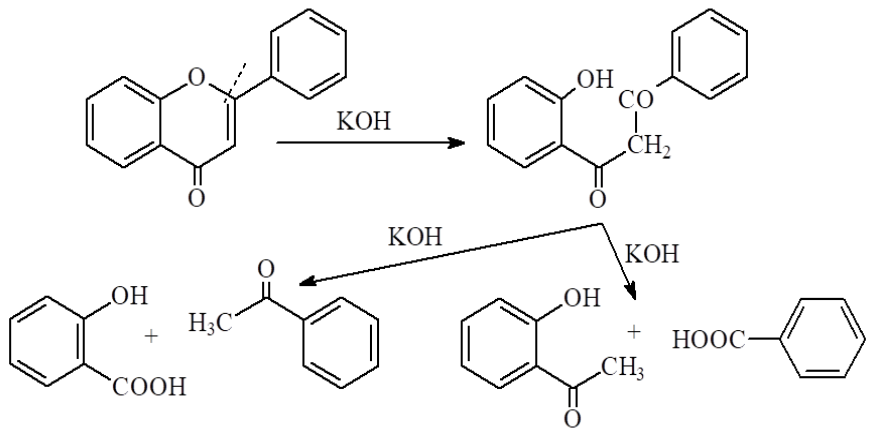


Structure-elucidation of some flavonoids

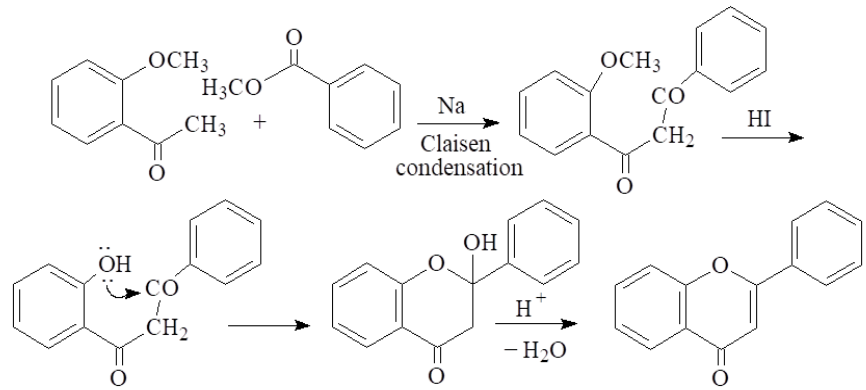
Flavone, 102, $C_{15}H_{10}O_2$



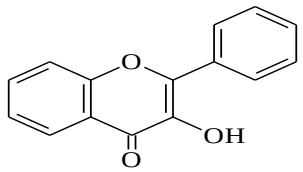
102



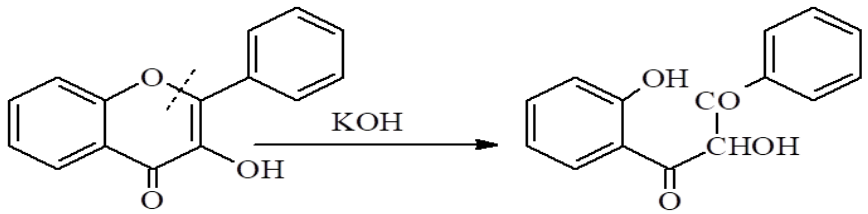
general method for synthesizing flavones

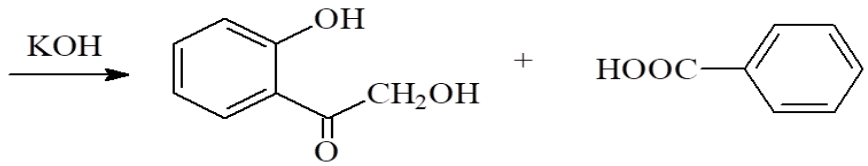


Flavonol (3-hydroxyflavone), 103, $C_{15}H_{10}O_3$

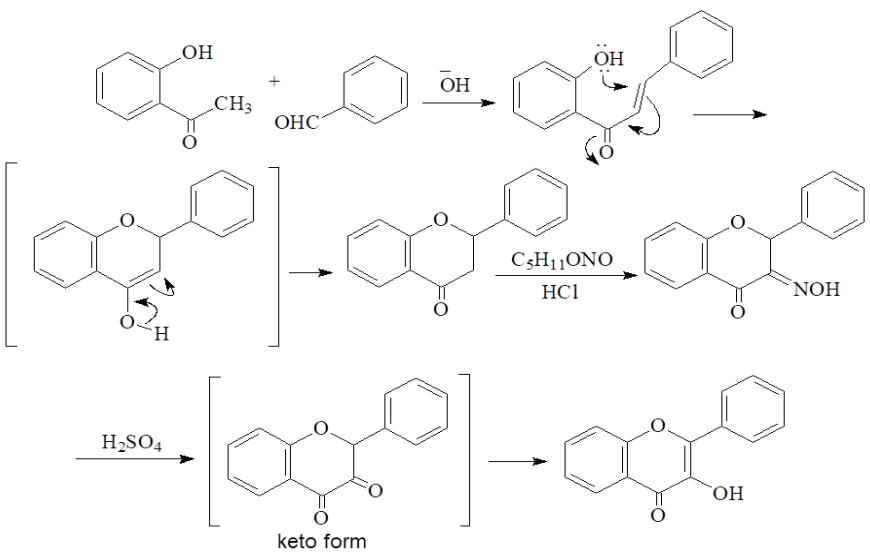


103





Kostanecki synthesis of flavonol



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- **2- The chemistry of natural products, R. H. Thomson, 2014.**
- **3- Organic chemistry of natural products volume I, Gurdeep R. Chatwal, 2017.**
- **4- Organic chemistry of natural products volume II, O. P. Agarwal, 2018.**
- **5- Chemistry of natural products, jaswant Kaur, 2019.**
- **6- Chemistry of natural products (A unified approach) second edition, N. R. Krishnaswamy, 2020.**
- **7- Pharmaceutical, Medicinal and Natural product chemistry, P. S. Kalsi, Sangeeta Jagtab, 2021.**
- **8- Chemistry of natural products, S. V. Bhat, B. A. Nagasampagi, M. Sivakumar, 2019.**

- **9- Natural products (chemistry & applications) Sujata V. Bhat, B. A. Nagasampagi, S. meenakshi, 2021.**

- **10- Comperhensive natural products chemistry volume 7, Sir Derek Barton, Koji Nakanishi, 2020.**

Chemistry OF Dyes

2nd Year Students Faculty of Education South Valley University

second term 2022/2023

Dr/ Ibrahim Abdul-Motaleb Mousa

Dyes

General characters of the dye molecule:

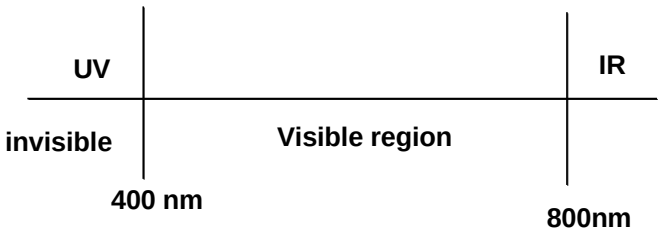
1- **It must have a suitable color.**

2- **It must be fixed to the fabric.**

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

Introduction on dyes

- **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)**

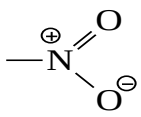
<u>Relation between color and chemical constitution:</u>

The organic compound to be colored it must have

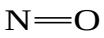
a) **Chromophores.**
b) **Auxochromes.**
c) **Quinoid structure.**

<u>A) Chromophores:</u>

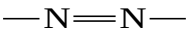
- Chromophores are these groups with multiple bonds examples of chromophores



nitro

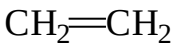


nitroso

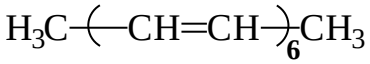


azo

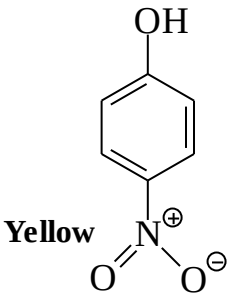
- **The compound contain the chromophores is called chromogen.**
- **Single chromophore is not sufficient to produce color but a number of chromophores must be attached in conjugation to produce color and as number of chromophores increase degree of color increase.**

e.g. 

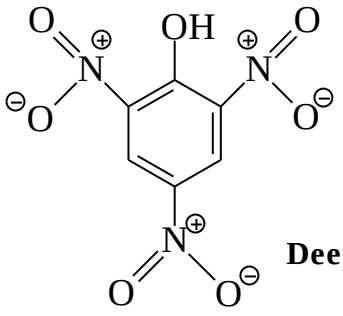
Colourless



Yellow



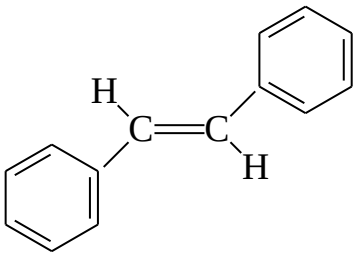
Yellow



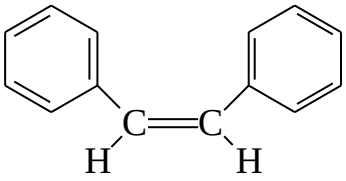
Deep Yellow

The position of groups in space can affect on color

e.g. stillbene



Trans
(Coloured)



Cis
(Colourless)

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

B) Auxochromes:

- **Auxochromes are groups, which deepen the color.**
- **It classified into acidic (phenolic) e.g. OH or basic e.g. NH_2, NHR, NR_2**
- **Auxochromes are known as bathochromic groups, which makes shift from violet to red *(red shift)*.**

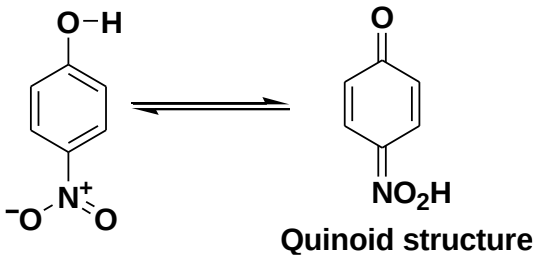
- **Groups which decrease the depth of color are known as hypochomic groups e.g $NHCOCH_3$ such groups shift the color from red to violet *(blue shift).***
- **Presence of auxochromes with chromogen make chromogen dye because it:**

1- Deepen the color.

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

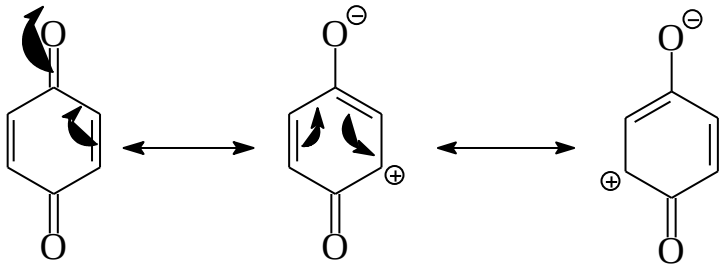
C) Quinonoid structure:

- **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**

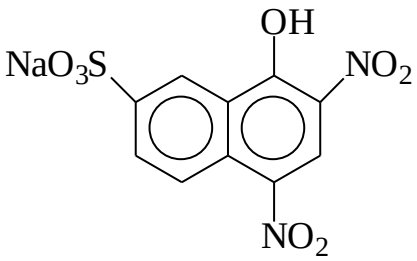
Chemical classification of dyes:

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

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

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

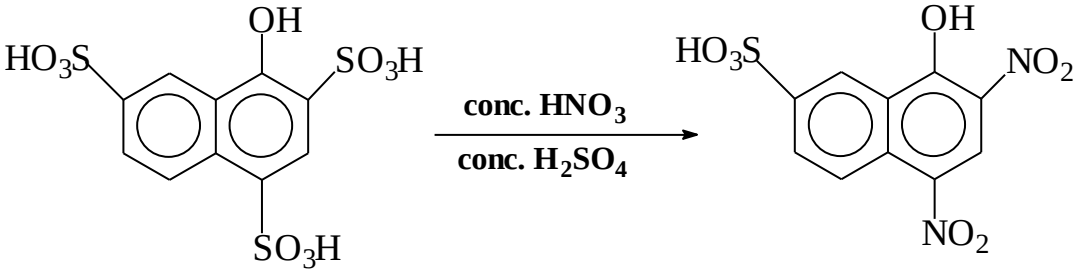
Dyes contain -NO_2 as chromophore and OH as auxochrome e.g.



Naphthol Yellow S

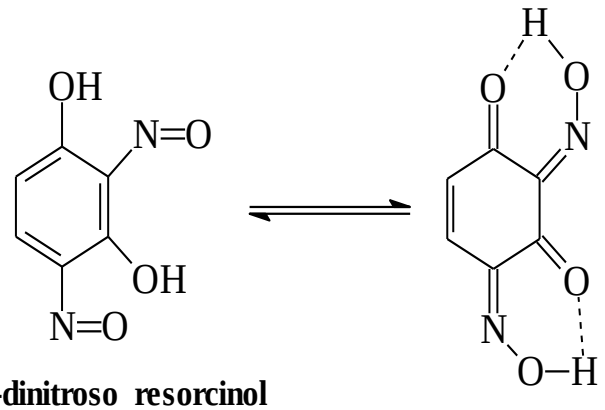
2,4-dinitro Naphthol-7-sulphonic acid sod. salt

Preparation:



2) Nitroso dyes:

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



2,4-dinitroso resorcinol

3) Azo dyes:

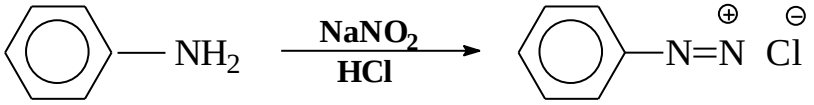
- **Azo dyes which contain N=N as chromophre and NH_2 or OH as auxochromes and both chromophore (-N=N-) and auxochrome attach with one more aromatic system.**
- **The dye is called monoazo if contain one N=N and is called diazo if it contain two N=N and so on.**
- **Azo dye is prepared through two steps:**

1- Diazotization.

2- Coupling.

1- Diazotization:

- **Diazotization is conversion of 1ry aromatic amine to diazonium salt.**



benzene diazonium chloride

<u>Mechanism of diazotization:</u>

It occur by the following steps:

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

$$\overset{\oplus}{N}O\ ,\quad NOCl\ ,\quad H_2\overset{\oplus}{O}-N=O\ ,\quad N_2O_3$$

2- Conversion of N-nitroso to diazonism salt.

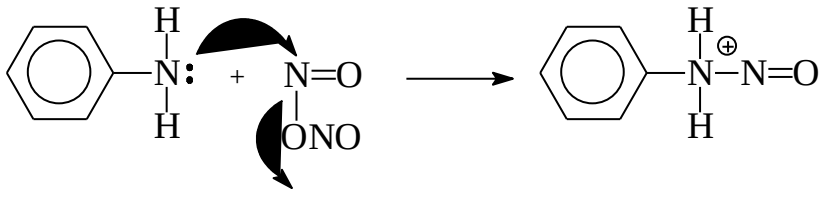
A) Mechanism of diazotization of 1ry aromatic amine:

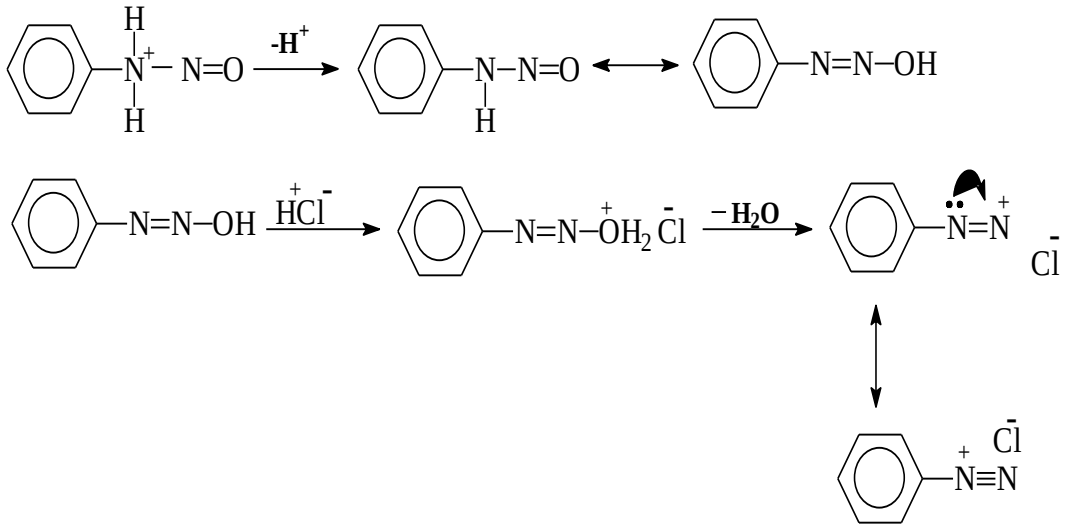
$$NaNO_2 + HCl \longrightarrow NaCl + HO-N=O$$

Nitrous acid

$$2\,HO-N=O \longrightarrow H_2O + N_2O_3$$

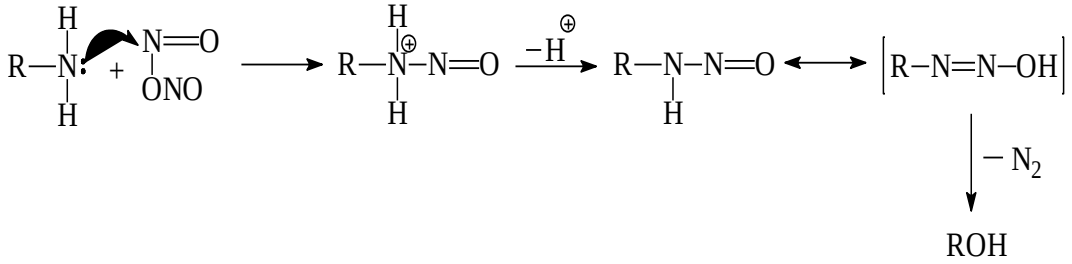
Dinitrogen trioxide





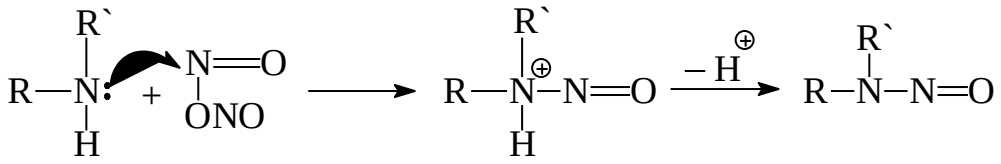
benzene diazonium chloride

B) 1ry aliphatic amines:



i.e. No diazotization of aliphatic amines.

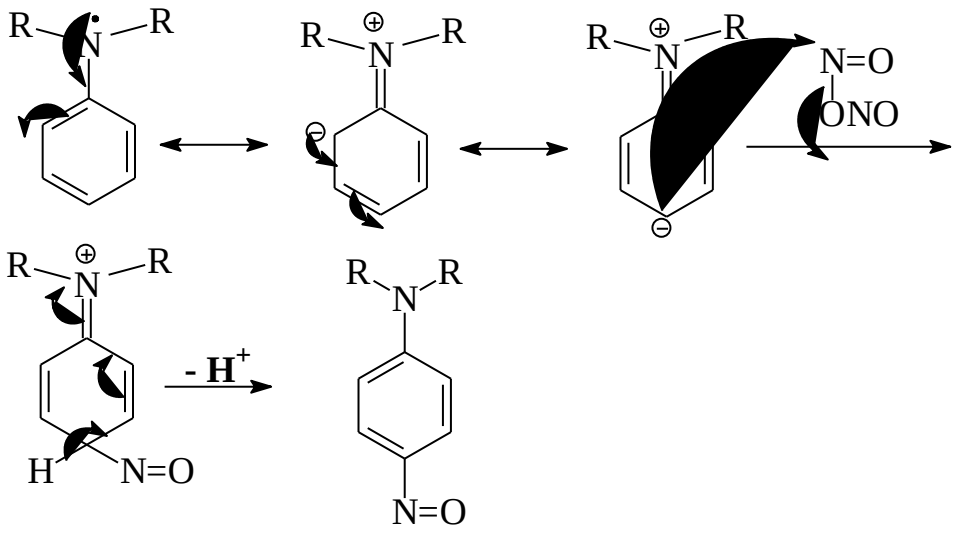
C) 2nd aromatic and aliphatic amines:



R may be aliphatic or Aromatic

N Nitroso compound

a) t- aromatic amines



P-Nitroso-N,N-dialkylaniline

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

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

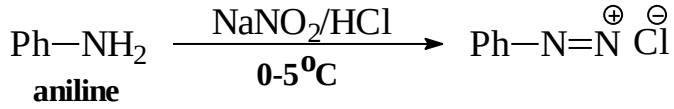
Effect of substituents on diazotization:

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

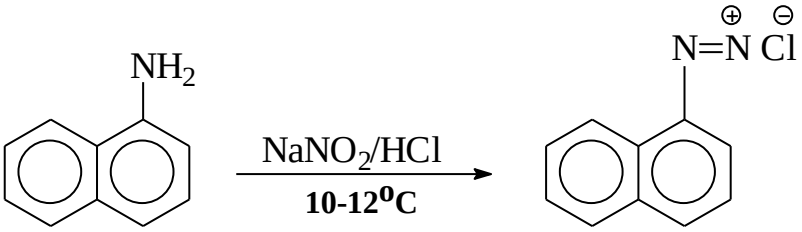
1- for unsubstituted 1ry aromatic amine:

It need equimolar of $NaNO_3$ and 3 equivalent of HCl

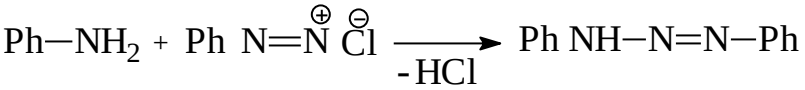
e.g.



