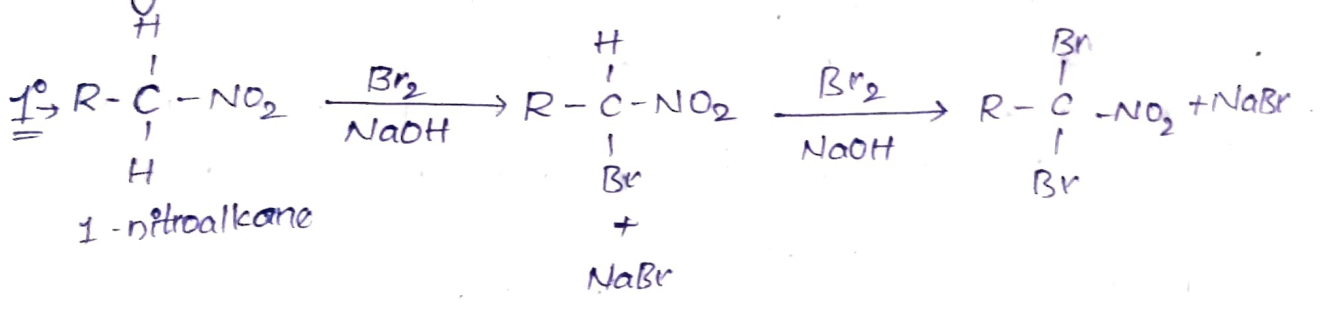
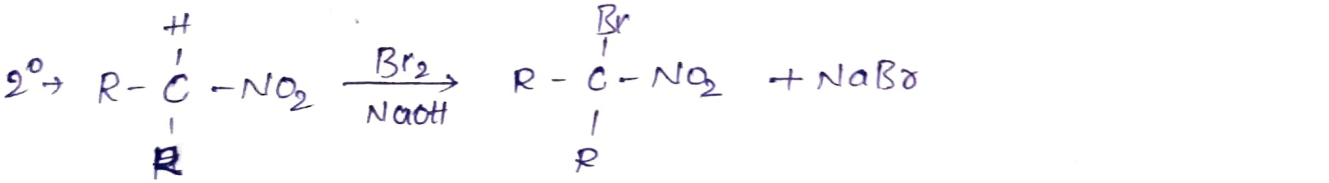
• Discuss about reactivity of Halogenations using nitrous oxide, Henry reaction, Mischaels addition reaction & Nef reaction?

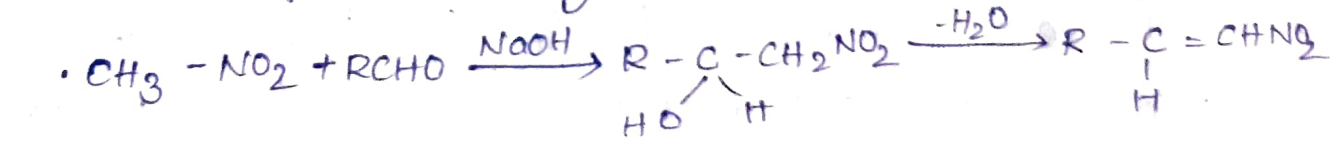
Ans:

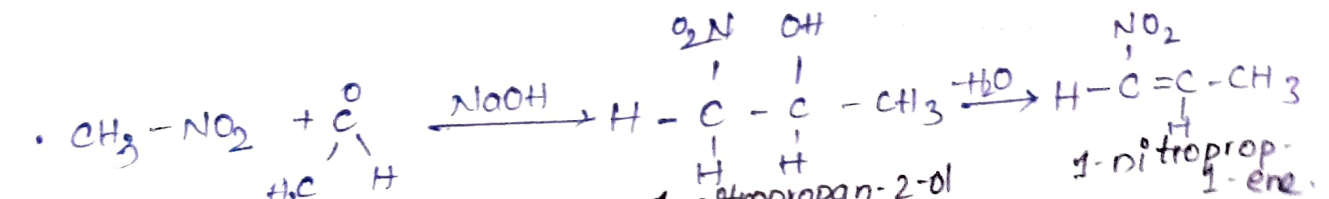
Halogenation: Primary and secondary nitroalkanes are readily halogenated with chlorine or bromine in the presence of base to form chloro or bromo nitroalkanes. During the reaction all hydrogens are replaced by halogens.



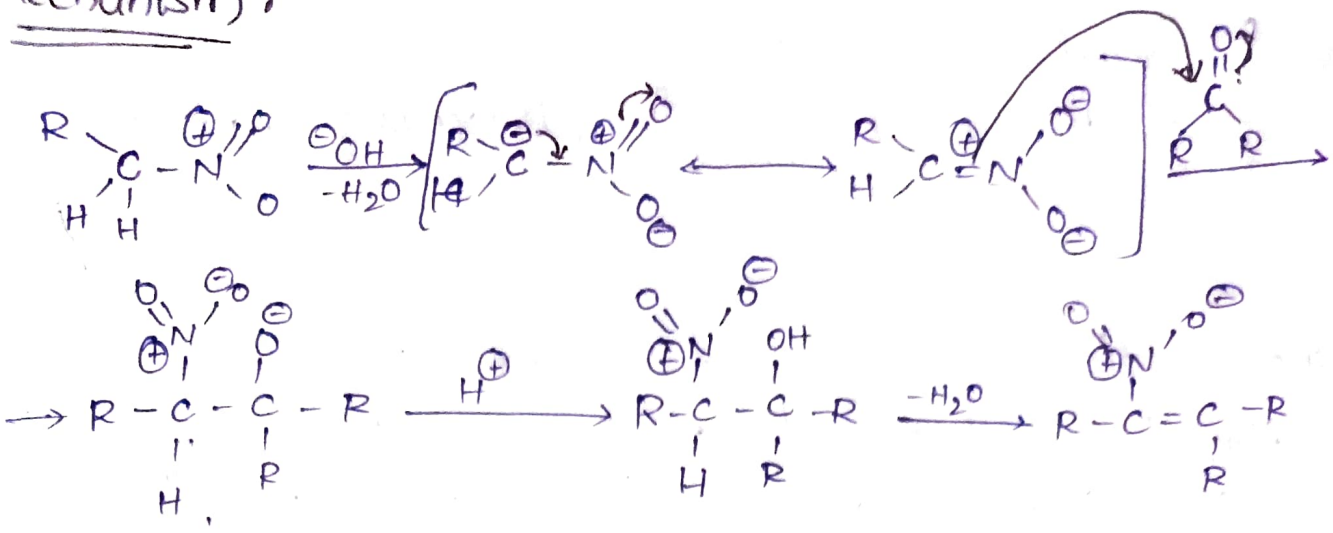


Henry reaction: A reaction in which a carbon-carbon is formed by reaction of nitrocompound having hydrogen with aldehyde or ketone to form nitro alcohol. The nitro alcohol may also lose a molecule of water to give nitroalkane.