For amino naphthalene



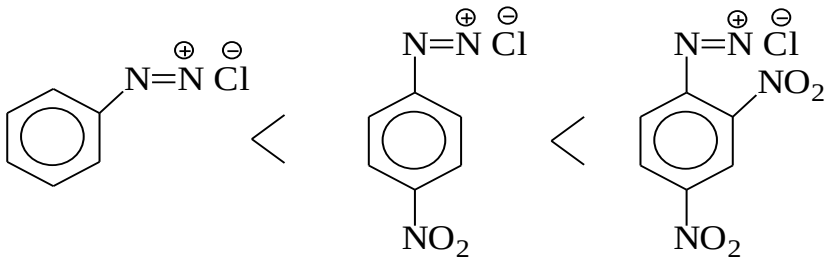
Secondary reaction can occur if some aniline is unreacted.



2- for nitro anilines:

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

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



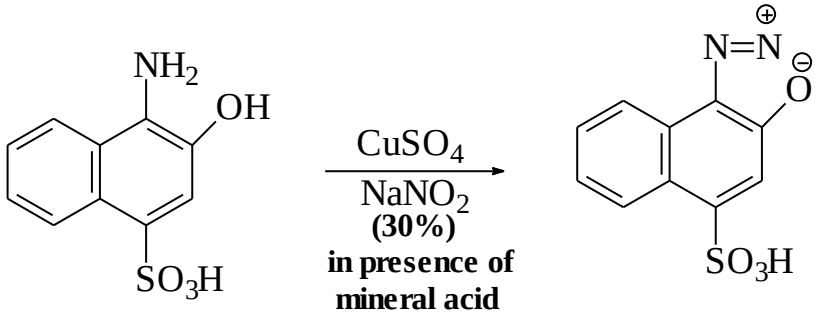
3- In case of acidic substituent:

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).

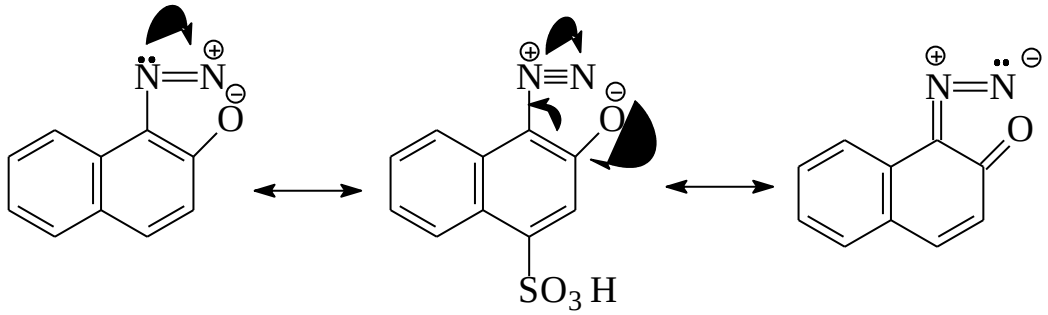
4- In case of aminophenol and aminonaphthol:

- **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 not form diazo-oxides**

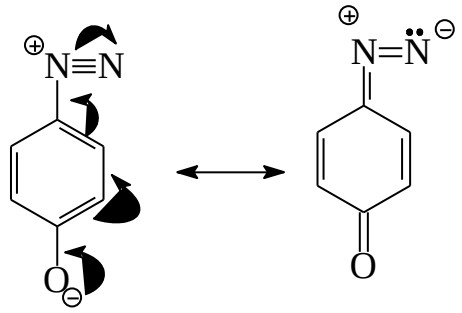
e.g.



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



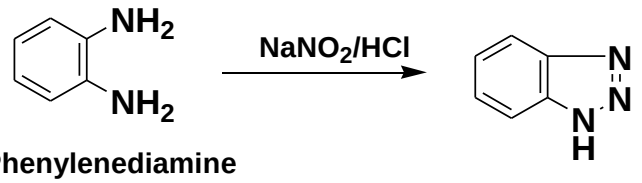
Also 1,4 aminophenol



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

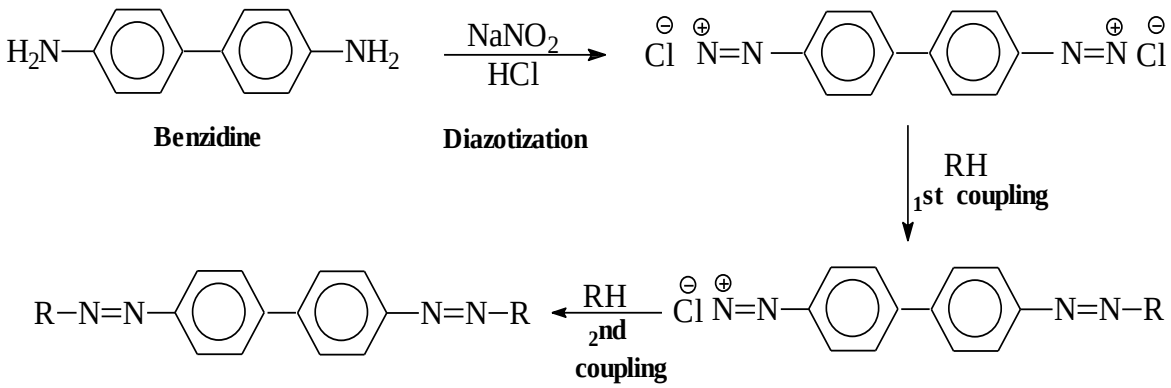
5- for diamines:

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.

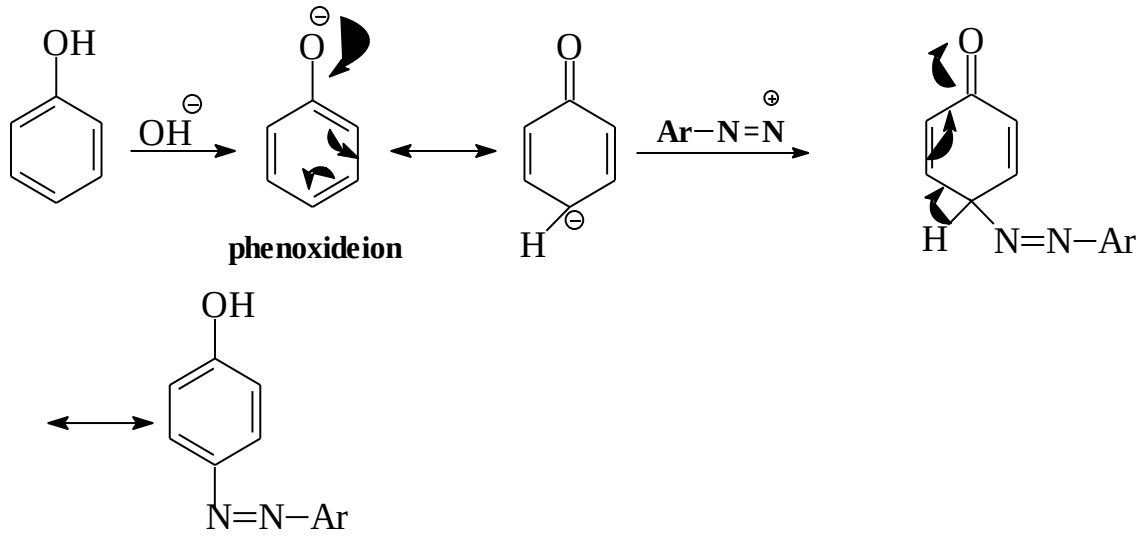


The 2nd coupling occurs slower than 1st.

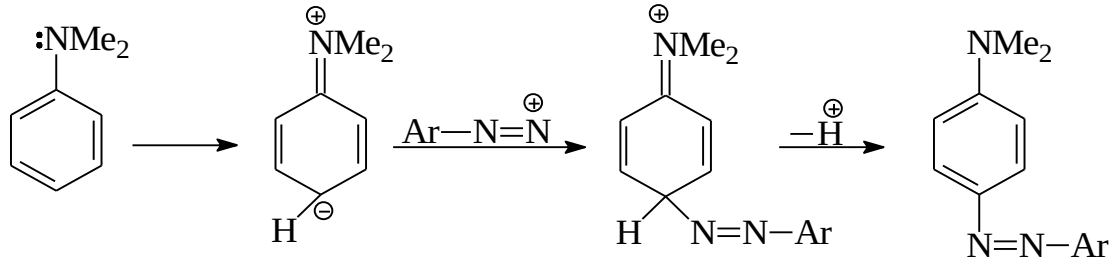
Diazo coupling

- **Diazo coupling is electrophilic substitution by diazonium cation.**
- **It occurs often in para-position.**
- **Coupling occurs for phenols in alkaline medium and for amines in slightly acidic medium.**

Mechanism of Diazo coupling of phenols:



Mechanism of Diazo-coupling of aromatic amines:



Coupling component:

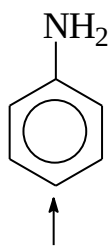
1) Benzene derivative:

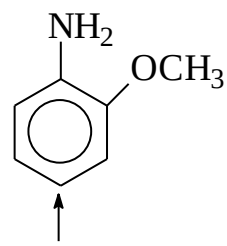
A) Amines:

- **Medium of coupling: acidic medium**

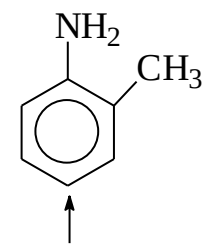
- **Position of coupling: para-position of amino group.**

i- Primary amines:

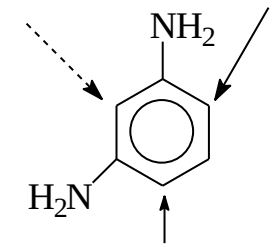




o-Ansidine



o-Toludine

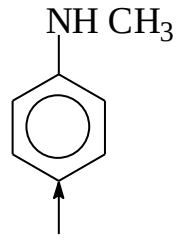


m–phenylenediamine

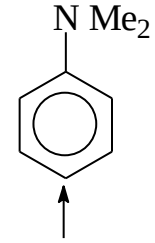
The arrow indicates the coupling position.

The arrow ⇢ indicate the less reactive position

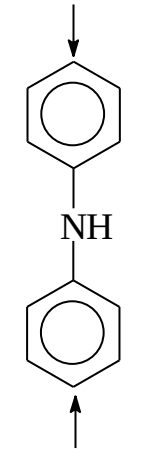
ii- Secondary and t–amines:



N–methyl aniline



N,N dimethyl aniline

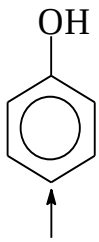


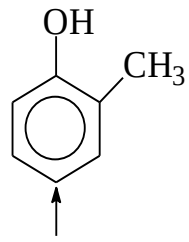
diphenyl amine

B) Hydroxy derivatives:

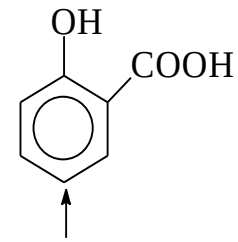
Medium of coupling: alkaline medium.

Position of coupling: para-position of –OH

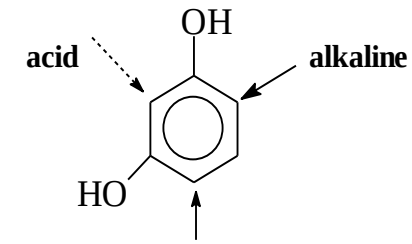




o- Cresol



Salicylic acid



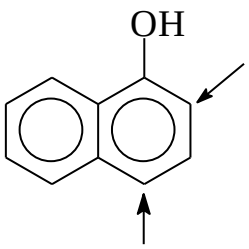
alkaline resoricnol

2) Naphthalene derivatives:

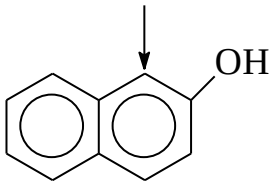
A) Naphthols:

Medium of coupling: alkaline

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



1 Naphthol or α–Naphthol

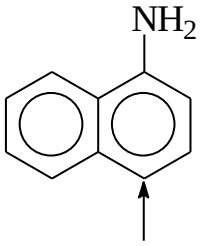


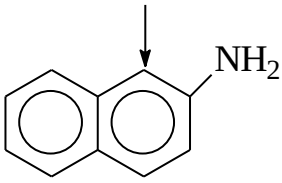
2-Naphthol or β-Naphthol

B) Naphthyl amines:

Medium: acidic

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

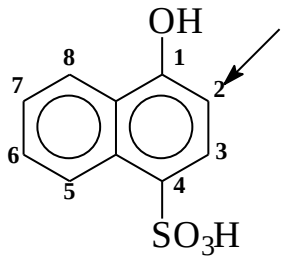




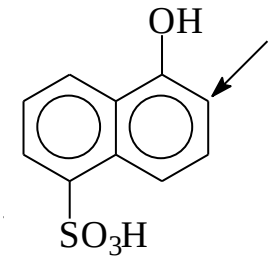
C) Naphthol sulphonic acid:

Medium: alkaline.

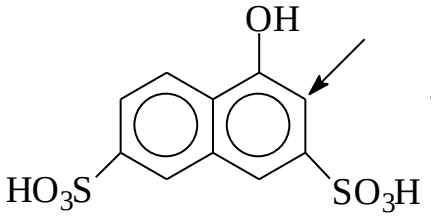
Position of coupling: ortho-position of OH.



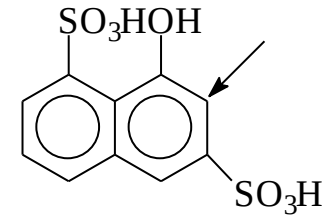
1-Naphthol-4-Sulphonic acid



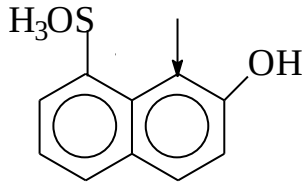
1-Naphthol-5-Sulphonic acid



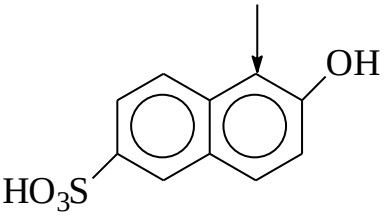
1-Naphthol-3,6-diSulphonic acid

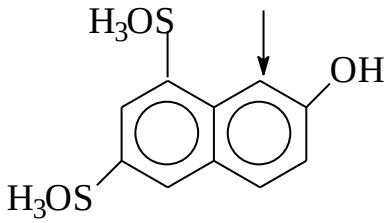


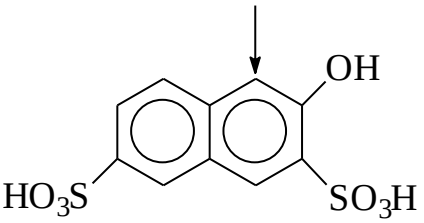
1-Naphthol-3,8-diSulphonic acid



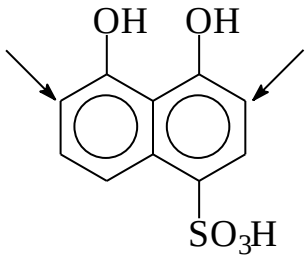
2-Naphthol-8-sulphonic acid

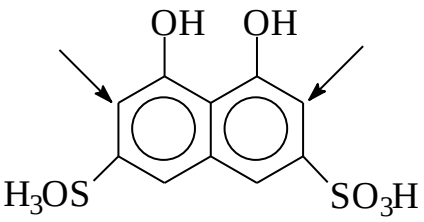






For dihydroxy naphthalene sulphonic acids





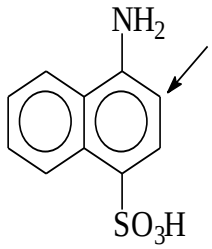
4,5 dihydroxy Naphthalene
1- sulphonic acid

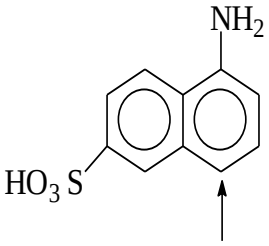
D) Naphthyl amine sulphonic acids:

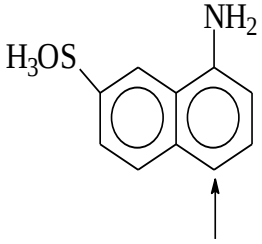
Medium: acidic

Position of coupling: position 4- for 1-Naphthylamine

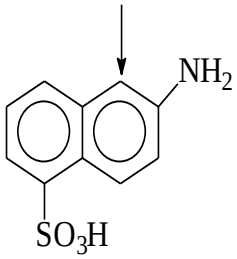
Position 1- for 2-Naphthylamine



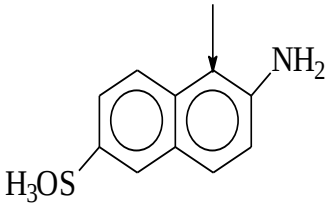




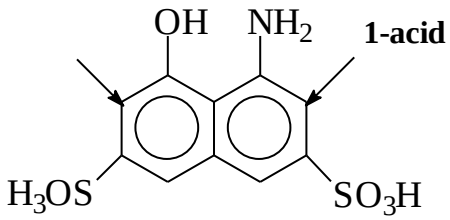
1-amino-7-Naphthalensulphonic acid acid



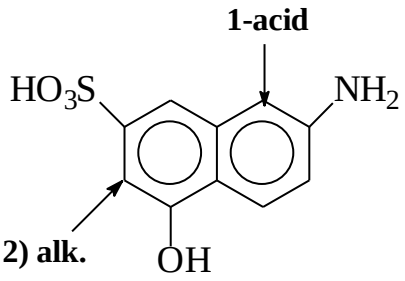
2-amino 5-Naphthene
sulphonic acid



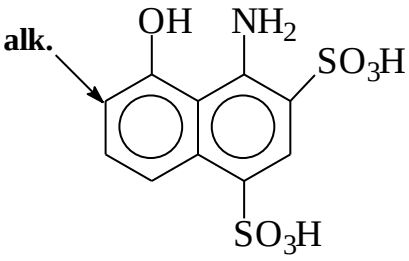
E) Amino naphthol sulphonic acids:

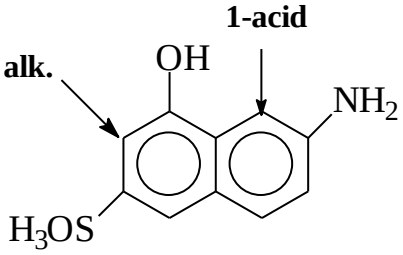


1- amino- 8-Naphthol 3,6 disulphonic acid



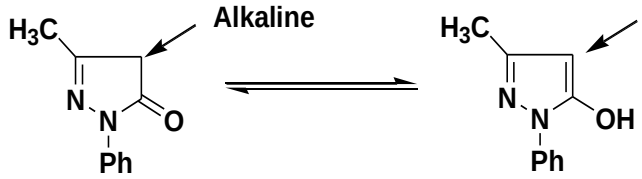
2-Amino-5-hydroxy-7-Naphthlene Sulphonic acid



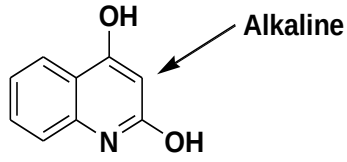


Active methylene component

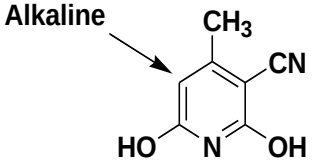
A) Hetero cyclic



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

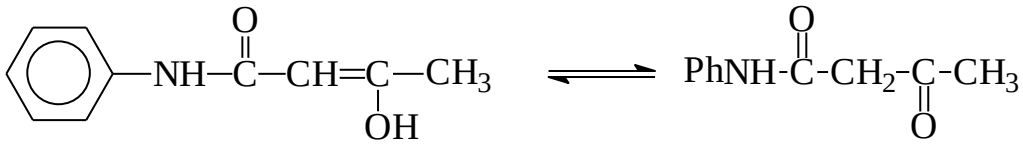


2,4-Dihydroxy-quinoline



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

Other example of active methylene acetoacetanilide



e.g of direct and acid dye

Questions

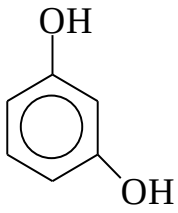
1- Give structure of Azo dyes prepared from aryl diazonium cation (ArN_2^+) and the following coupling agent.

a- Acetoacetanilide.

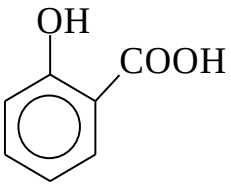
b- 1- amino–8-naphthol-3, 6-disuphonic acid.

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

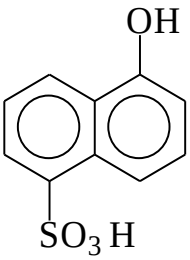
2- Give the structure of the following azo dyes which could be obtained from the interaction of diazonium cation (ArN_2^+) with the following coupling component



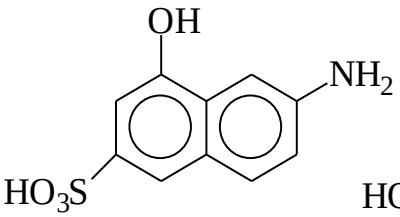
(1)



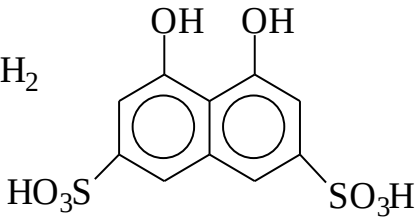
(2)



(3)



(4)



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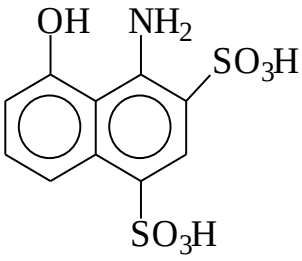

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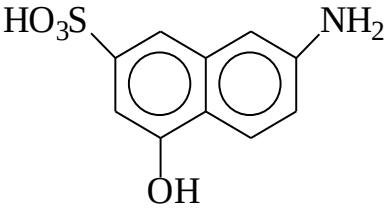
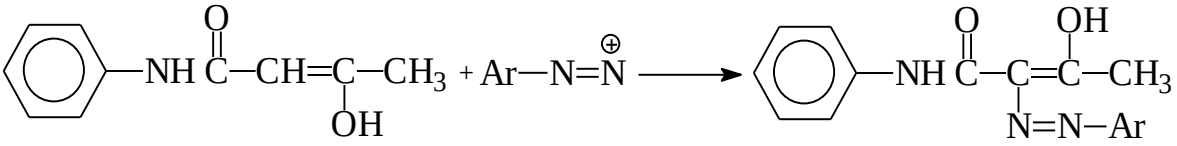


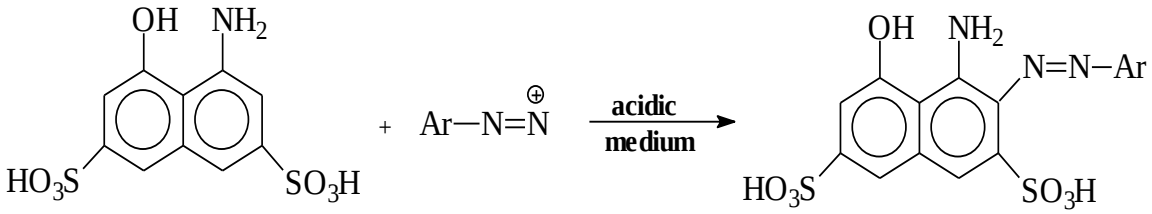
(7)

ـ بالنسبة لإجابة السؤال الأول

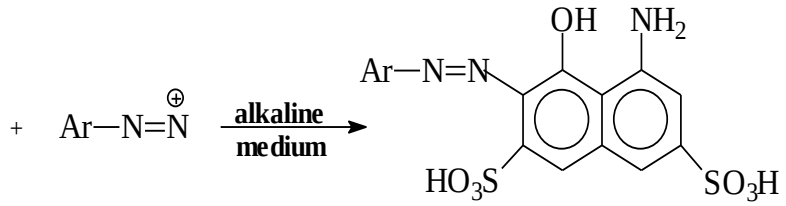
1) Acetoacetalide:



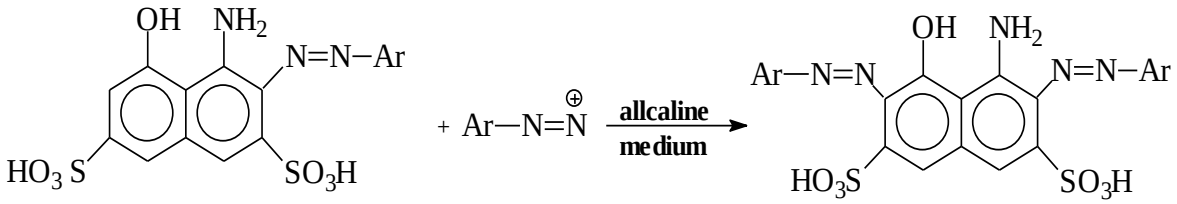
2) 1-amino–8-naphthol–3,6-disulphonic acid:



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

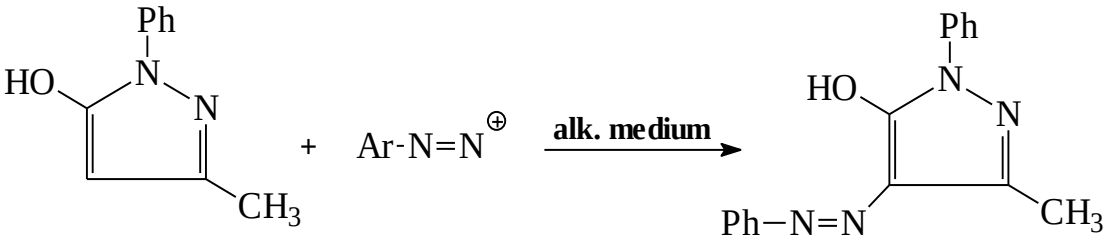


7-Arylazo-1- amio
-8-naphthol- 3,6 disulphonic acid



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

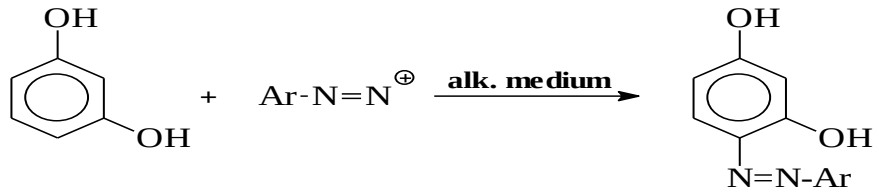
3) 3-methyl-1-phenyl-2-pyrazolin-5-one:



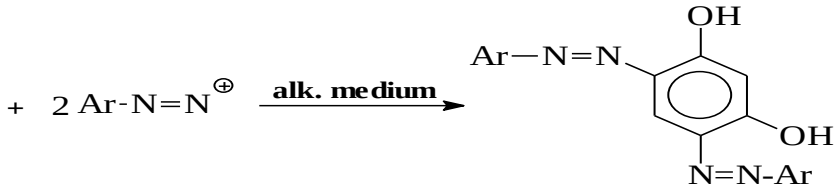
4-arylazo-3-methyl-1-phenyl-2- pyrazolin-5-one

- إجابـــــــــــــــــة الســـــــــــــــــؤال الثـــــــــــــــــاني

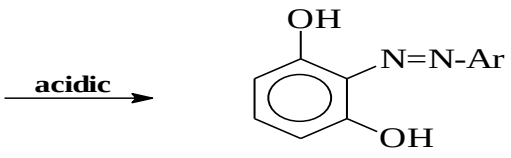
(1)



Resorcinol **4-arylazo resorcinol**

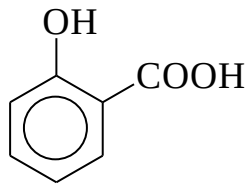


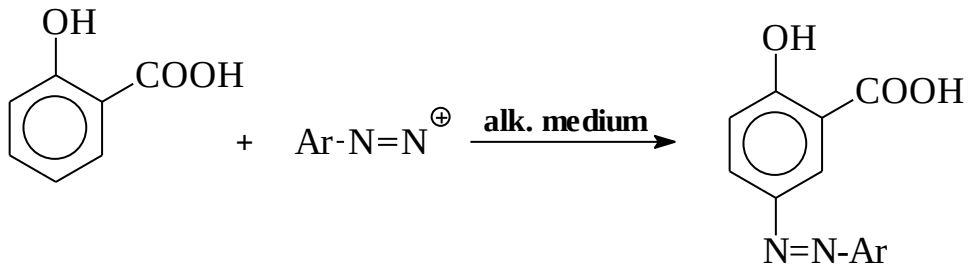
4,6-arylazo resorcinol



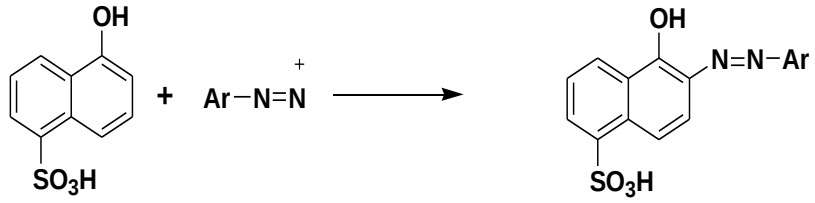
2-arylazo resorcinol

(2)





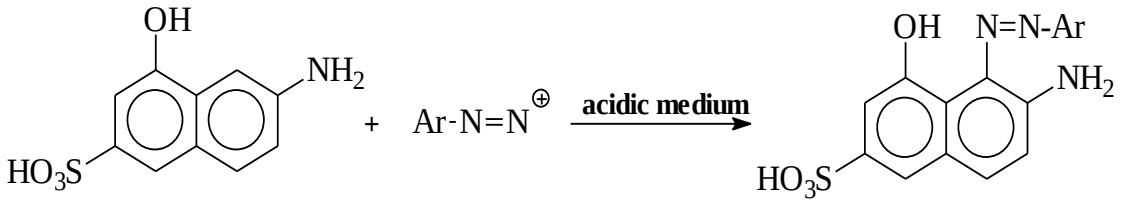
4-arylazo salicylic acid



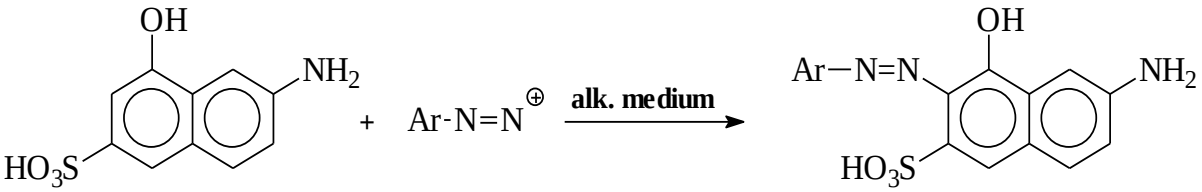
5-Hydroxy-naphthalene-1-sulfonic acid

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

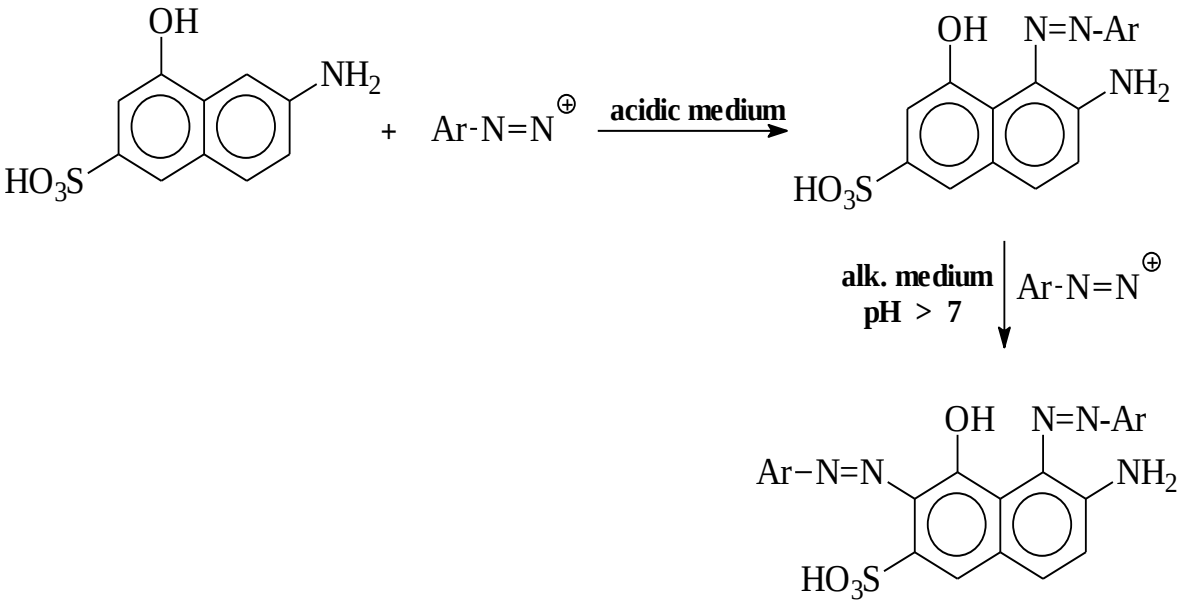
(a)

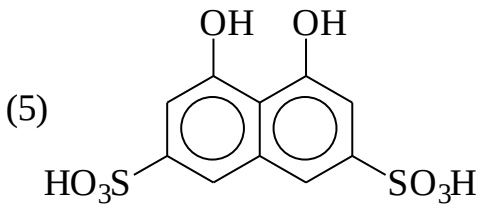


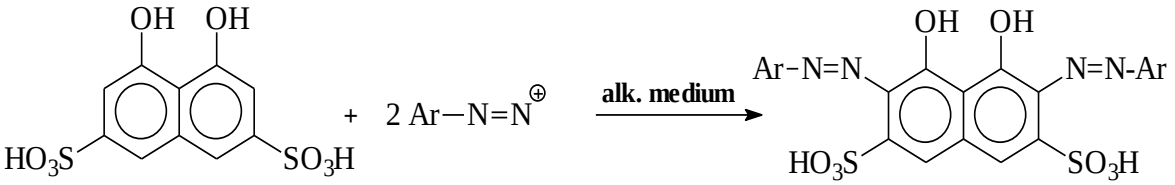
1-arylazo-2-amino-8-hydroxy naphthlene-6-sulphonic acid



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

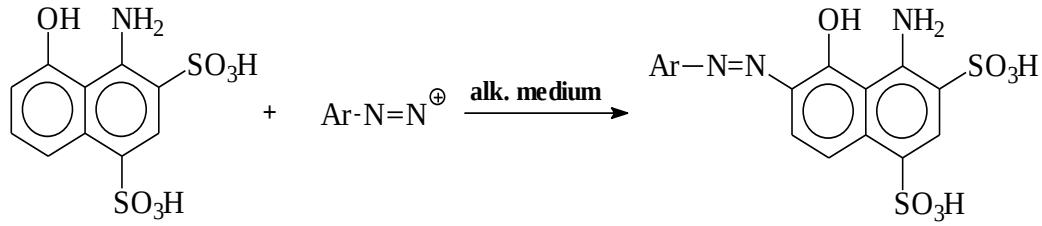






2,7-diarylazo-1,8-dihydroxy naphthalnene 3,6-disulphoric acid

(6)



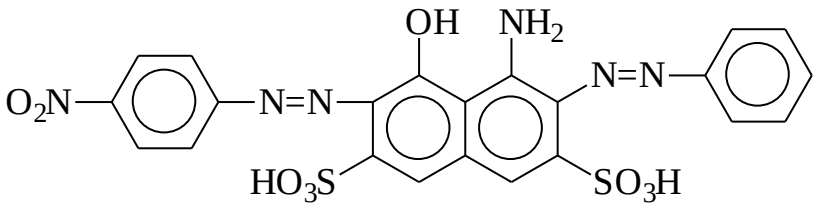
7-arylazo-1-amino-8-hydroxy naphthalnene 2,4-disulphoric acid

(7) Like (4).

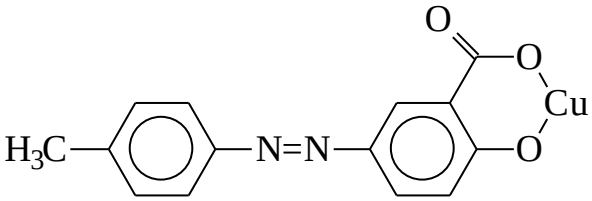
Question:

Synthesis of the following dyes:

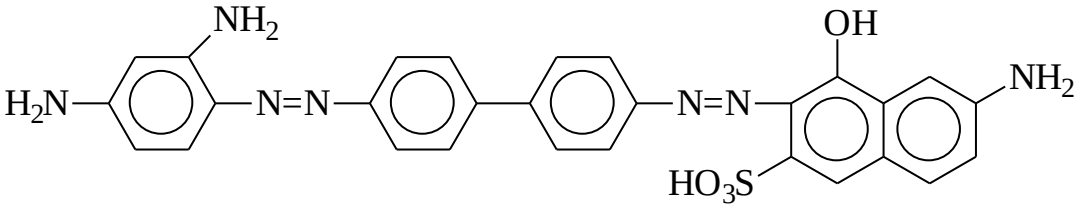
(1)



(2)

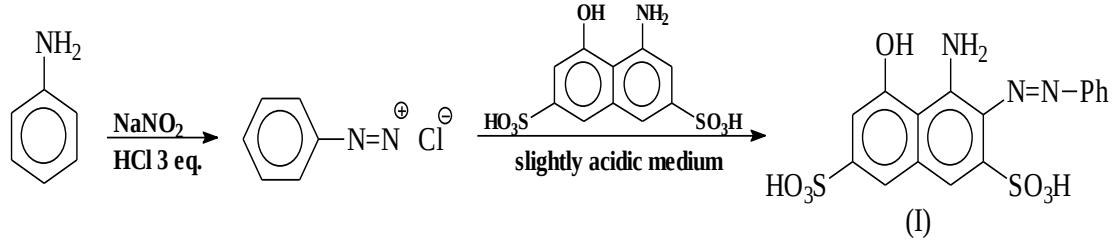


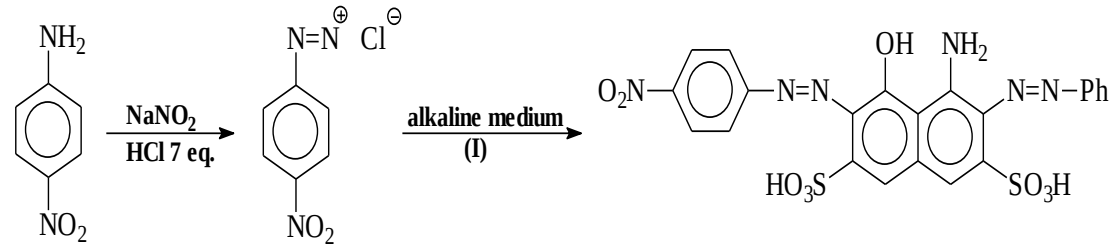
(3)