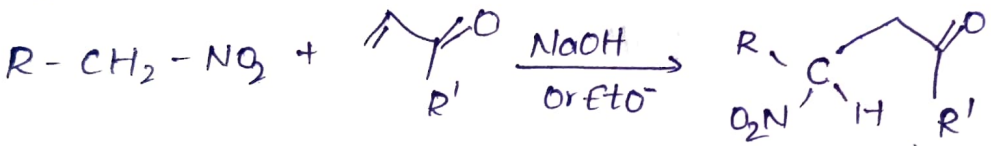




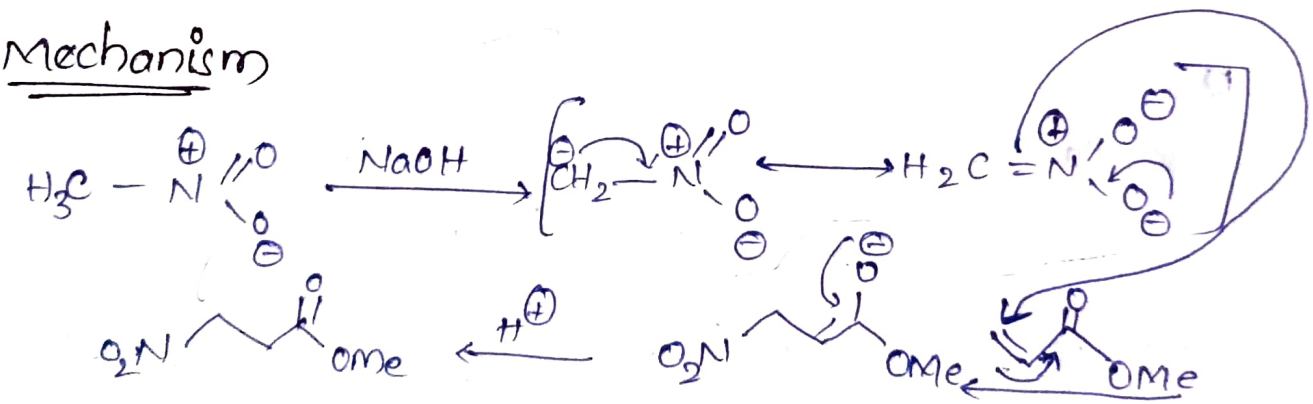
Mechanism:



- **Mischael addition reaction:** Unsaturated esters and carbonyl compounds react with primary and secondary nitro alkanes in presence of basic catalyst like sodium ethoxide or diethyamine in an alcohol solvent to give Mischael addition product in good yield.



Mechanism

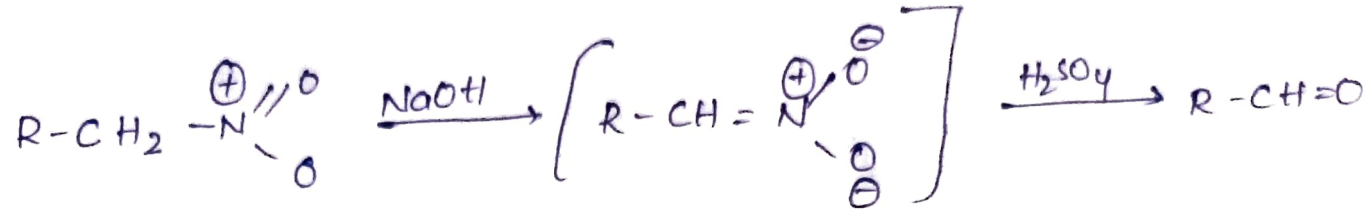


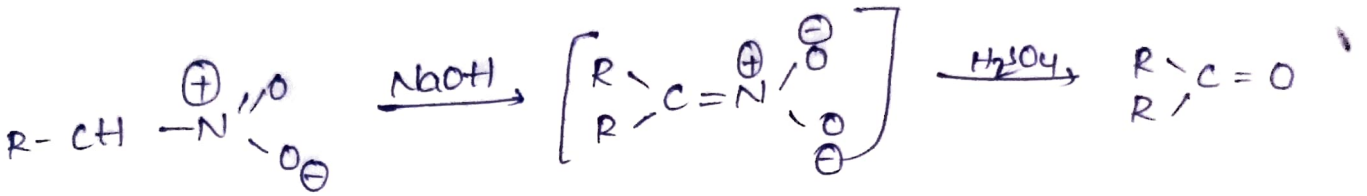
methyl 3-nitro propanoate.

- **Nef Reaction:** The reaction involves hydrolysis of primary and secondary nitroalkanes to aldehydes or ketones and nitrous oxide.

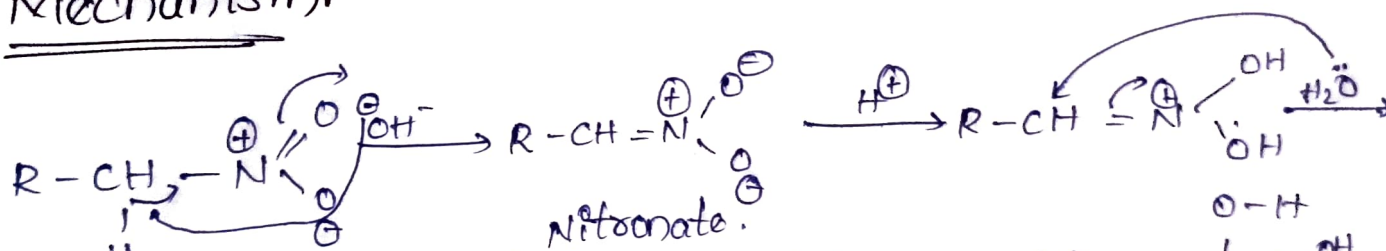
(2)

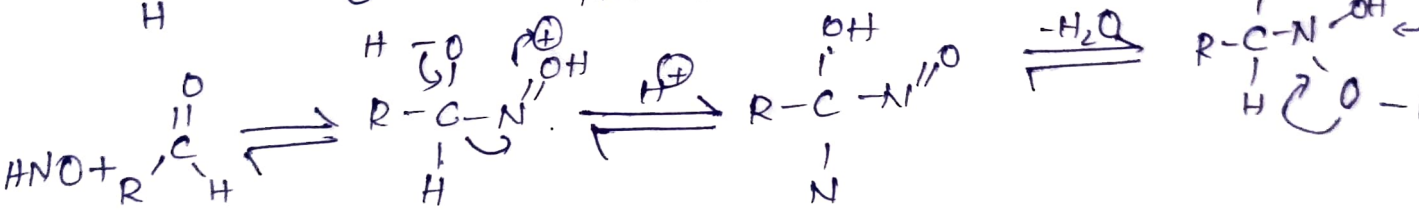
· Nitroalkanes are first converted to their sodium salt and then hydrolysed by concentrated H_2SO_4 to aldehydes and ketones.