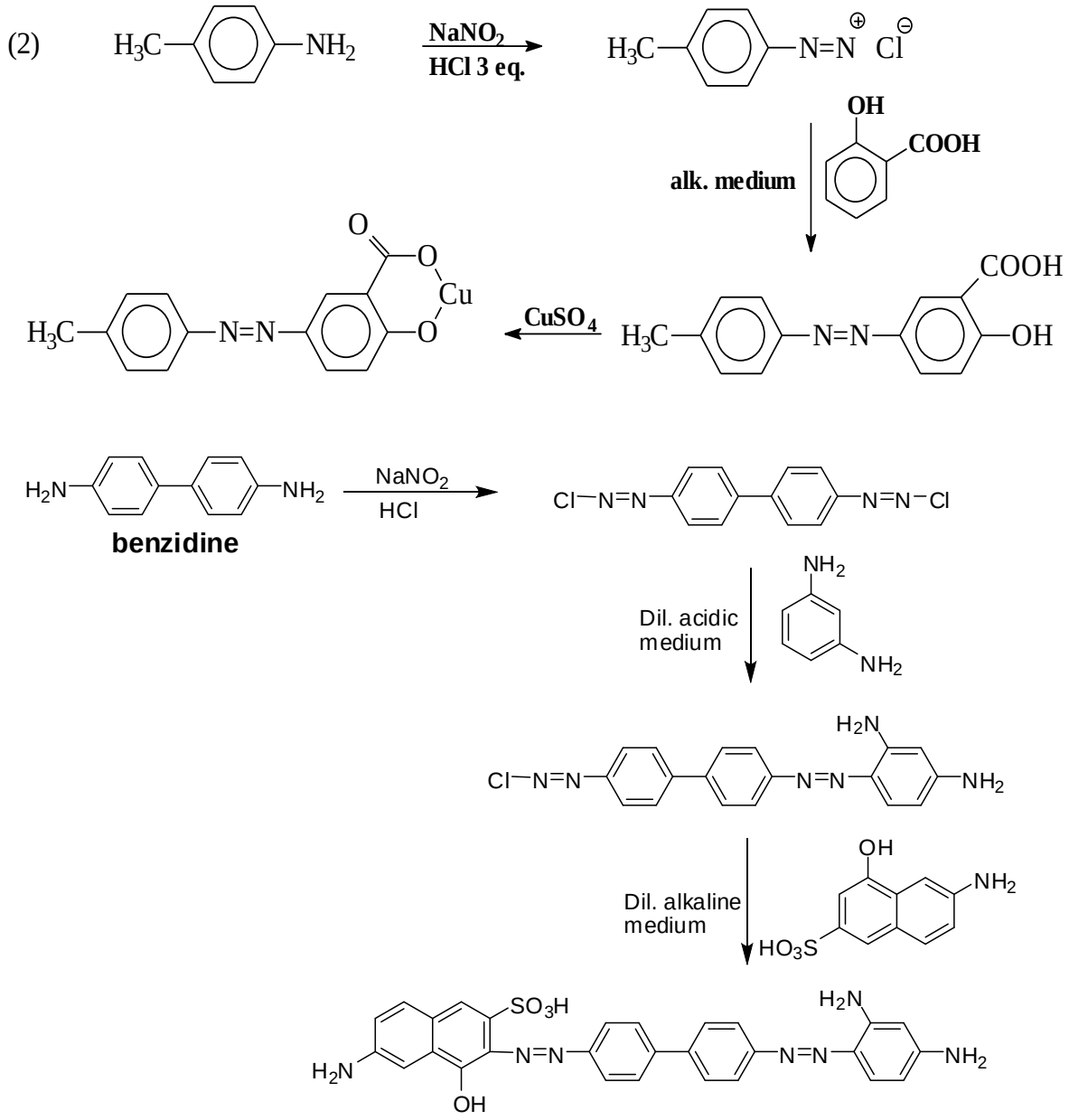
Solution:

(1)



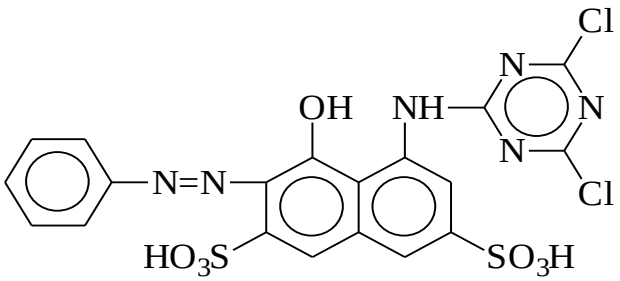


(2)

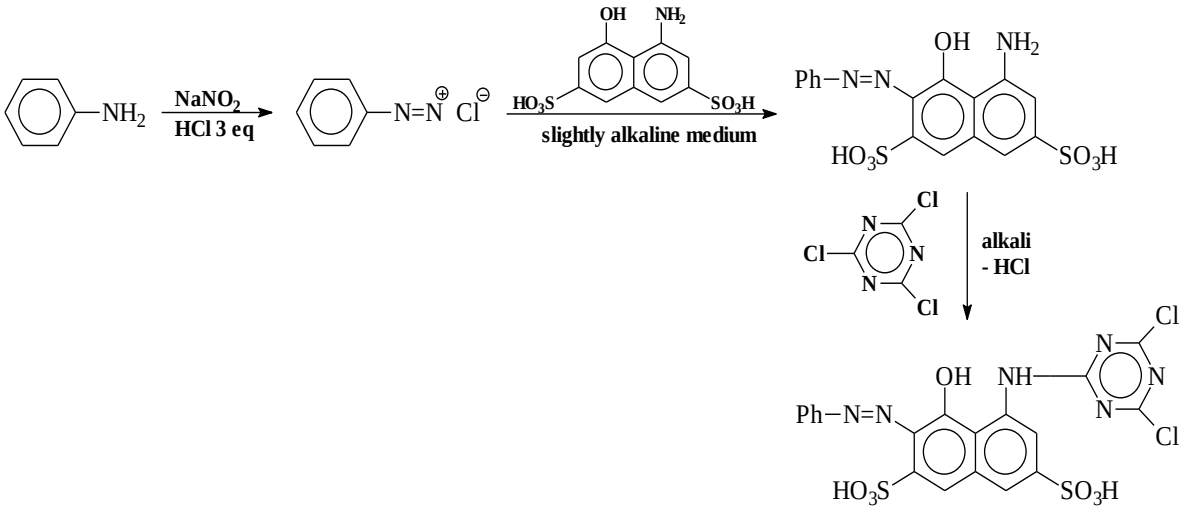

H3C
NH2
NaNO2
HCl 3 eq.
N=N
Cl
OH
COOH
alk. medium
CuSO4
Cu
O
H2N
benzidine
Cl—N=N
Dil. acidic medium
Dil. alkaline medium
HO3S
SO3H

Question:

Synthesis



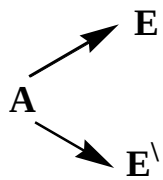
Solution:



Types of Disazo dyes

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

  1. **A→ E→ E\ or A→ M→ E**

2. 

3. **A→ E← A**

4. **A→ E.X.E ← A**

   Where A is diazo component (amine)

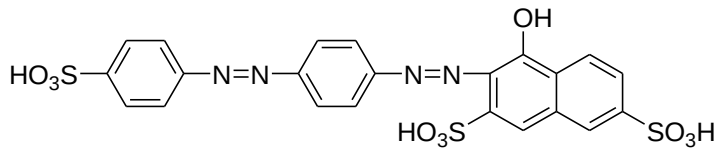
   E is coupling component

   X is agent used for binding two amines

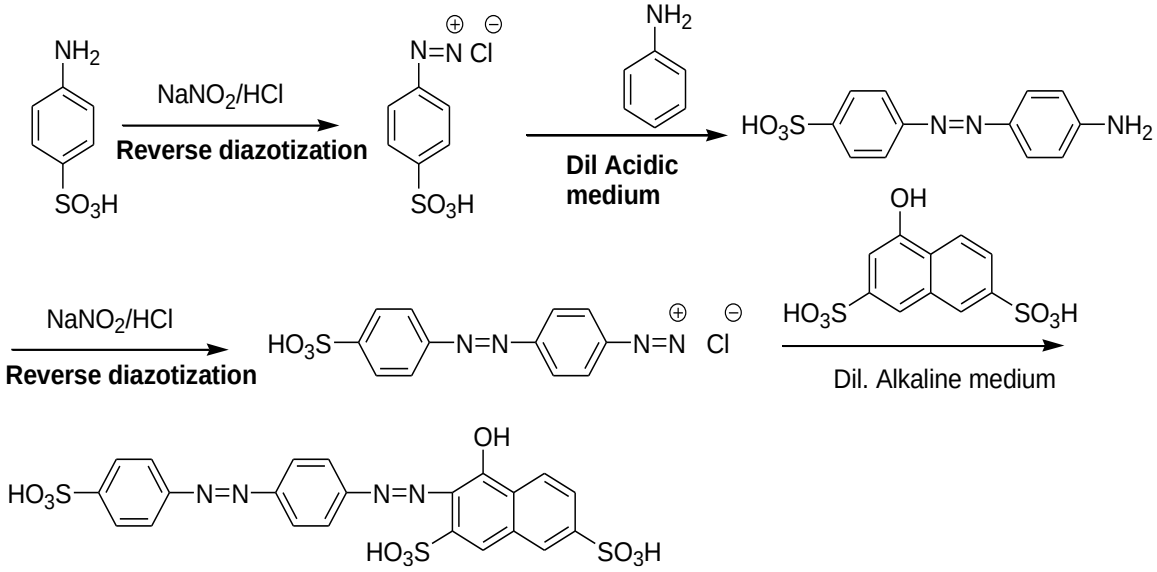
5. **<u>Type 1</u> A→ E→ E\ or A→ M→ E**

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

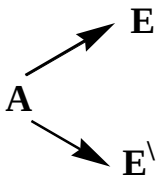
  <u>e.g.</u>



  <u>Synthesis</u>

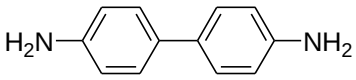


Type 2

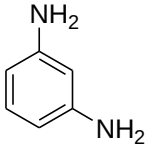


- **In this type we use Diamine as benzidine and couple it with two coupling component**

A as

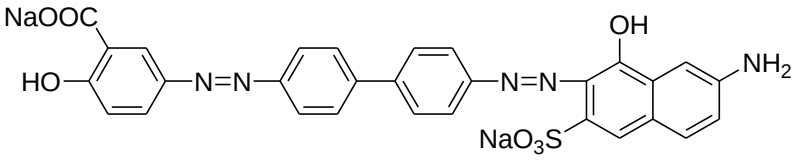


Benzidine

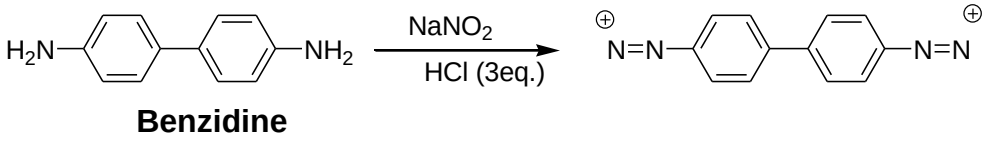


m-phenylenediamine

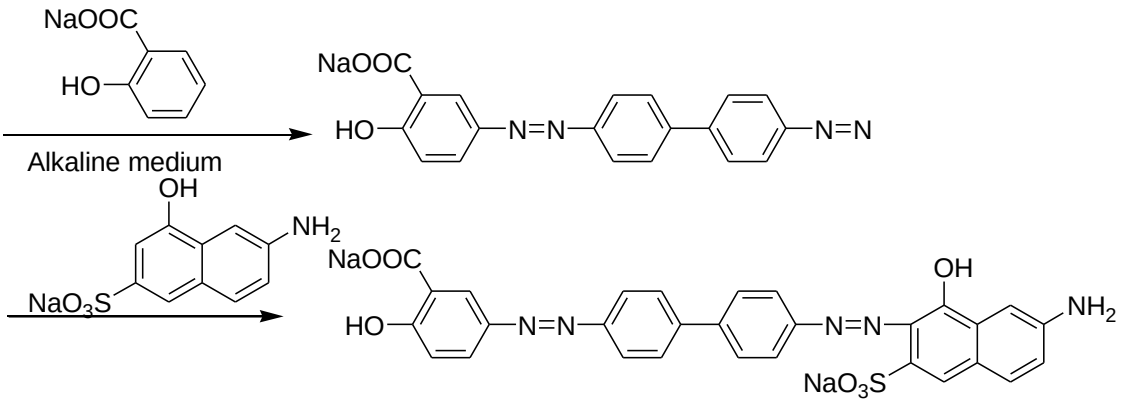
e.g.



Synthesis

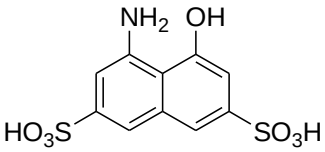


Benzidine



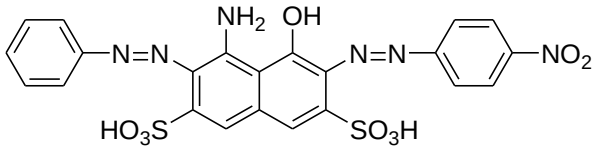
Type 3 A→ E← A

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



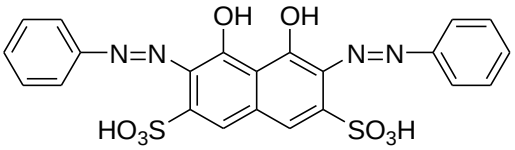
4-amino-5-hydroxynaphthalene-2,7-disulfonic acid

e.g.



See synthesis page 20

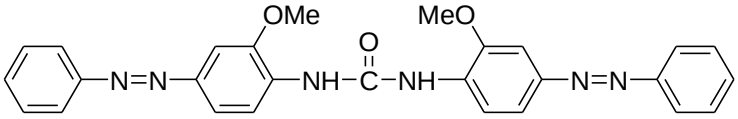
Example of A→ E← A



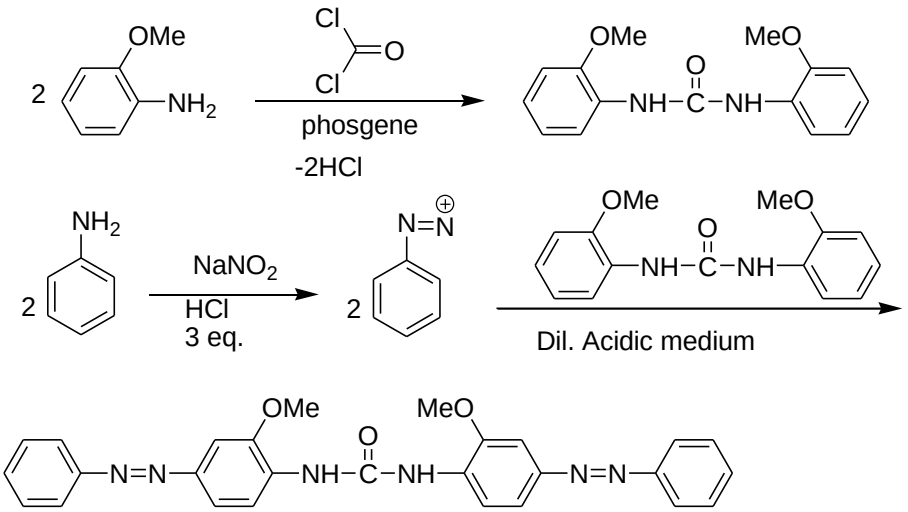
Type 4

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

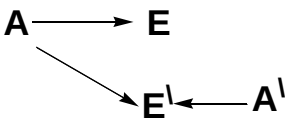
E.g.



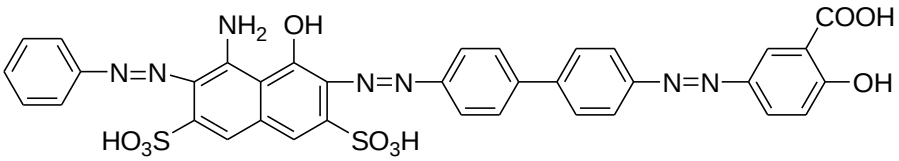
Synthesis



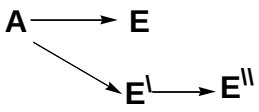
1. **Triazodyes**



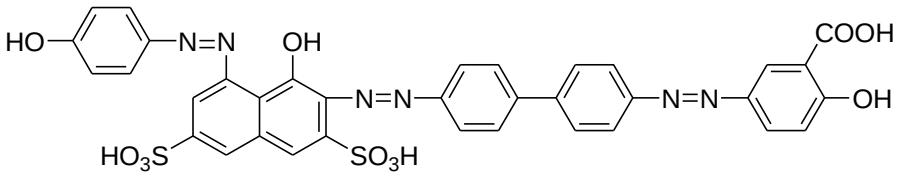
- **Like 3 but we introduce other coupling component on E**



2.

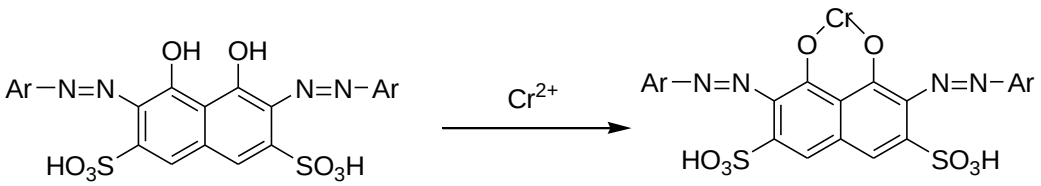


- **$E^{\backslash}$ must contain NH_2 which can be converted into diazonium salt can couple other coupling component**



<u>Metalazo compounds</u>

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



Some notes

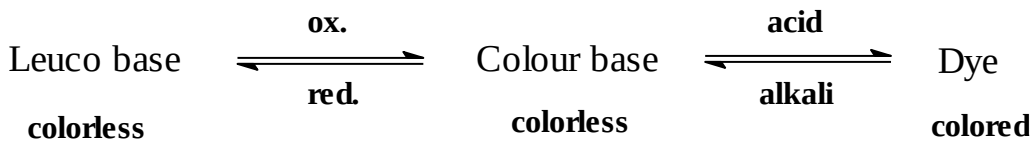
- **The diazonium salt produced from diamines such as benzidine are called tetrazonium salt and the dye produced is called bisazo dye**

The bis azo dyes can be prepared by many methods as explained in

Triphenyl methane dyes

- **Triphenyl methane dyes are obtained by introduction of NH_2, NHR, NR_2 or OH groups in para-position of two rings at least of three phenyl groups.**

- **The compounds obtained are colorless (leuco-base) on oxidation converted into t-alcohol (color-base), which forms quinoniud structure in the presence of acid.**



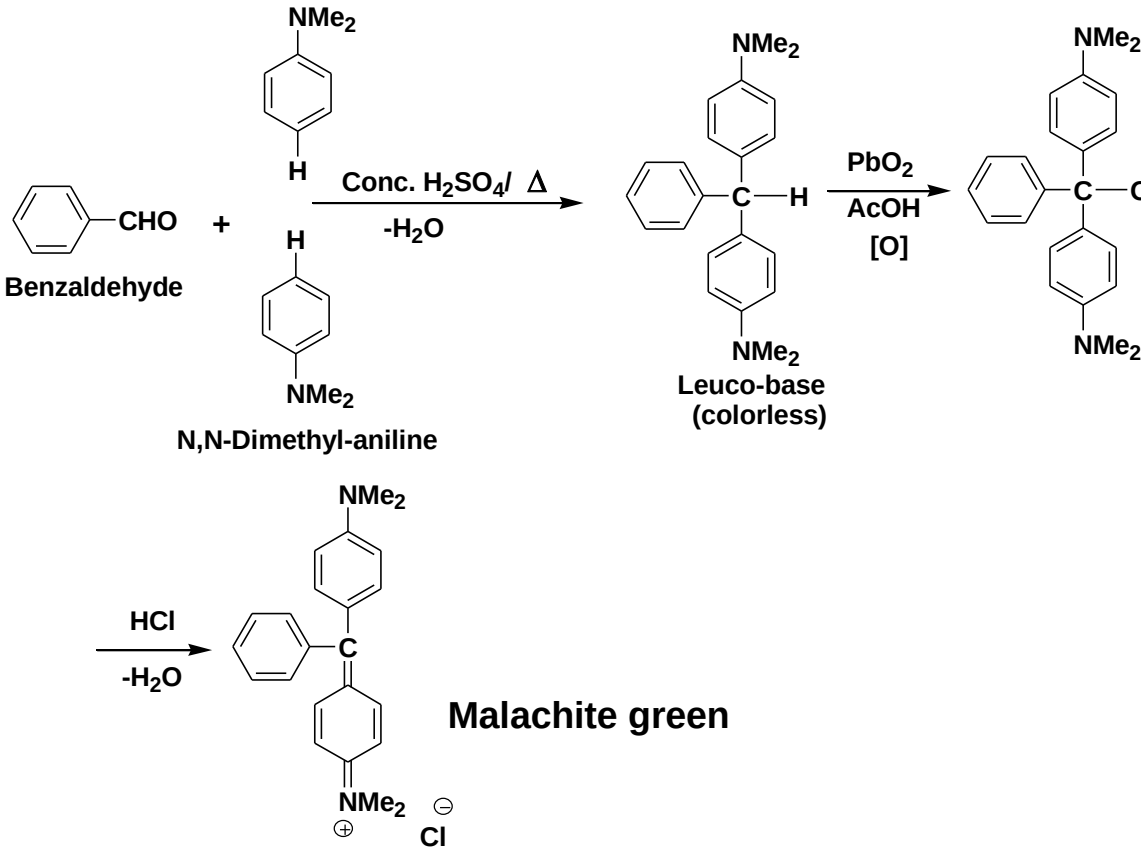
- Triphenyl methane dyes are classified into:

1- Base Dyes or cationic dyes.

2- Acid Dyes or anionic dyes.

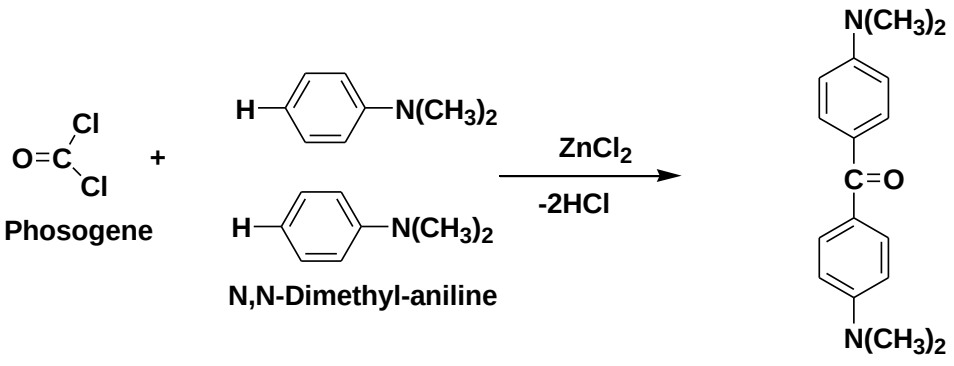
1) Base Dyes or cationic dyes

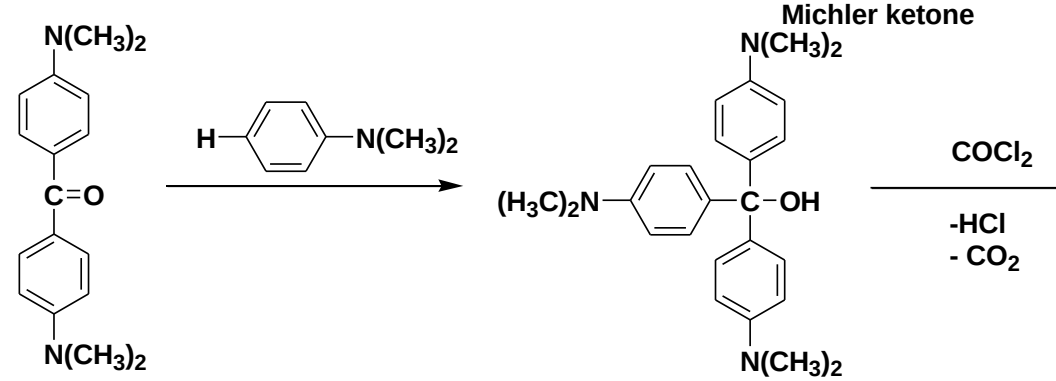
A) Malachite green

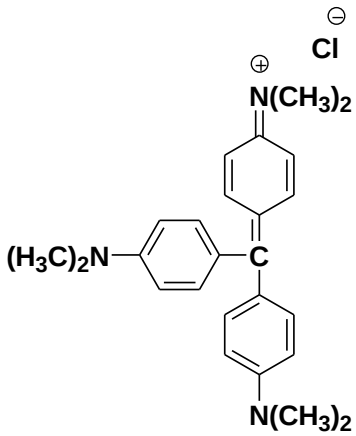


- ***Malachite green is used for dying cotton and polyacrylonitrile***

B) Crystal violet

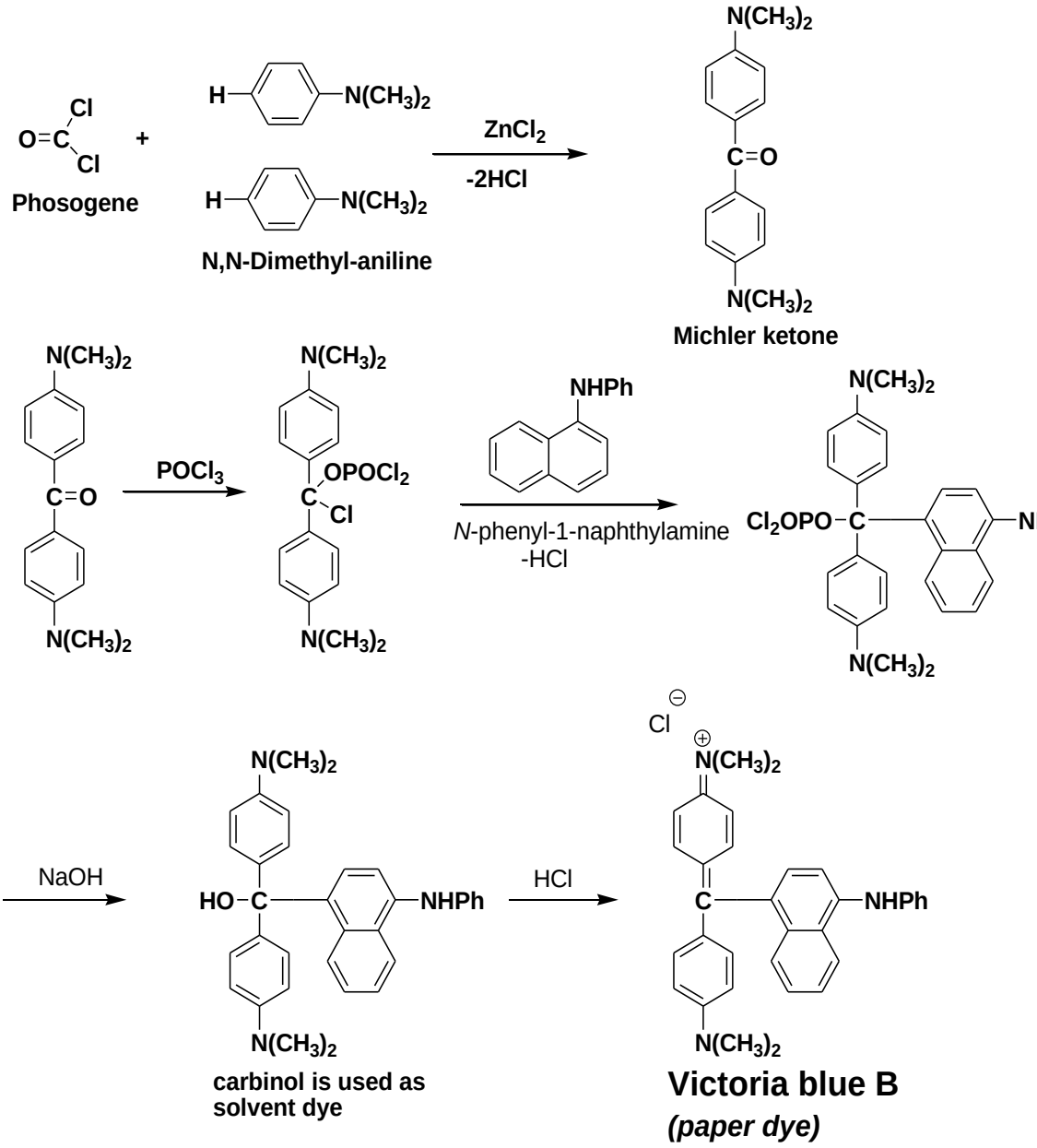






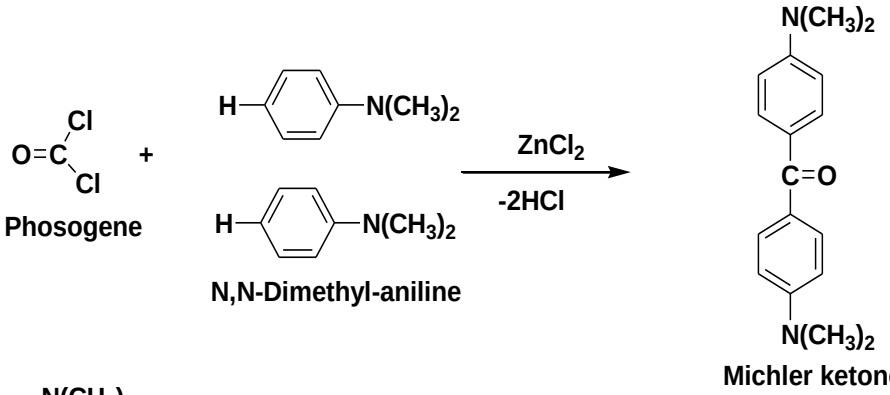
Crystal violet

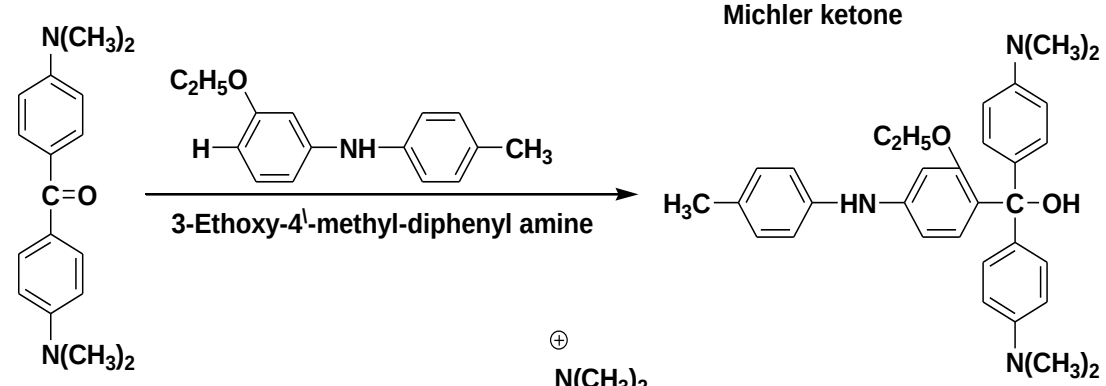
C) Victoria blue B (paper dye)

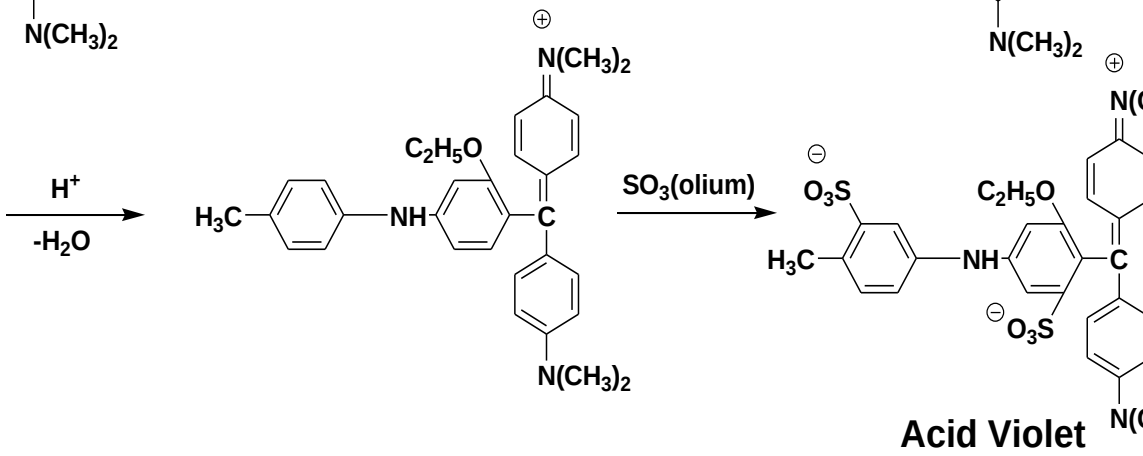


Acid dyes

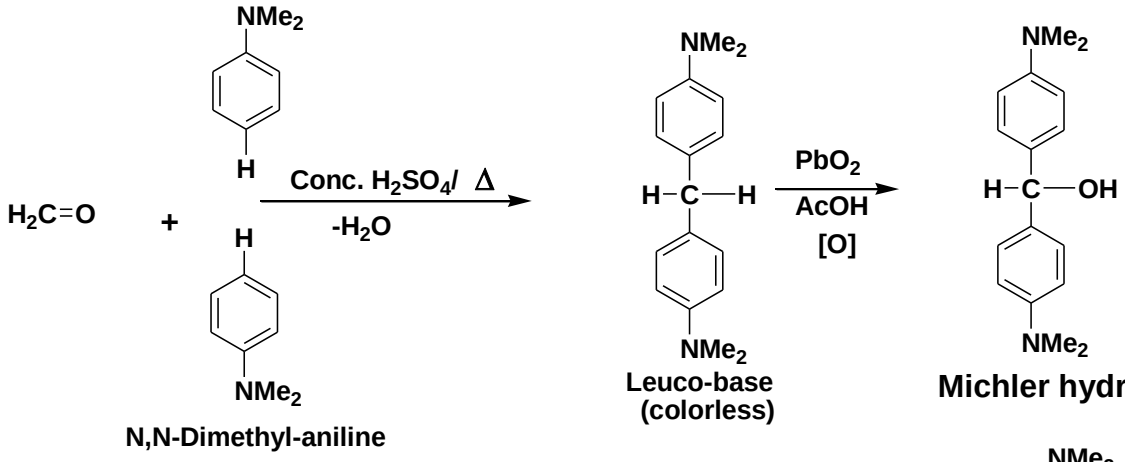
1) Acid violet

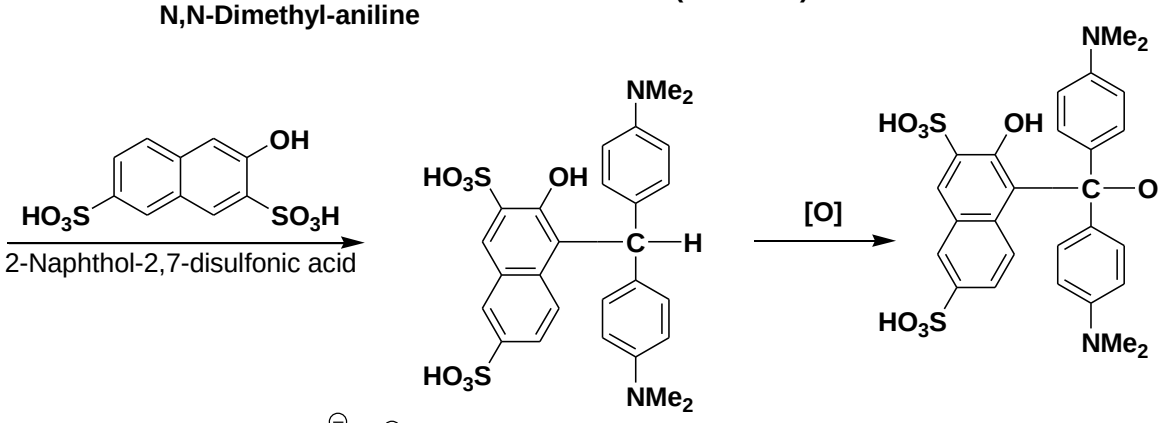


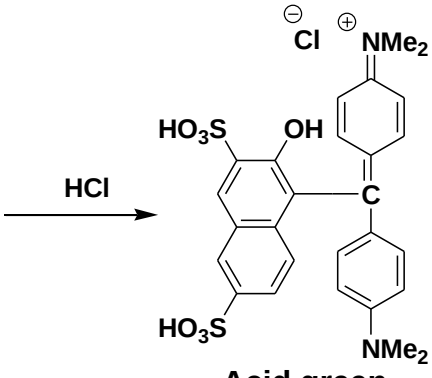




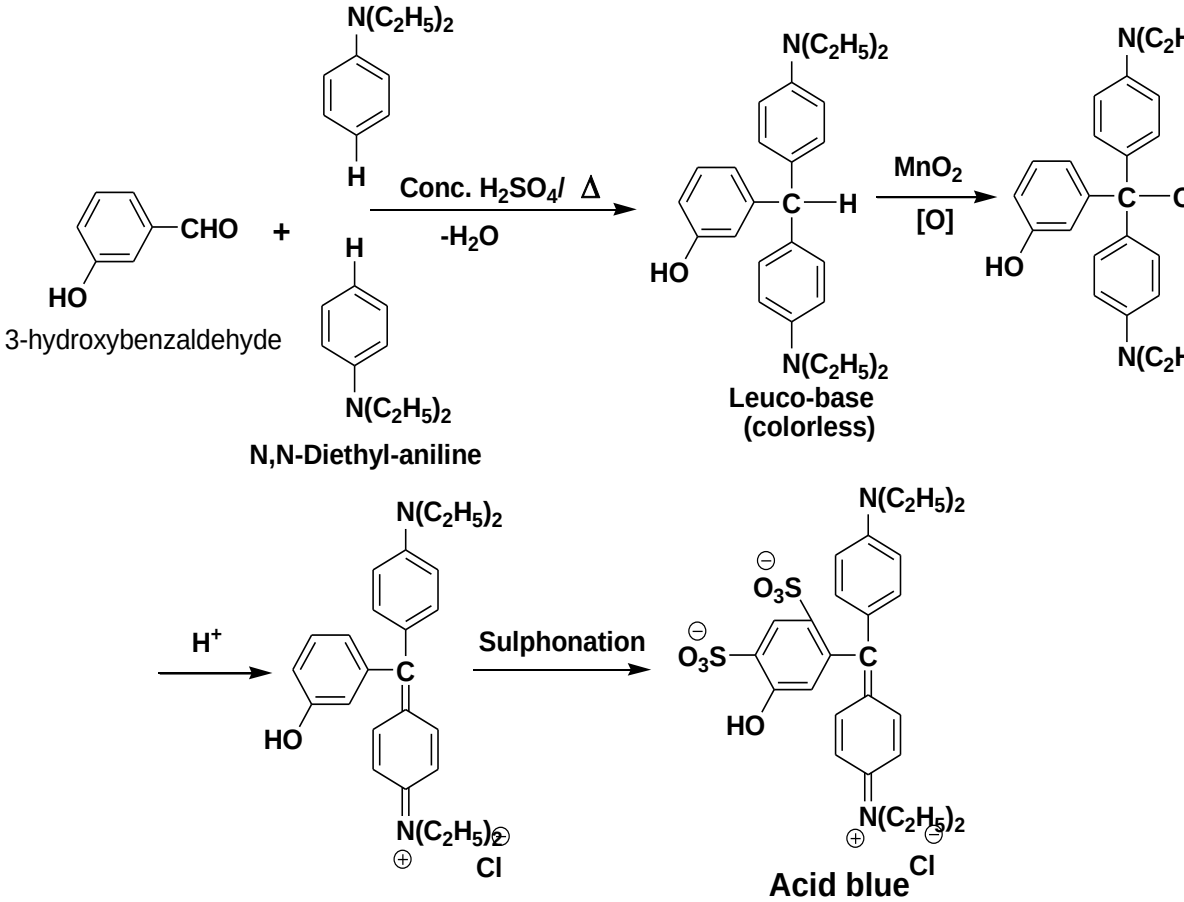
2) Acid green (wool green):