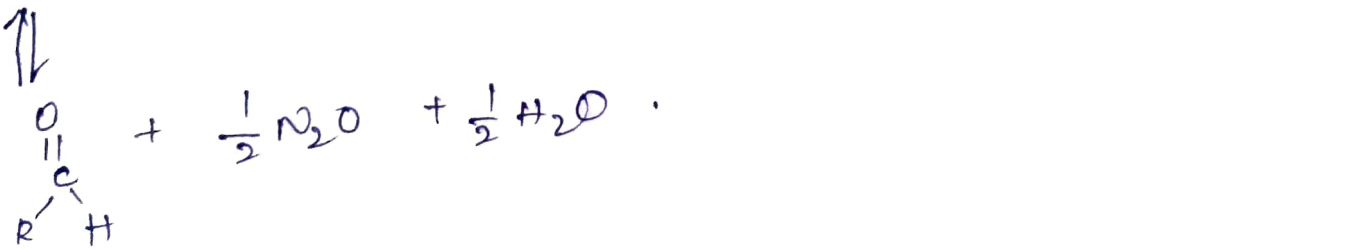




Mechanism:



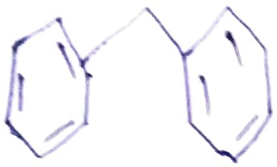




2. write the synthesis is medicinal uses of diphenyl methane naphthalene, anthracene, phenanthracene

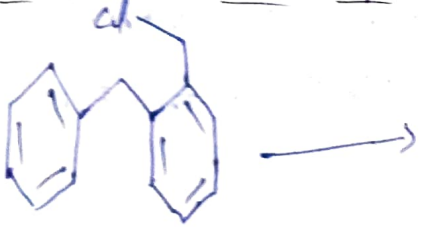
diphenyl methane

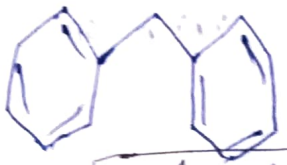
Diphenyl methane is an organic Compound write the formula $(C_6H_6)_2CH_2$ abbreviated by (CH_2ph_2) the Compound consist of methane where in two hydrogen atoms are replaced by two phenyl groups It is a white solid



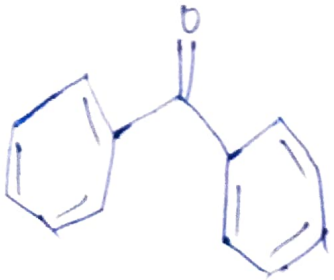
Diphenyl methane

preparation of diphenyl methane

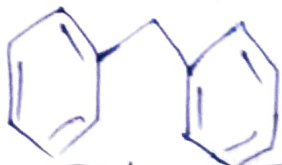




Diphenyl methan

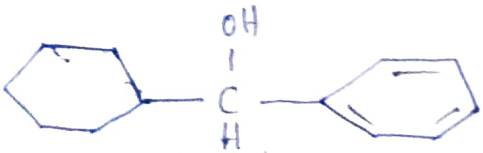


HIP

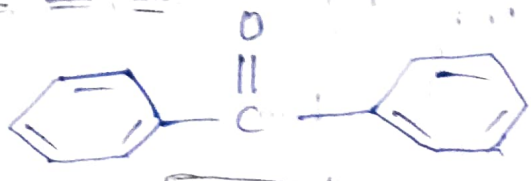


Diphenyl methane

Derivatives of diphenyl methane



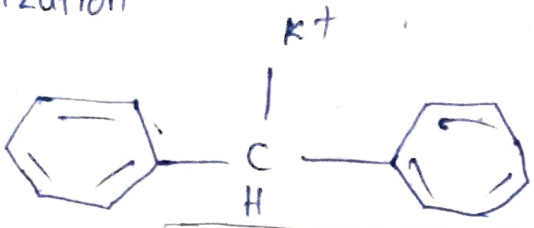
Benzhydrol



Benzophenone

medicinal uses of diphenylmethane

1. diphenylmethane is widely used in the synthesis of luminog
for aggregation induced emission
2. diphenylmethyl potassium used in the preparation of polym
-rization



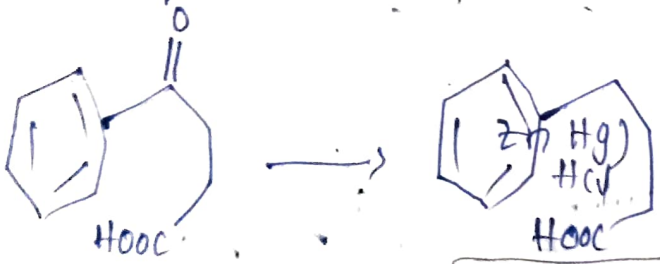
diphenyl methyl pottassium

Naptholene

preparation of Naptholene

i. From 3 Benzoyl propanoic acid

when 3 benzoyl propanoic acid is heated with sulphuric acid α napthol is formed, which on distillation with zinc dust forms napthalene.

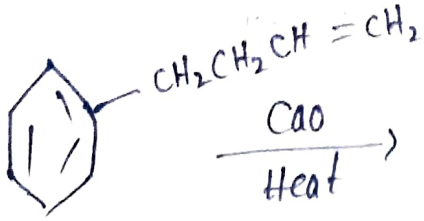


3 benzoyl propanoic acid

4 phenyl butanoic acid

ii. From 4-phenyl-1 butene

when 4 phenyl 1 butene is passed over red hot calcium oxide napthalene is formed



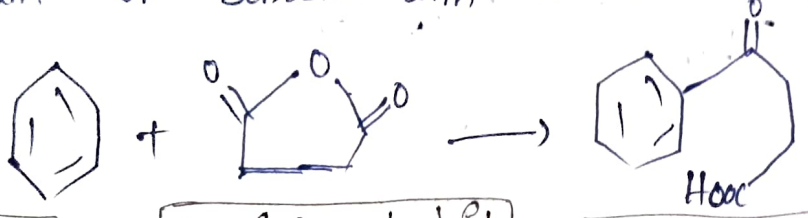
4 phenyl 1 butene

Naphthalene

iii. Haworth Synthesis

It involves five steps.