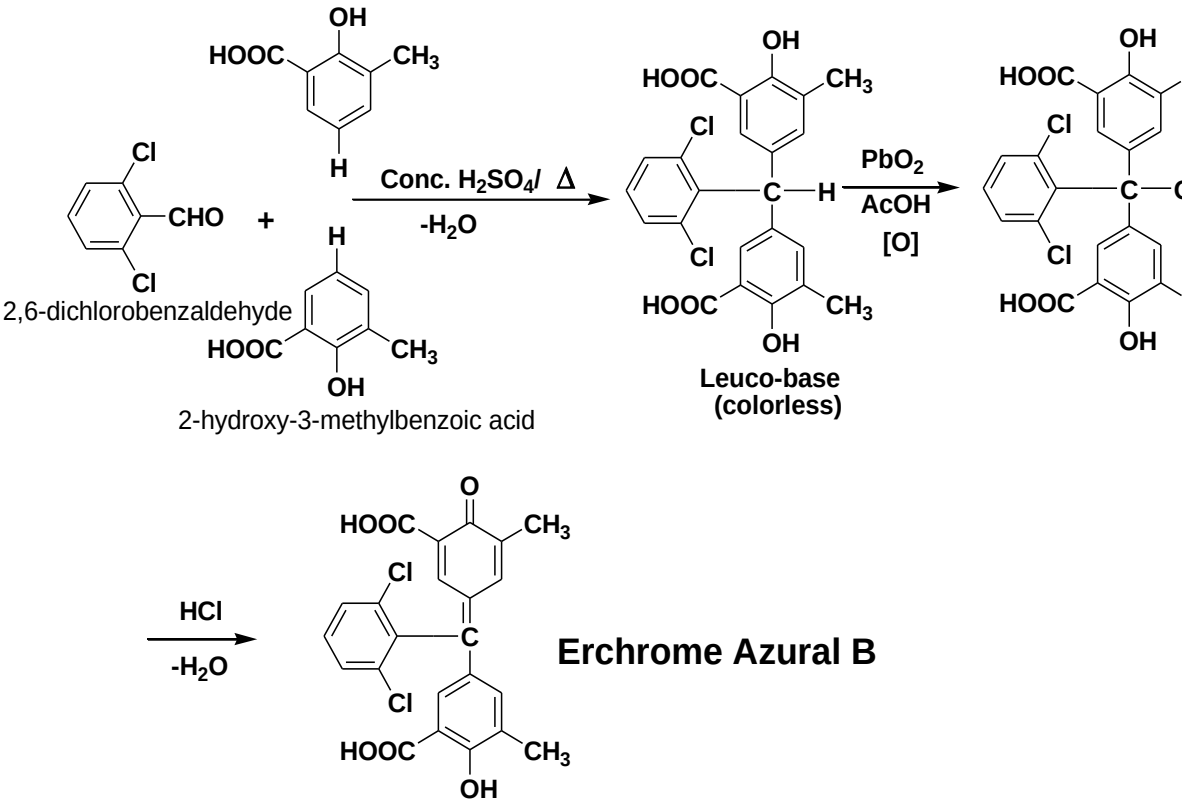


3) Acid blue (patent blue):

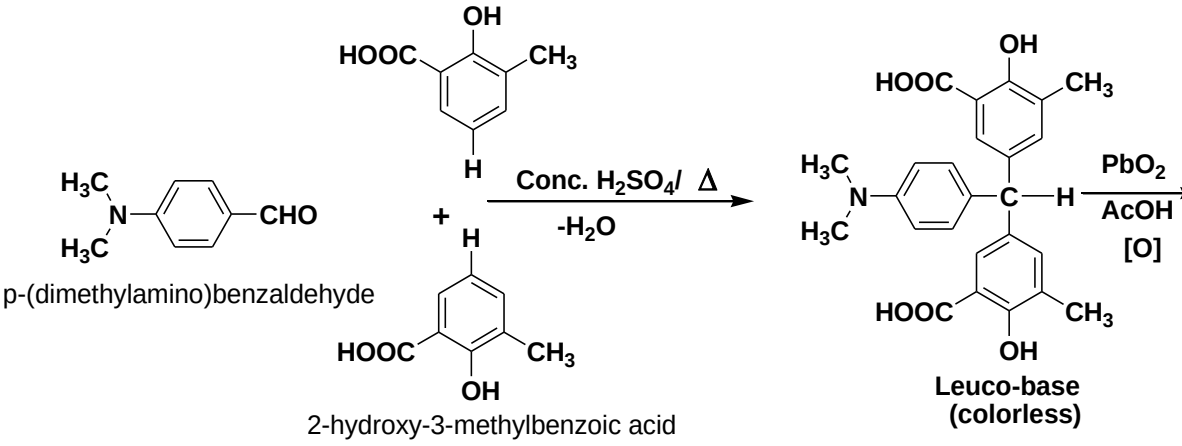


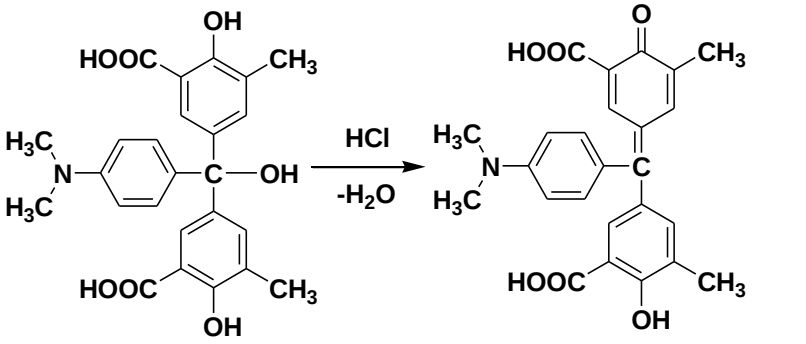
Hydroxy triaryl methane dye

1-Erichrome azurol B:

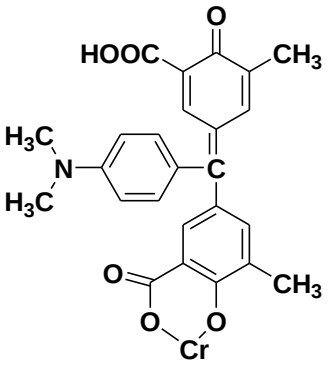

OH
HOOC
CH3
H
Cl
CHO
Cl
+
Conc. H2SO4/ Δ
-H2O
2,6-dichlorobenzaldehyde
2-hydroxy-3-methylbenzoic acid
Cl
C
H
PbO2
AcOH
[O]
Leuco-base
(colorless)
HCl
-H2O
O
Erchrome Azural B

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:

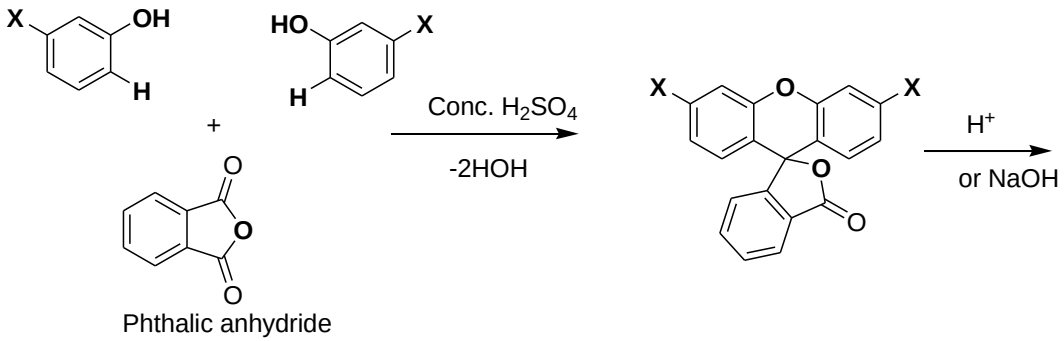
X = auxochromes (NH_2, NHR, NR_2, OH).

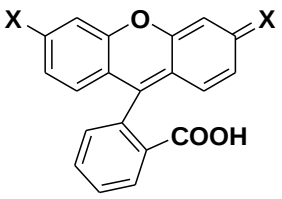
X must be in para-position to CR_2

- The color is due to formation of quinoid structure.

Xanthene dyes

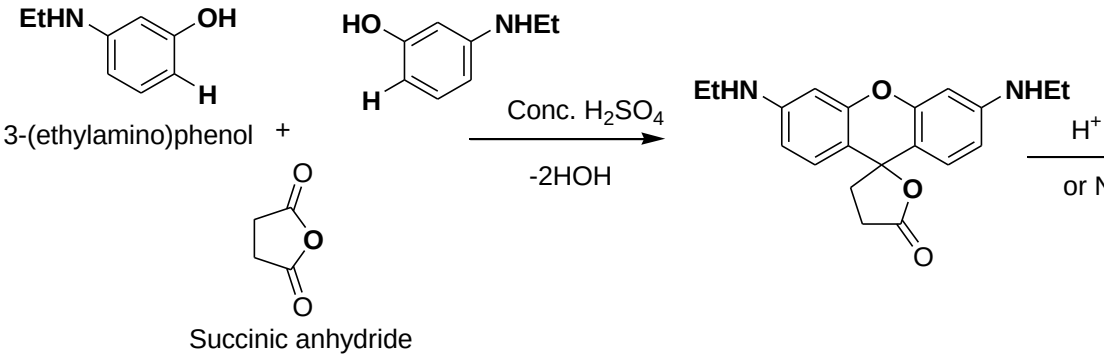
General procedures

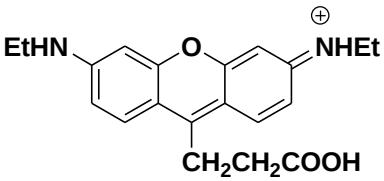




Where X = NH_2 or NHR or NR_2 the dye is called rhodamine

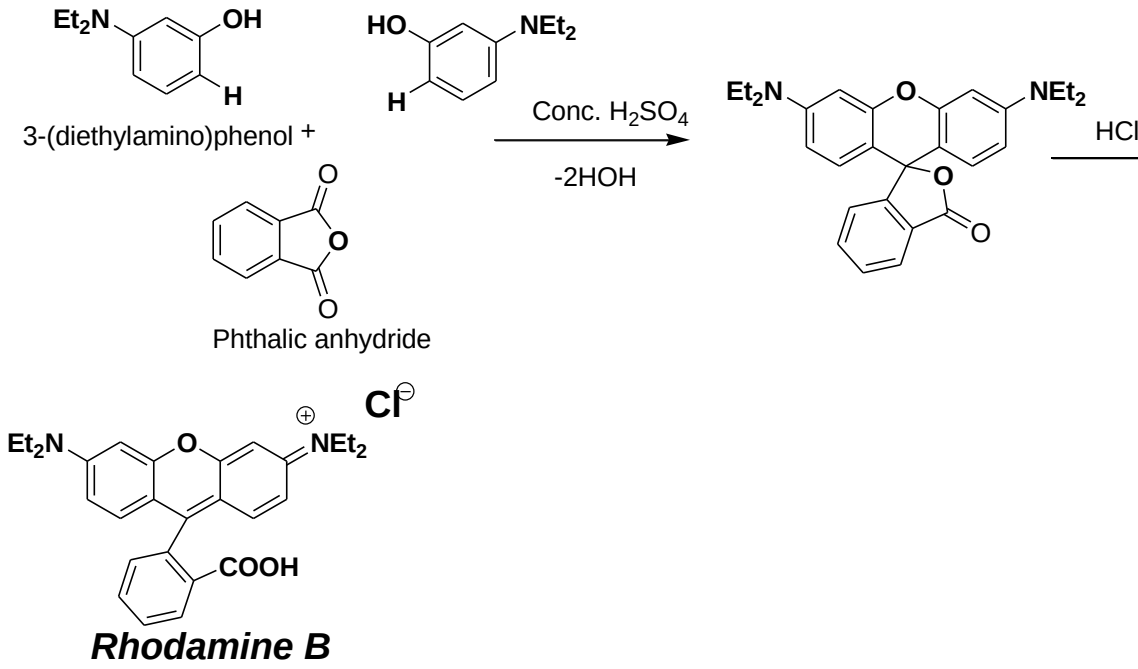
1- C.I. Basic red



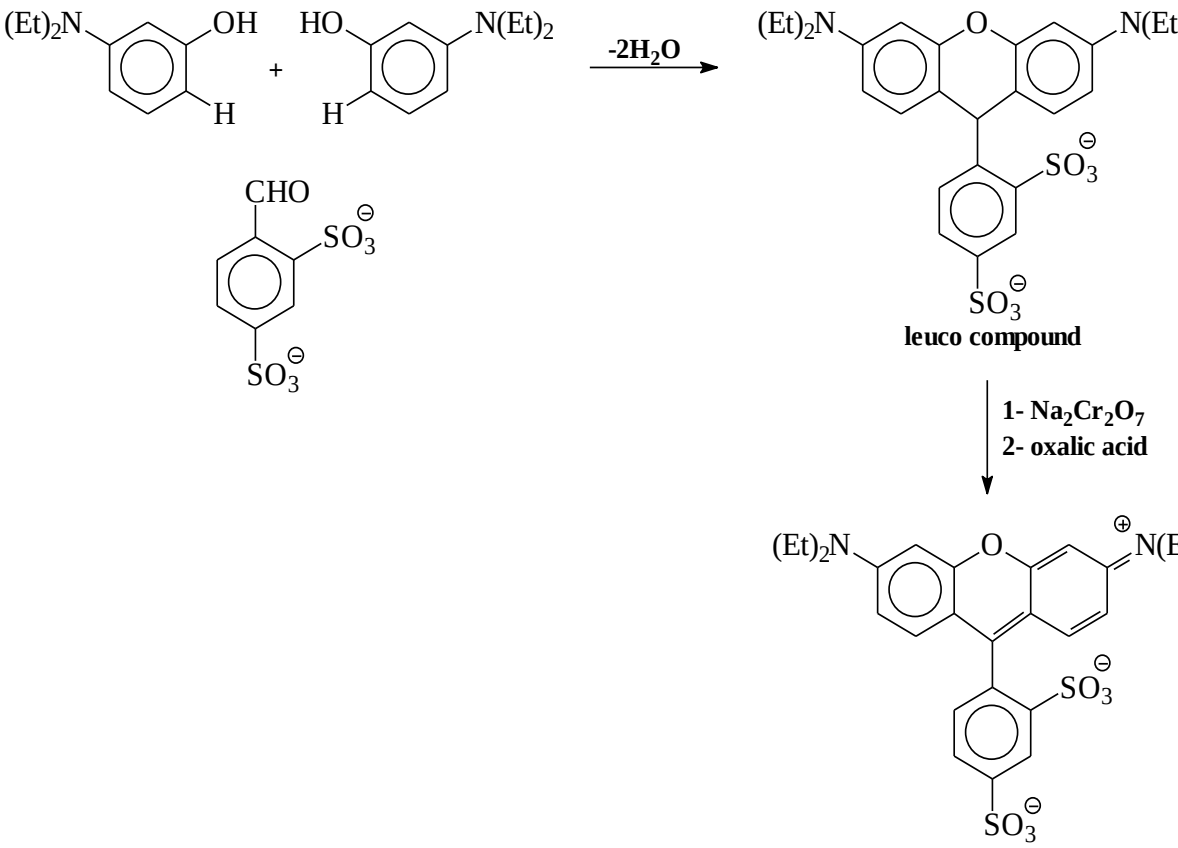


C. I. Basic red

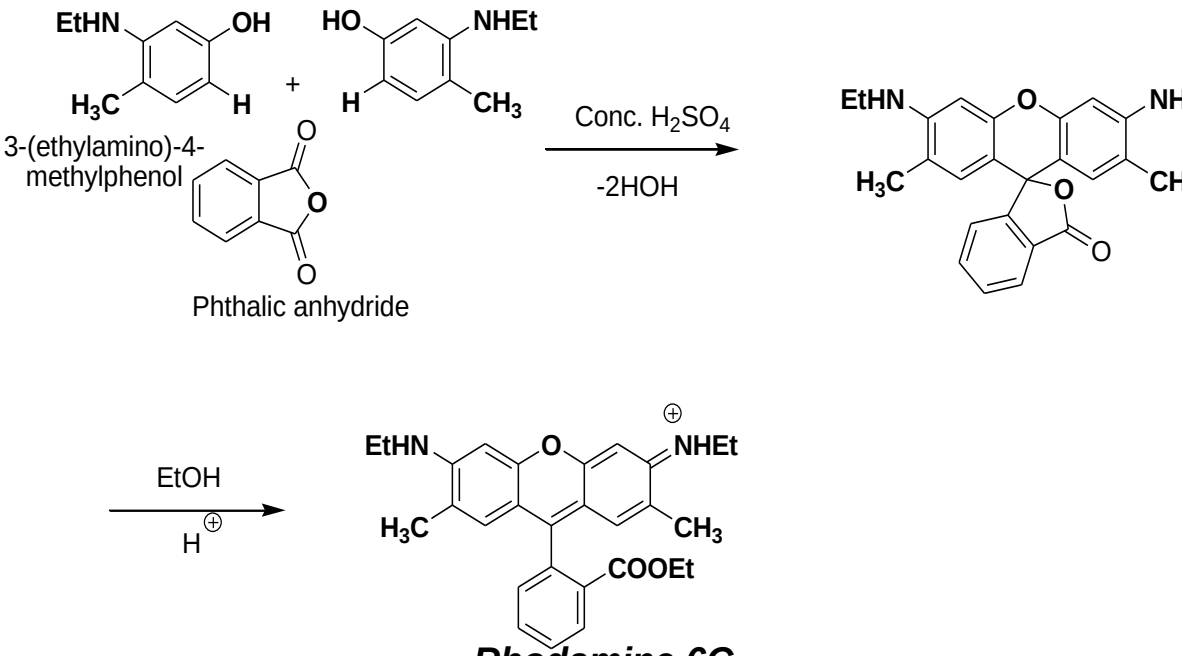
2) Rhodamine B



3) Sulphorhodamine (Rosamine dye)

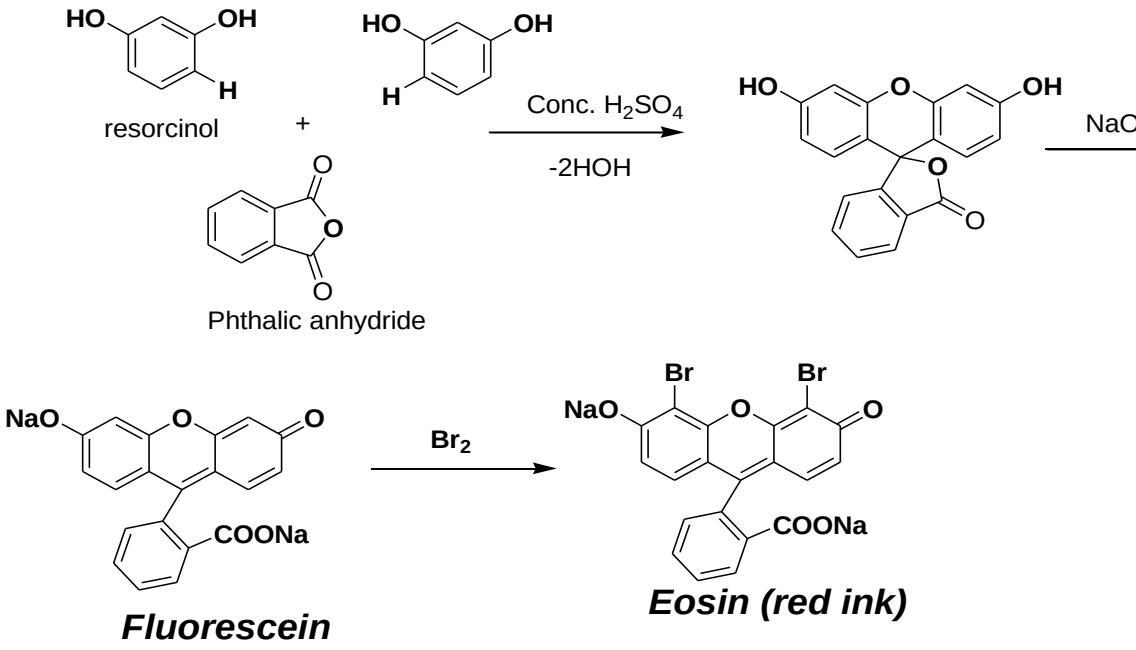

(Et)2N
OH
H
+
HO
N(Et)2
H
CHO
SO3
SO3
-2H2O
(Et)2N
O
N(Et
SO3
SO3
leuco compound
1- Na2Cr2O7
2- oxalic acid
(Et)2N
O
N(E
SO3
SO3

4) Rhodamine 6G



Rhodamine 6G

5) Fluorescein dye and its derivative (Eosin)



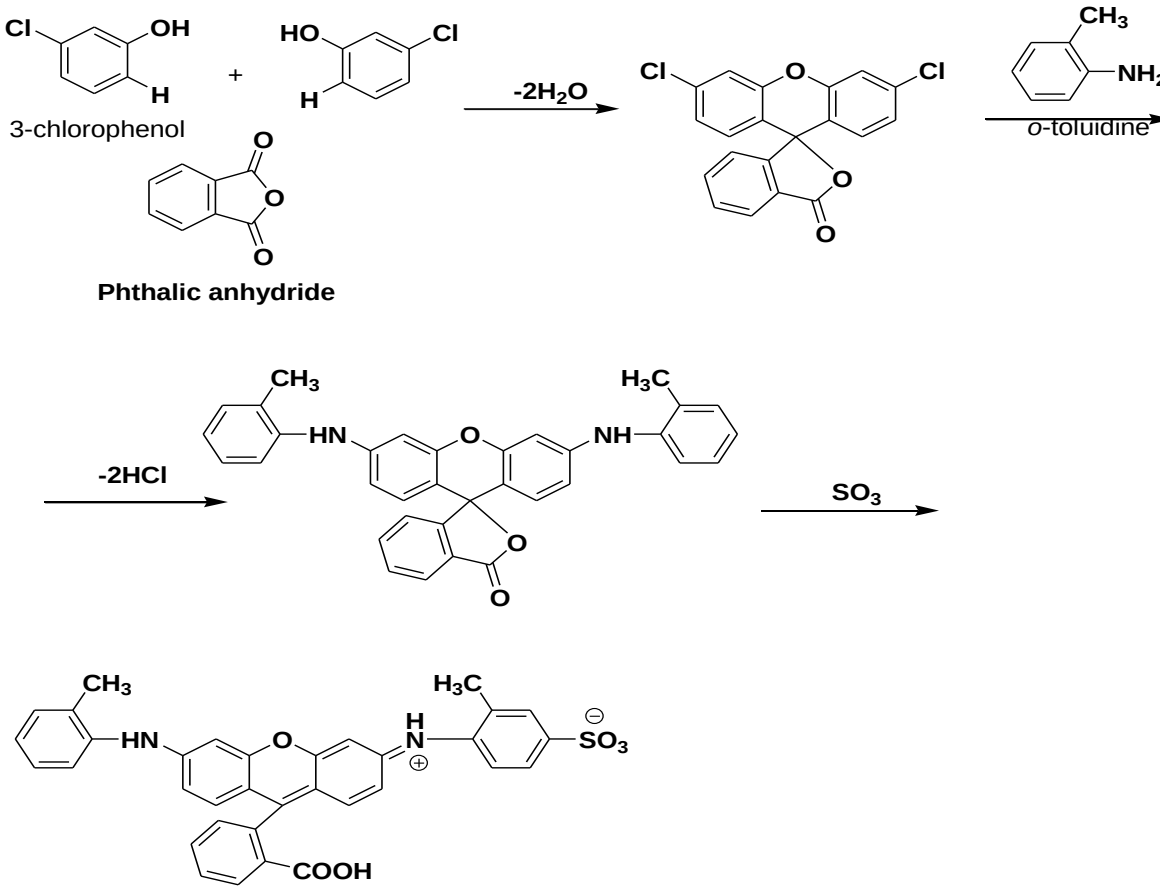
3-Kiton fuchine A_2R:

It is wool dye.