Step I : formation of 3 benzoyl propanoic acid by the treatment of benzene with succinic anhydride.

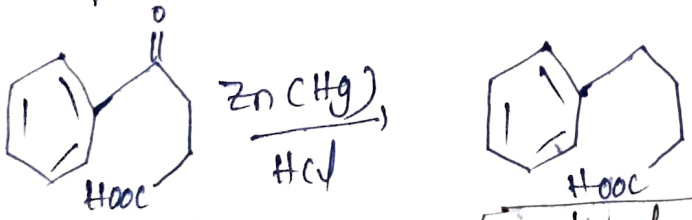


Benzene

succinic anhydride

3 benzoyl propanoic acid

Step II : 3 benzoyl propanoic acid is treated with amalgamated zinc to produce 4 phenyl butanoic acid.



3 benzoyl propanoic acid

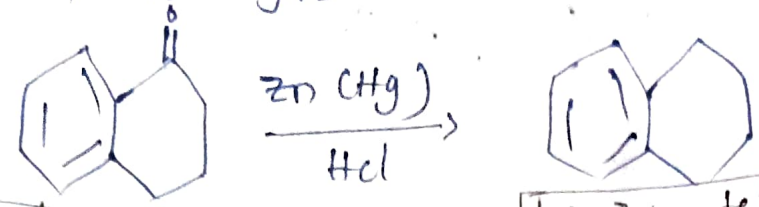
4 phenyl Butanoic acid

Step III : 4 phenyl butanoic acid is heated with conc. sulphuric acid to form Tetralone (ring closer reaction)

4 phenyl butanoic acid

Tetralone

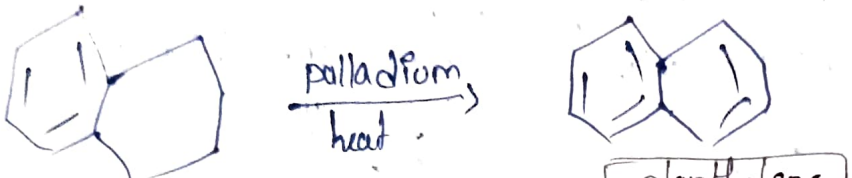
Step IV: Tetralone is again heated with amalgamated zinc and Hcl to give tetraline



3,4 Dihydro 2H-napthalen-1one
Tetralone

1,2,3,4 tetrahydronapthalene Tetraline

Step V: Tetraline is heated with palladium to yield napthalene



Tetraline

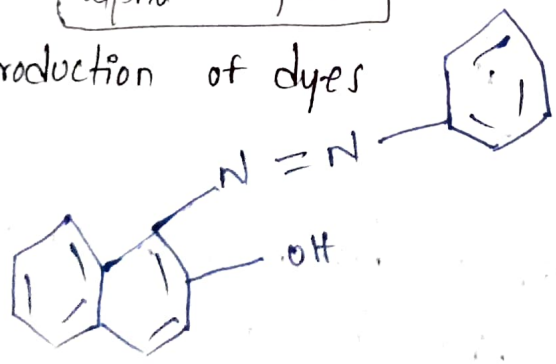
Napthalene

medicinal uses of Napthalene

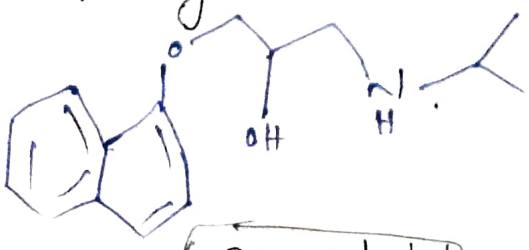
1. production of Napthols

alpha - Napthol

2. production of dyes



3 preparing of beta blocker drugs

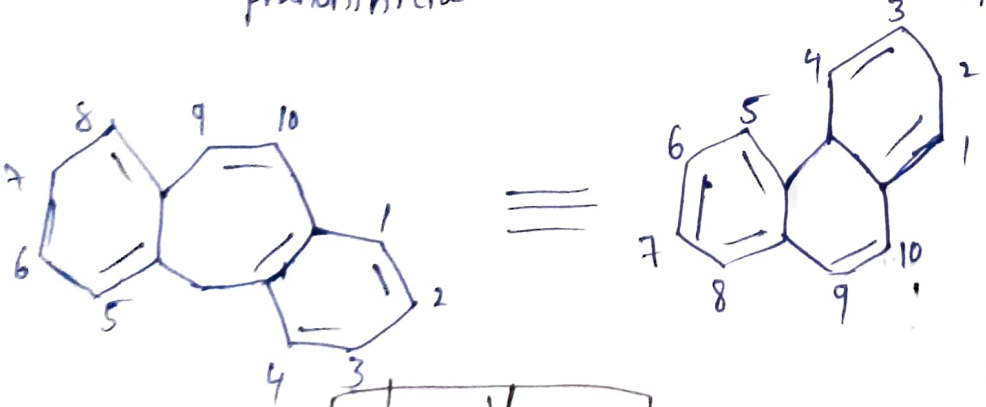


propanalol

4. To synthesize synthetic dyes
5 Useful insecticide
6. Veterinary medicine – dusting powder
7 polyethylene napthalene to prepare plastic bottles
8. Naphthalene sulfonic acids are used to prepare plasticizers, natural rubbers, etc..
9. Napthalene drugs to Cure Cough urine infection eye trouble etc..

Phenanthrene

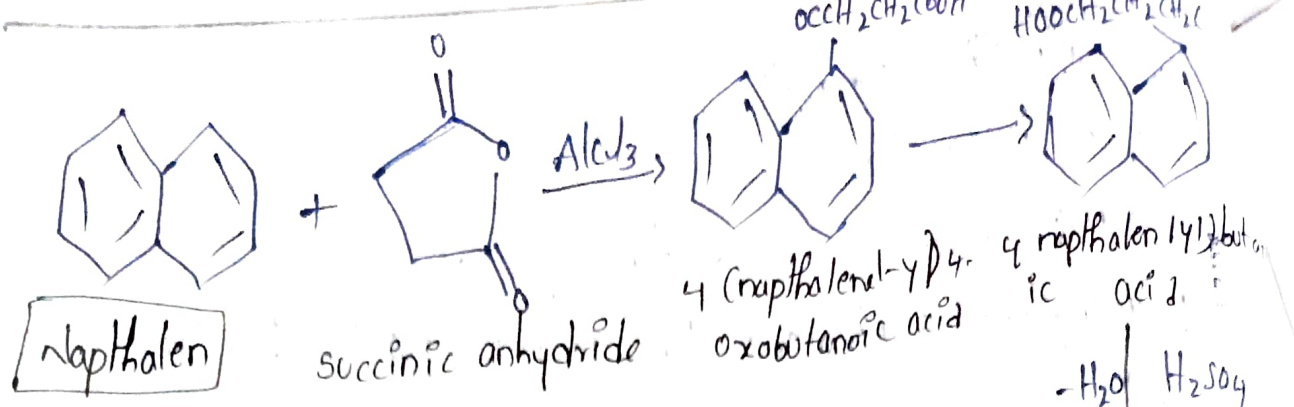
phenanthrene is apolycyclic aromatic hydrocarbon composed of three fusedbenzenerings In its pure form it is found inciga retter Smoked is a knownrirriant photosensitizing skin to light phenanthrene appear as a white powder. having blueflo rescene phenanthrene is the backbone morphine

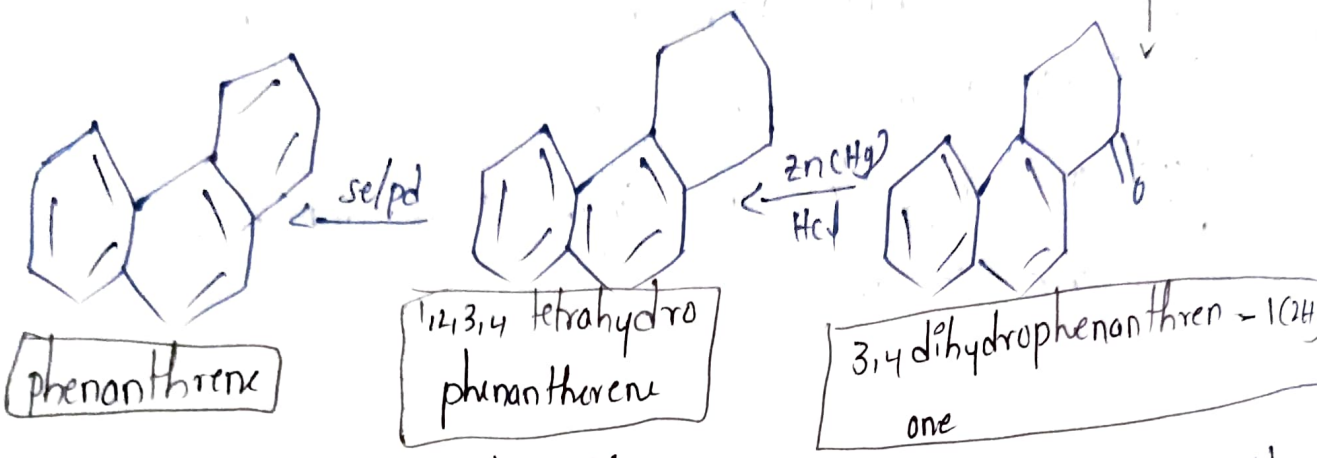


phenanthrene

preparation of phenanthrene

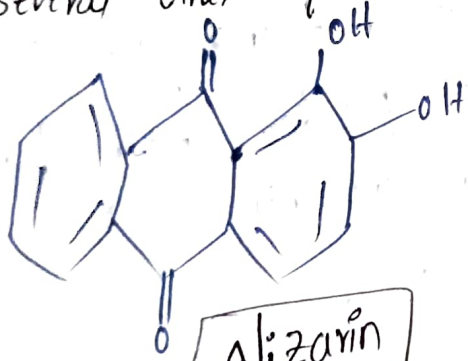
i. haworth phenanthere Synthesis





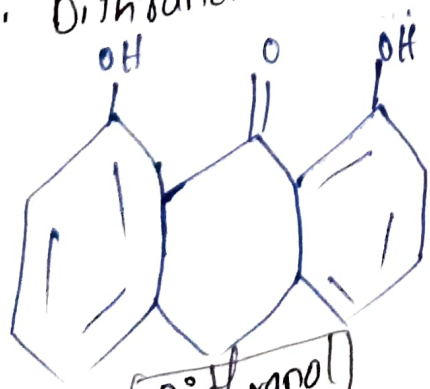
medicinal uses of phenanthrene

1. Anthraquinone is used in the manufacture of alizarin and several other dyes.



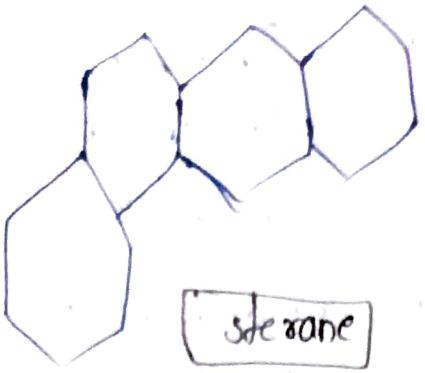
Alizarin

2. Dithranol antifungal.



Dithranol

moiety contain phenanthrene nucleus

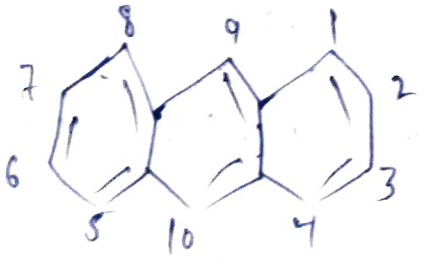


Sterane

4. Sex hormones and bile acids
5 Steroid used as oral contraceptive and anti inflamatory agent
6. Cardiac glycosides morphine codeine.