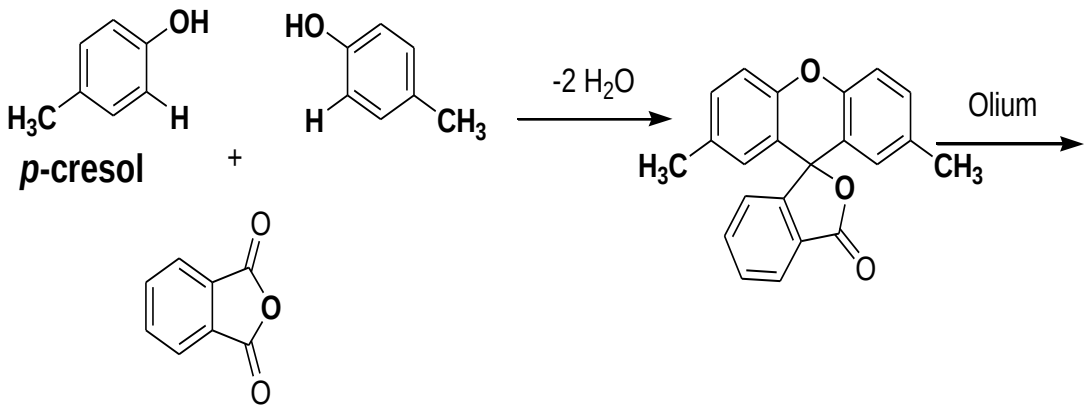
It is reddish violet dye with good fastness.

It can be used for paper coloration.

It can be prepared as follow.



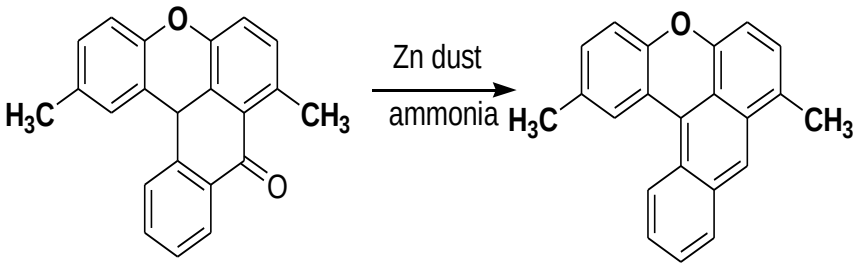
4-Fluorol 5-G: (Coloring mineral oil)



***p*-cresol**

+

Phthalic anhydride



Fluorol 5G
Coloring mineral oil)

Vat dyes

It classified into two types:

1- **Indigo dyes.**

2- **Anthraquinone dyes.**

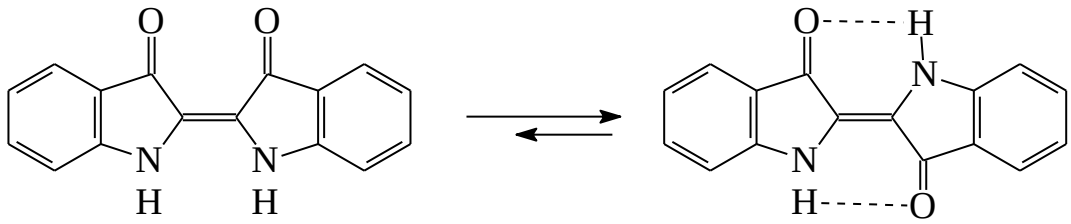
Vat dye (insol. dye) $\xrightarrow{\text{Reduction}}$ Leuco compound (soulble colorless)

$\downarrow$ [O]

Colored insoluble dye

Structure of indigotin:

Indigotin can exist in both cis and trans form.

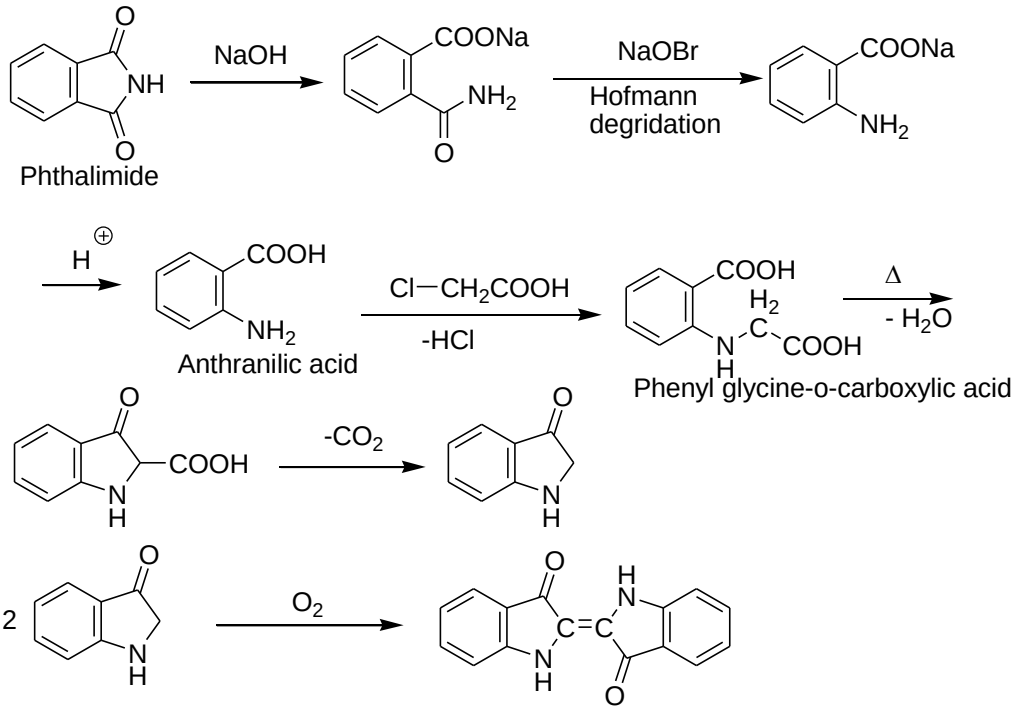


cis form
less stable

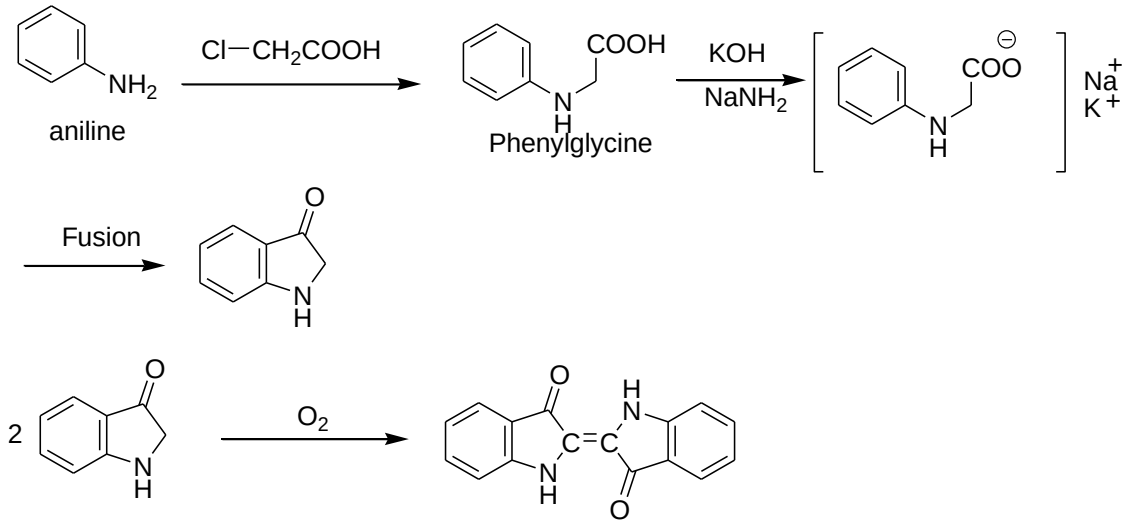
trans form
more stable due to formation of H.b.

<u>Synthesis of Indigo</u>

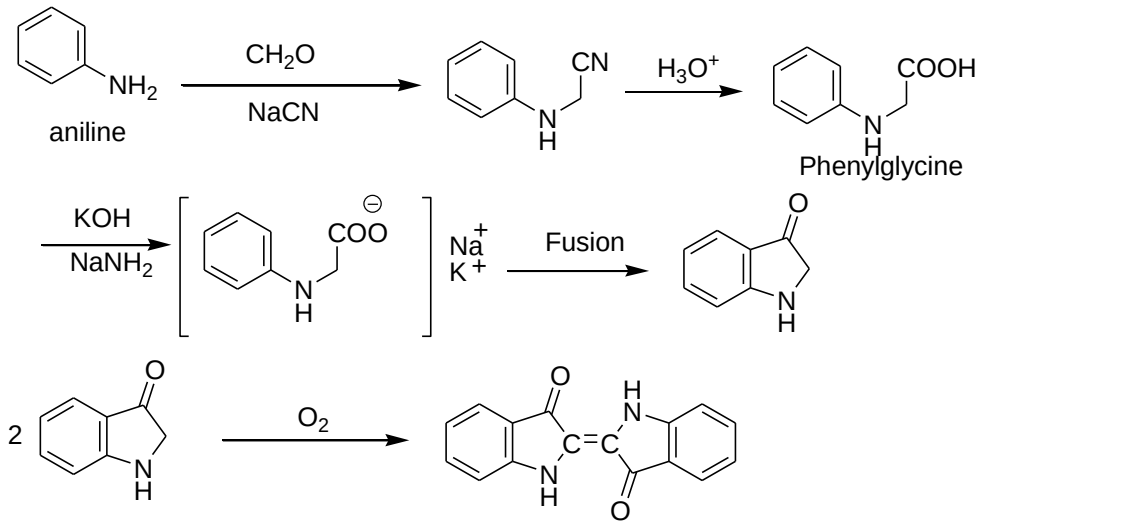
1. Heumann process



2. Sodamide process

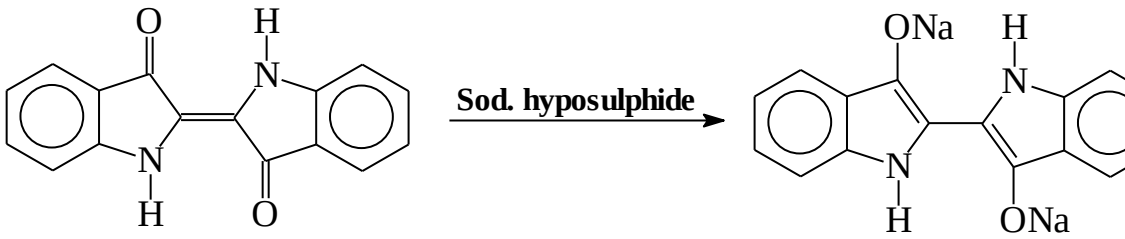


3. From aniline and sodium cyanide



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).**



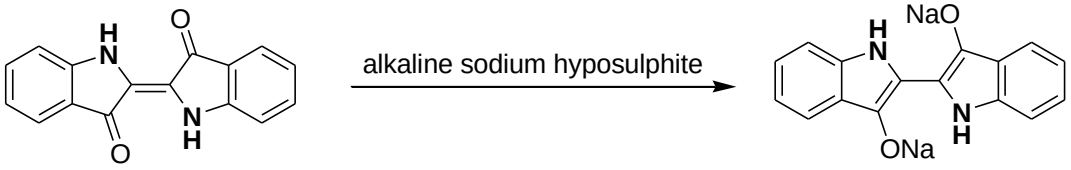
indigotin blue oxidized form water insol.

indigotin colorless redu form water soluble

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

Indigotin derivatives

1) Indigotin white

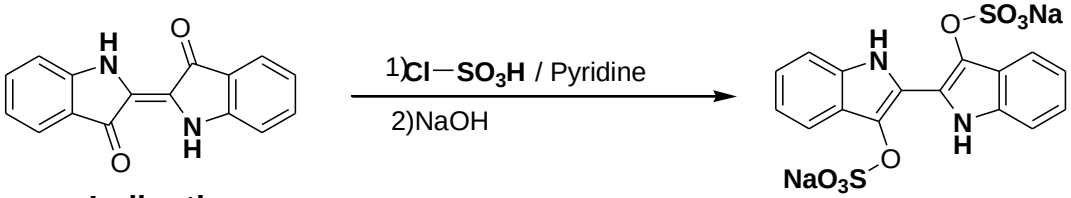


Indigotin
dark blue
water insoluble

White Indigotin
colorless
water soluble

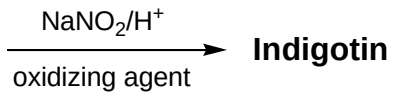
2) Indigosol O

- **It is used for dying wool**



Indigotin

Indgosol O
Water soluble



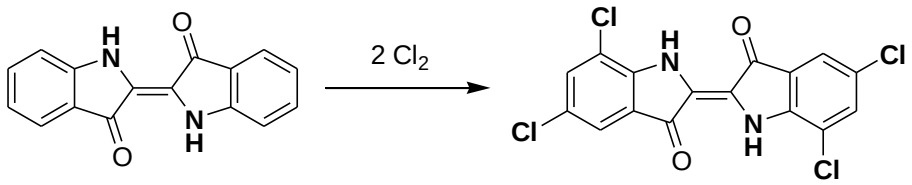
Indigotin

Application of Indigosol on fibres

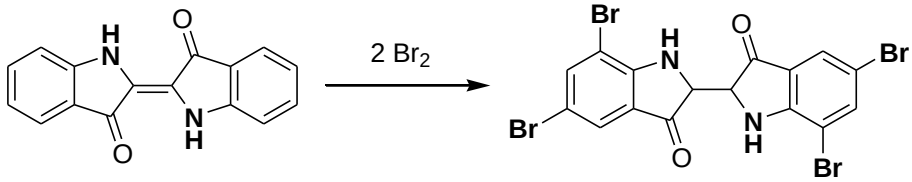
- **Indigosol O is applied on both animal and vegetable fibres by soaking نقع the fabic in the**

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



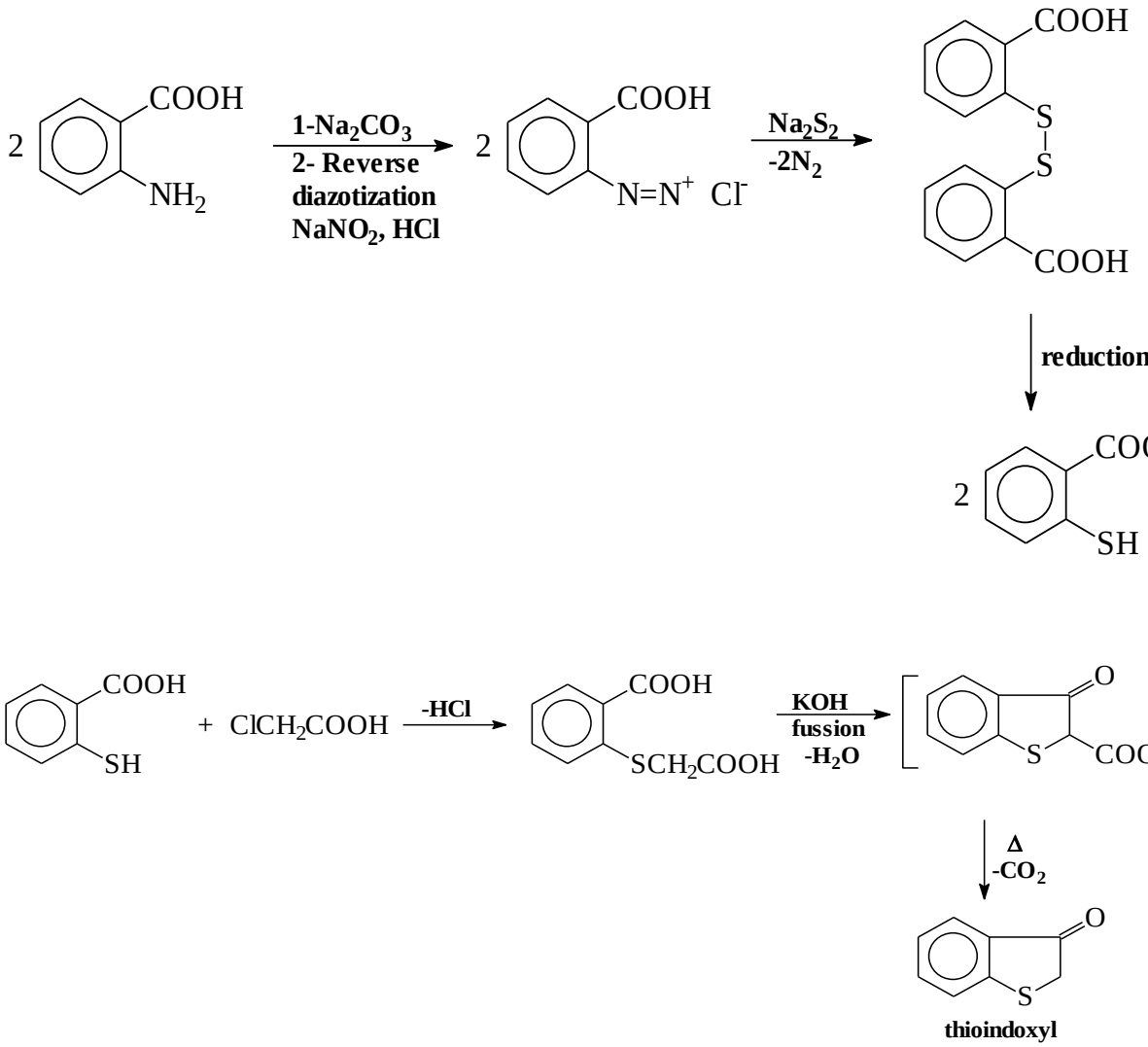
Indigotin **Brilliant Indigo B**

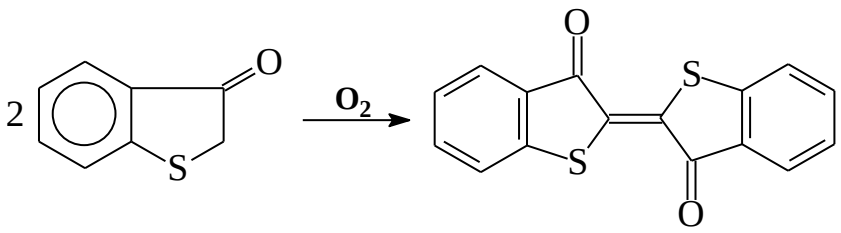


Indigotin **Brilliant Indigo 2B**

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

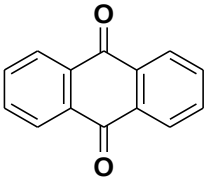
Preparation of thio-indigo:





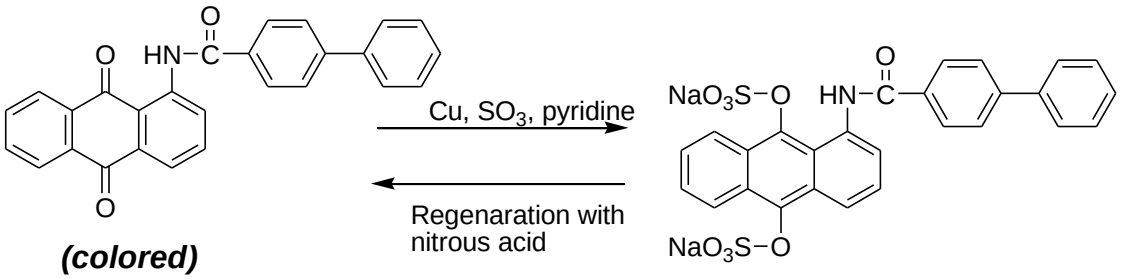
Thioindig red

Anthraquinone vat 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**

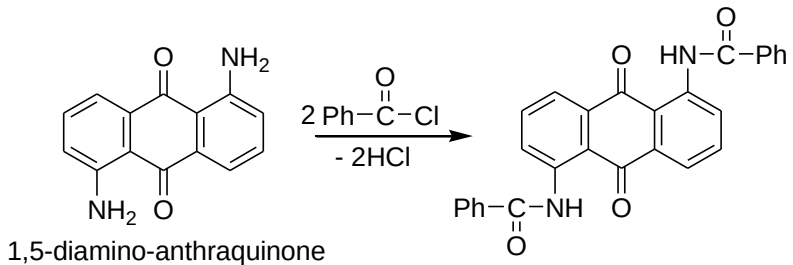


(colored)

Leuco form (colorless)

1) Indanthrone dyes:

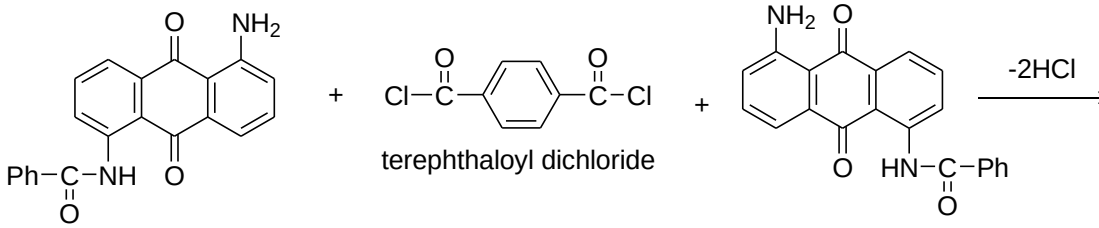
Synthesis of C.I vat yellow(cibanone yellow FGK), (Indanthrene yellow GK)



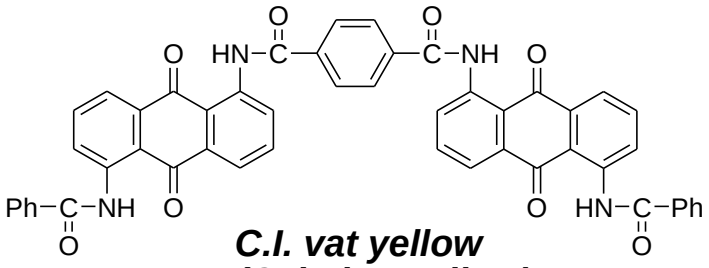
1,5-diamino-anthraquinone

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

Synthesis of C.I vat yellow (Caledon yellow)



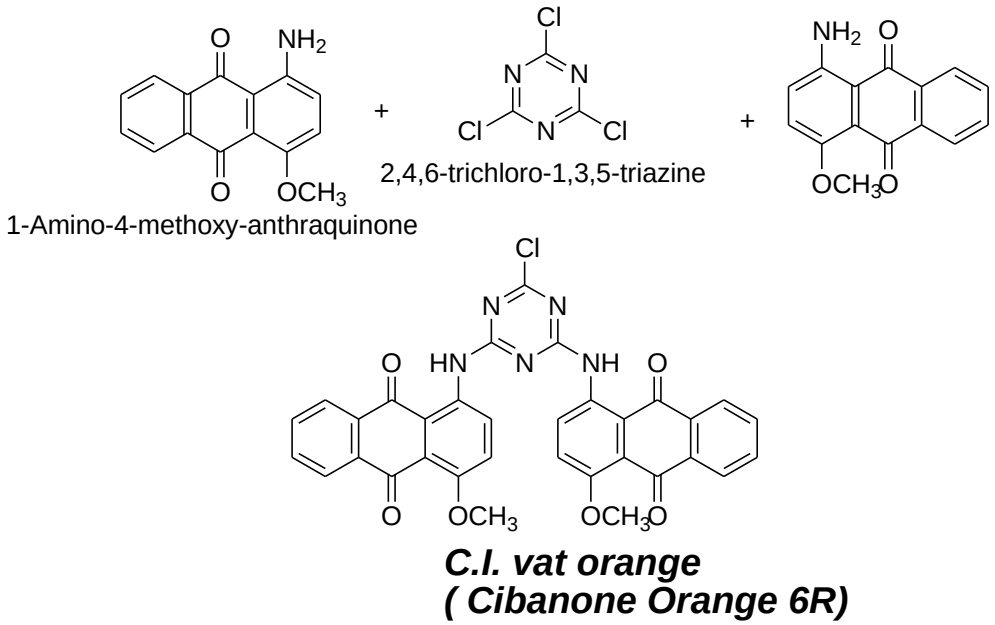
1-Amino-5-benzoylamino-anthraquinone



C.I. vat yellow (Caledon yellow)

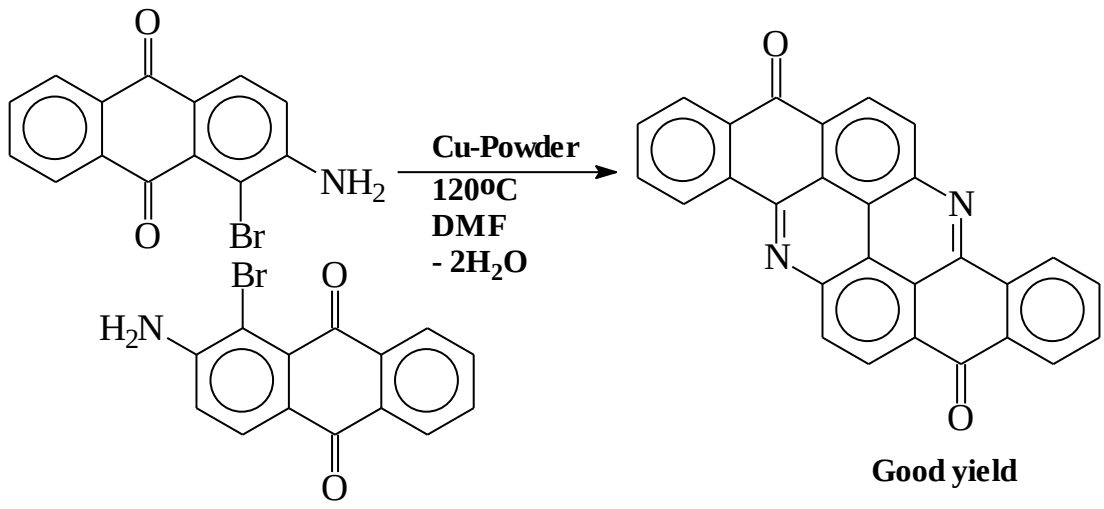
Synthesis of C.I. vat orange (Cibanone Orange 6R)

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



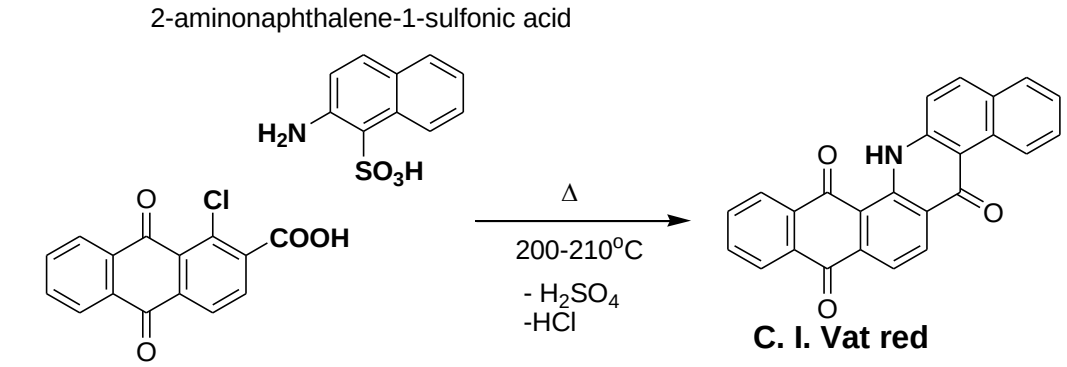
C.I. vat orange
(Cibanone Orange 6R)

C) Flavanthrone (Indanthrone yellow G):

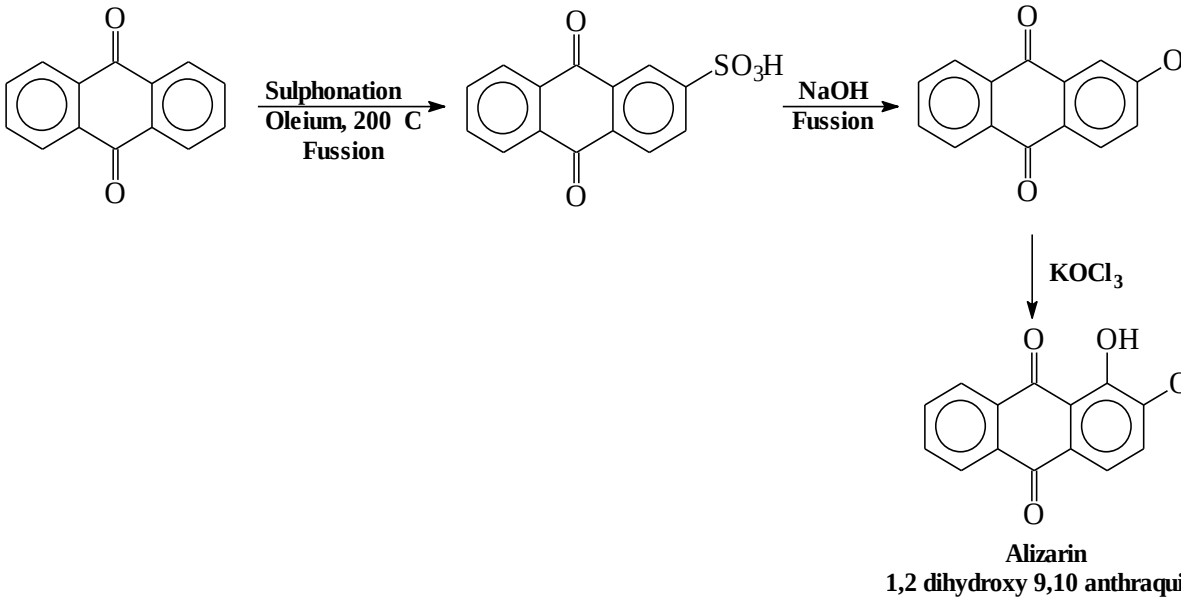


Anthraquinonacridine

Synthesis of C.I Vat red



Alizarine



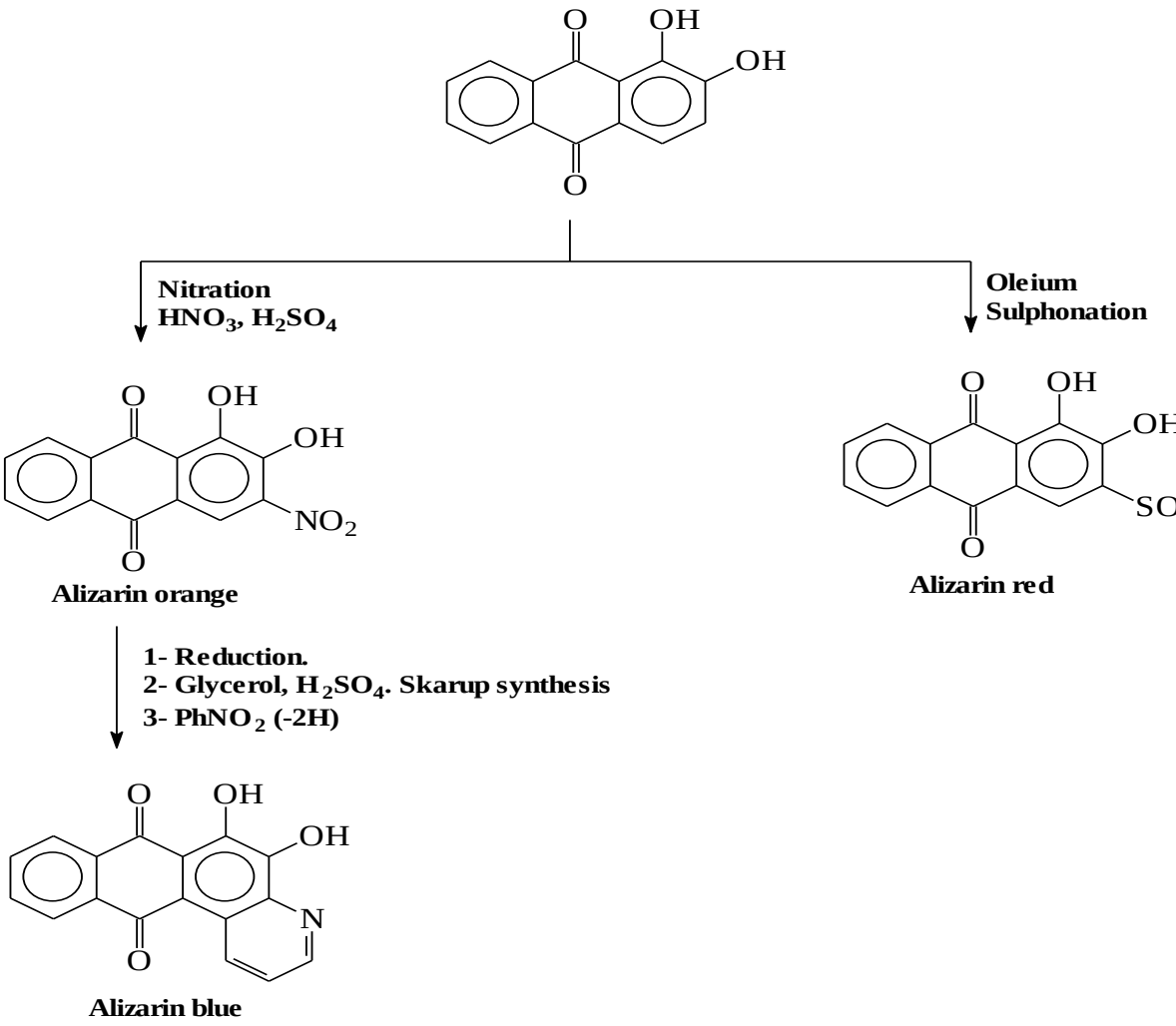
Alizarin is used to prepare:

a- Alizarin orange.

b- Alizarin red.

c- Alizarin blue.

As the following:



Cyanine dyes:

- **Cyanine dyes have no value as dyes, but it is very important as photographic sanitizers.**

- **Cyanine consists of two heterocyclic nuclei linked by odd number of conjugated double bond.**

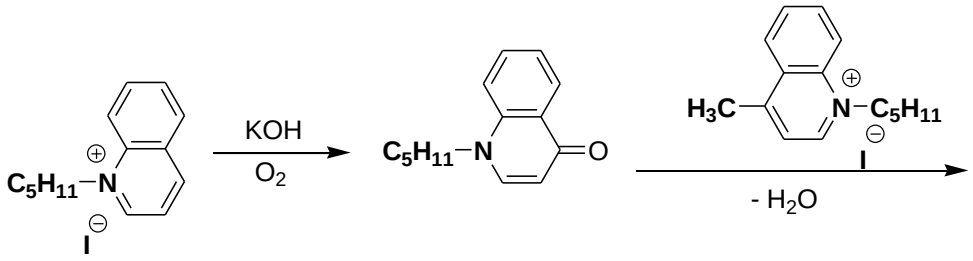
- **Photographic plates of AgCl are sensitive to light from (350-450 nm),AgBr (350-530). By using cyanine dyes, the sensitivity becomes from (350-600 nm) and some of cyanines make sensitive to (350-700 nm) i.e. cover all colors in the visible region.**

- **Cyanine dyes are two quinoline attached to each other by =CH from 4, 4` position.**

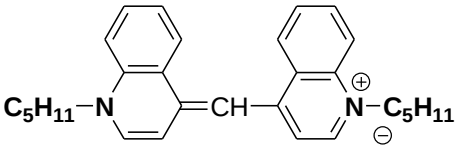
- **Isocyanines attachment from 4,2` by =CH-.**

- **Carbocyanines attachment from 2,2` by =CH-CH=CH- (e.g. sensitol red).**

1) Synthesis of cyanine dyes:

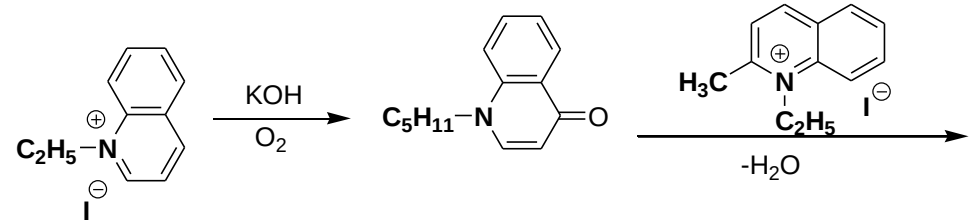


Amyl quinolinium iodide

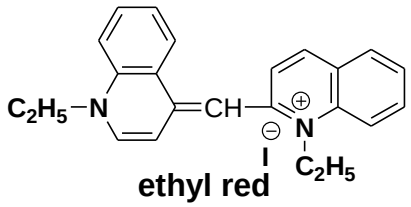


Cyanine

2)Synthesis of isocyanine: e.g. ethyl red



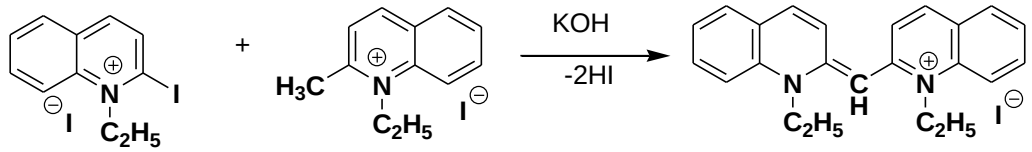
ethyl quinolinium iodide



ethyl red

- **Ethyl red is sensitive from orange to UV**

3) Synthesis of Pesudocyanine

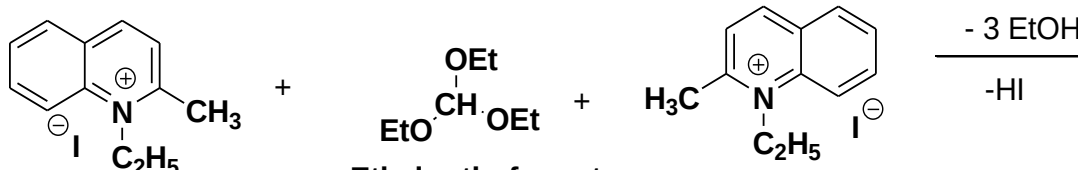


2-Iodo ethyl quinolinium iodie

Pesudocyanine dy

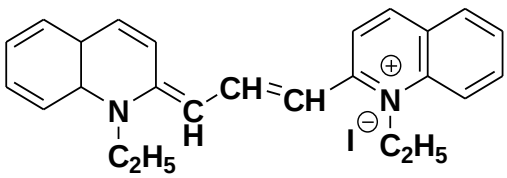
- **This dye has sensitivity from blue to green color**

4) Synthesis of carbocyanine



2methyl ethyl quinolinium iodie

Ethyl orthoformate



Sensitol red

- **This dye has sensitivity from red to orange color**