Anthracene

Anthracene is present is coal tar to the extent of 0.3 to 3.5 percent hence its name Greek anthrac meaning coal on distillation of tar it passes over in the high boiling fractions anthracene oil the molecule of anthracene is made of three . benzene nuclei fused in ortho positions It is a Colorless solid polycyclic aromatic hydrocarbon

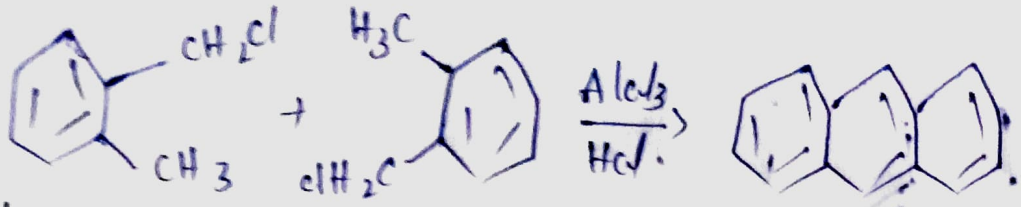


anthracene

preparation of anthracene

i. By friedel Craft reaction

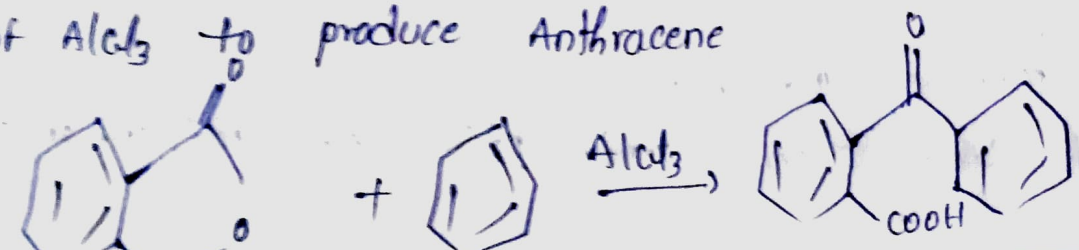
Two molecules of benzyl chloride is condensed in presence of $AlCl_3$ to produce Anthracene.



Anthracene.

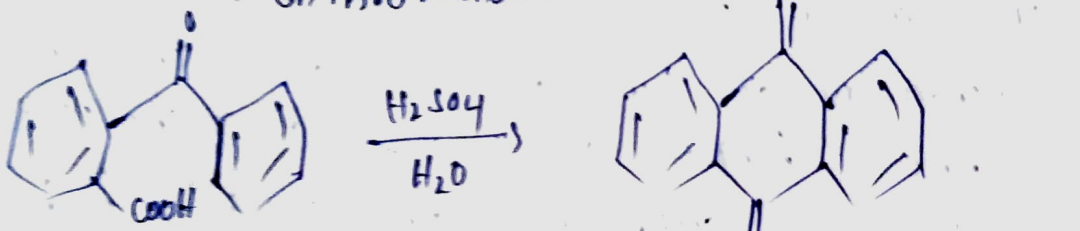
ii By Haworth synthesis

Step I: Benzene on reaction with phthalic anhydride in presence of $AlCl_3$ to produce Anthracene



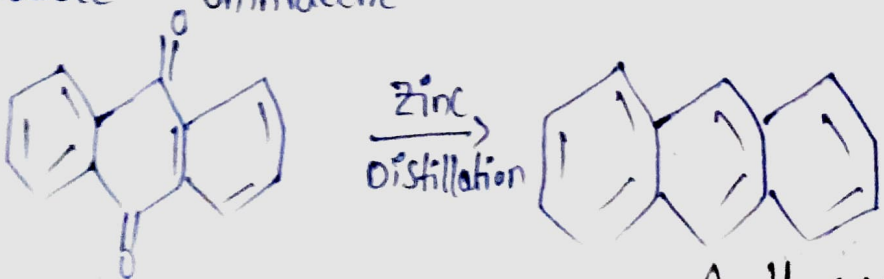
phthalic anhydride | Benzene | o benzoyl benzoic acid

Step II: o benzoyl benzoic acid is heated with conc H_2SO_4 to give 9,10 anthraquinone.



o benzoyl benzoic acid | 9,10 anthraquinone

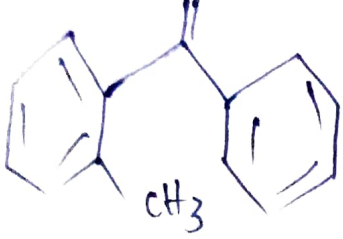
Step III Distillation of 9,10 anthraquinone with zinc dust will produce anthracene



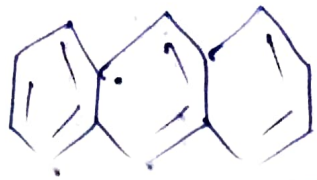
9,10 anthraquinone. Anthracene

iii. Elbs Reaction

Pyrolysis of o methylbenzophenone at 450°C can produce



o methyl bentophunone

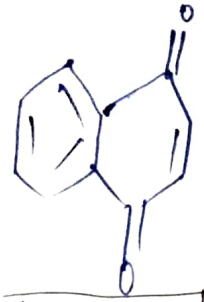


+ H_2O

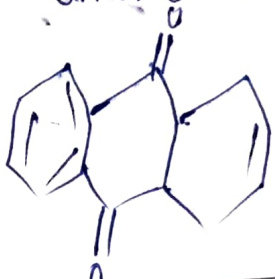
Anthracene

iv. By Diel alder reaction

This involves the reaction of 1,4 napthaquinone with 1,3 butadiene The product is oxidized with chromium trioxide in GAA to form 9,10 anthraquinone which on distillation (Zn) produce anthracene.



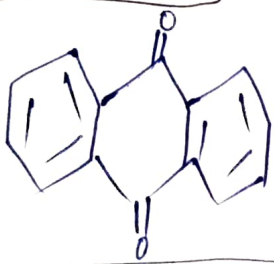
+ $CH_2 = CH - CH = CH_2$ —Sncly→



Diel alder adduct

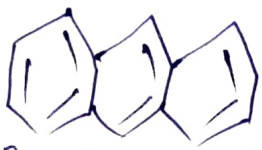
C1,4 napthoquinone

$\xrightarrow[CH_3COOH]{CrO_3}$



9,10 anthraquinone

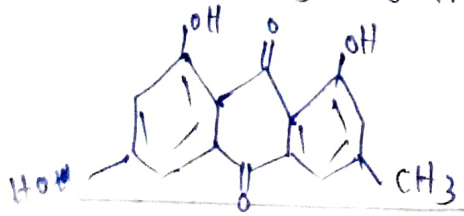
$\xrightarrow[\text{distillation}]{\text{Zinc}}$



anthracene

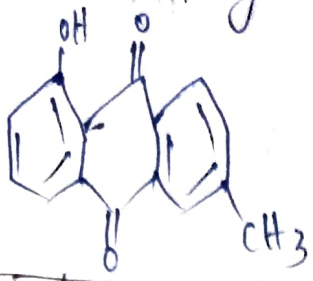
medicinal uses of anthracene

1. Anthracene glycolysides are oxygenated derivatives of pharmacological importance that are used as laxatives or catharatics antineoplastic agent polycystic kidney

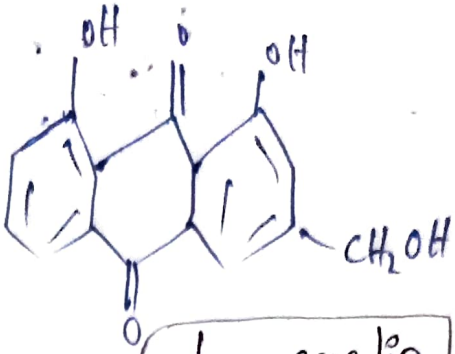


emodin

2. Anti inflomatory antibacterial antifungal andantiprolif-tive activity



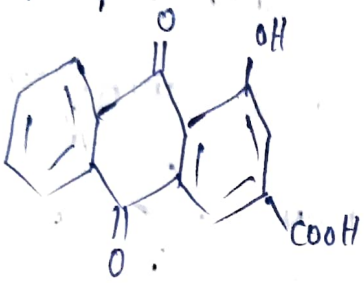
Chrysophanol



Aloe emodin

3. As natural dyes.

4 hepatoprotective ~~hem~~ nephroprotrctive antioxidant



Nitro compounds

These are the important class of Organic compounds that are recognised by the presence of one or more functional groups ($-NO_2$) bonded directly to the carbon of the hydrocarbon chain or aromatic ring.

Method of Preparation

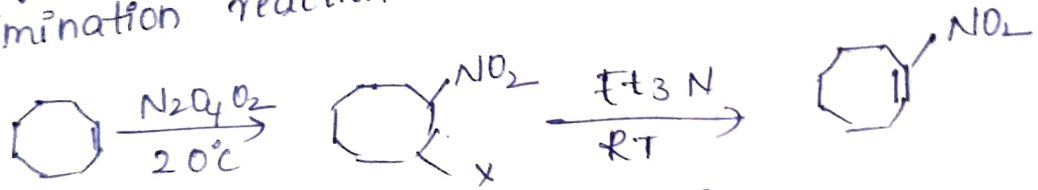
(a) Preparation of nitroalkanes

(i) From unsaturated hydrocarbon: Alkanes react with nitric acid or dinitro-tetraxide in liquid or vapour phase to form nitro derivatives.

$$CH_4 + HNO_3 \xrightarrow{675K} CH_3NO_2 + H_2O.$$

(Nitromethane)

(ii) From unsaturated hydrocarbons: Alkenes are nitrated in good yield by dinitrogen tetroxide in the presence of oxygen to give a mixure of vic dinitro compounds. Base catalyzed elimination reaction leads to generation of nitro alkanes.



X = NO_2 ONO or ONO_2

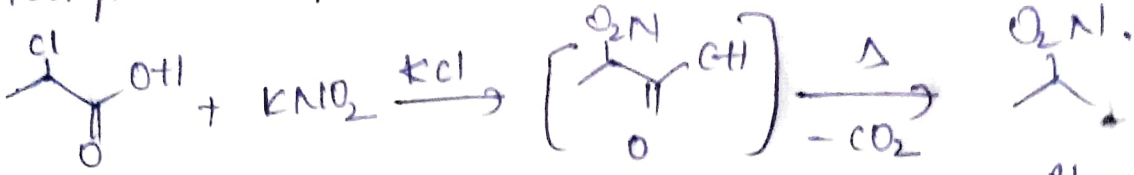
(iii) From alkyl halides: 1° & 2° nitro alkanes are synthesised by heating alkyl bromides or iodides with Li, K, Na Sodium nitrate in dimethylformide or dimethylsulphoxide.

2-iodobutane

~~2-butane~~ 2-nitrobutane. 2-butane nitrite.

From Halocarboxylic acids: It is prepared by [illegible] chloroacetic acid with sodium nitrite or potassium nitrite.

- Nitroacetic acid, which is formed as an intermediate product decarboxylates to yield nitromethane.

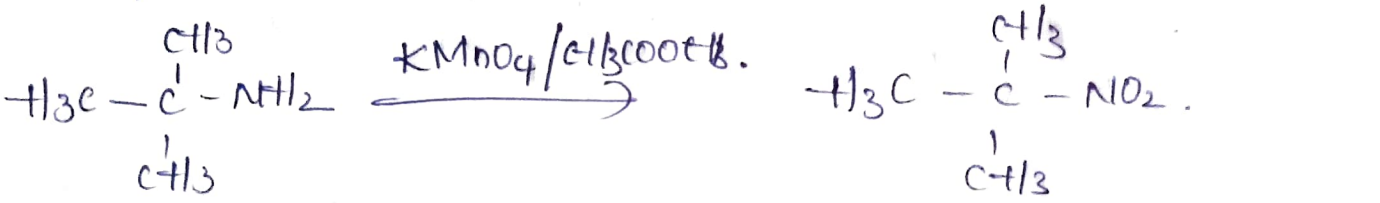


2-chloropropanoic acid.

2-nitropropane

From amines: 1° amines on oxidation with peracids through yield nitro compound.

Primary amines in which the amino group is bonded to a 3° carbon can be oxidized with potassium permanganate in aqueous acetone to nitrocompound in 70-83% yield.

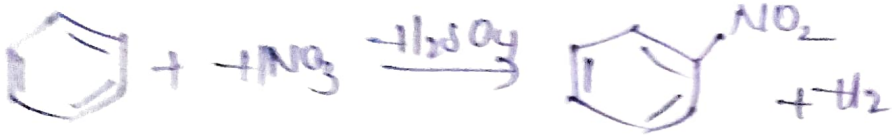


2-methylpropane-2-amine.

2-methyl-2-nitropropane

Preparation of nitro arenes

Aromatic hydrocarbons react with conc. nitric acid directly in the presence of strong acid catalyst namely sulphuric acid to form nitro derivatives.



Nitrobenzene

Medicinal uses of Nitro Compounds

- Antimicrobial Agents: Nitromidazoles (Metronidazole, Ornidazole, Ornidazole) fight anaerobic bacteria, protozoa, Nitrofurans (Nitrofurantoin) treat UTIs.

Cardiovascular Drugs: Nitroglycerin & isosorbide dinitrate (nitro esters) release nitric oxide causing vasodilation to treat angina & heart failure.

Anticancer agents: Nitro groups are used in hypoxia-activated prodrugs (like pimonidazole), targeting low oxygen tumor environments.

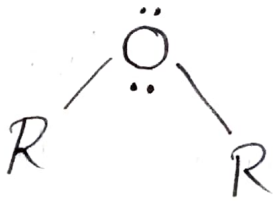
CNS & Others: Benzodiazepines like Nitrazepam (insomnia, epilepsy) & clonazepam (convulsant) contain nitro groups.

4. Explain the Synthesis of Ethers by william son's Ethers, Synthesis and acid dehydration method.

A. Ethers

* Ethers are a class of organic compounds that contain an ether group an oxygen atom connected to two alkyl or aryl groups.

* They have the general formula R-O-R, where R and R represent the alkyl or aryl group.



Ethers.

William son's Synthesis

* The most versatile method for making ethers is the willamsons ether synthesis, named for english chemist Alexander williamson, who devised the method. in the 19th century

* Alcohols are reacted with metallic sodium to form alkoxides. This alkoxide ion is a strong nucleophile

and readily reacts with alkyl halide to produce an ether.

$$2C_2H_5OH + 2Na \longrightarrow 2C_2H_5ONa + H_2$$

$$C_2H_5ONa + C_2H_5Br \longrightarrow C_2H_5OC_2H_5 + NaBr$$

Dehydration Method

* In the presence of acid, two molecules of an alcohol may lose water to form an ether.

* Biomolecular dehydration produces useful yields of ethers only with simple, primary alkyl groups, such as those in dimethyl ether and diethyl ether. Dehydration is used commerically to produce diethyl ether.

$$2\ ROH \rightleftharpoons[H^{\oplus}] ROR + H_2O$$

Examples

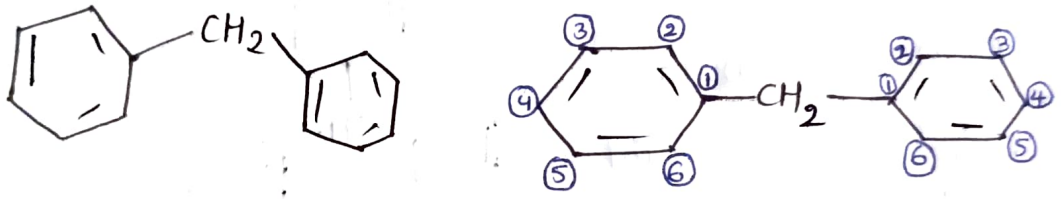
$$2\ CH_3OH \xrightarrow{H_2SO_4,\ 140^{\circ}C} CH_3OCH_3 + H_2O$$

$$2C_2H_5OH \xrightarrow{H_2SO_4,\ 140^{\circ}C} C_2H_5OC_2H_5 + H_2O$$

Describe the structure, property and uses of diphenyl Methane and triphenyl Methane and their derivatives.

Diphenyl Methane:

- Diphenyl Methane is an organic compound consists of methane where two hydrogen atoms are replaced by two phenyl group.
- It is a member of isolated ring hydrocarbons under the class of polynuclear hydrocarbons.
- It is also known as Benzhydrol.



Properties of Diphenyl Methane:

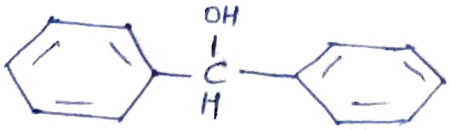
- Its chemical formula is $C_{13}H_{12}$
- It is a crystalline solid.
- Its Melting point is 22-24°C and Boiling point is 246°C.
- It is insoluble in water and soluble in organic solvents.

Uses:

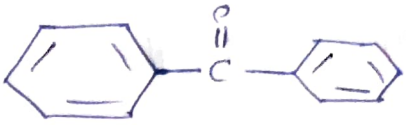
- It is used in Manufacturing of soaps, pesticides, Insecticides.
- Also used as Jet fuels.
- It is used for synthesis of dyes.
- Used as Anticulcer agent and also as anti-histamine agent.
- It is also used as Antianxiety drug.

Derivatives:

① Benzhydrol:



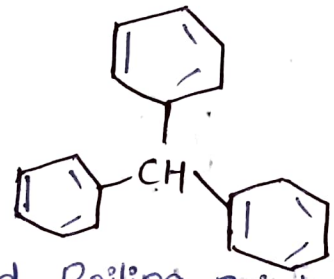
②. Benzophenone:



Triphenyl Methane: Triphenyl Methane is an organic compound in which 3 hydrogen atoms of Methane are replaced by phenyl groups.

- It is a part of isolated ring hydrocarbons under the class of polynuclear hydrocarbons.

Properties:



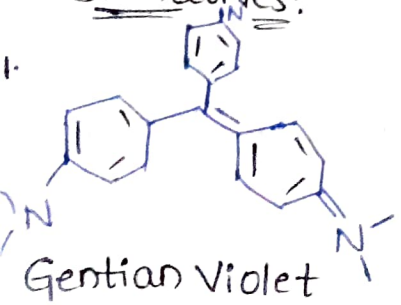
- Its chemical formula -
- It is a colourless solid.
- It Meltipoint is 92-94°c and Boiling point is 359°c
- It is insoluble in water and Soluble in organic solvents.

Uses: It is used for synthesis of various dyes.

- It also posses antimicrobial and antifungal properties.
- It is also used as disinfectant.
- Used as antimicrobial agent.

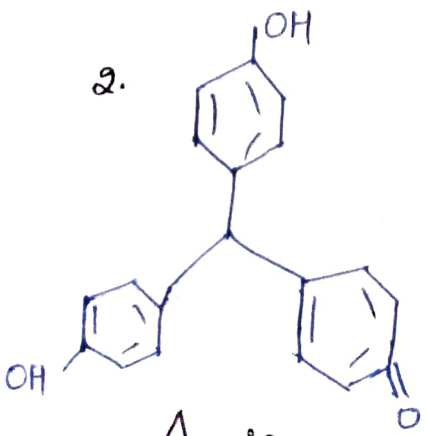
Derivatives:

1.



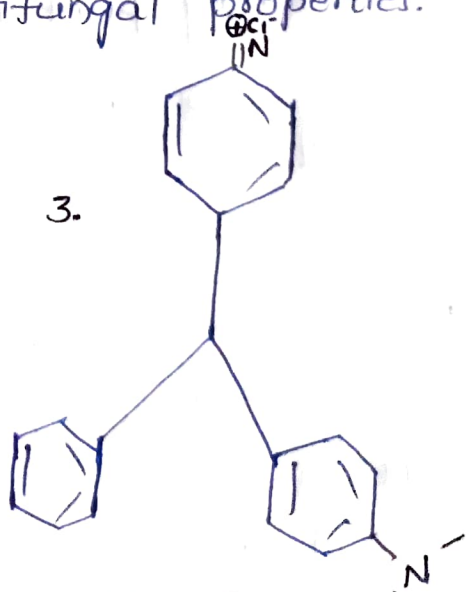
Gentian Violet

2.



Aurin

3.



Malachite green