JRG College of Pharmacy

JRG COLLEGE OF PHARMACY

UNIVERSITY SOLVED QUESTION WITH ANSWER

Year	:	**2022-23**
Subject	:	**Ph. Organic Chemistry-II**
Subject Code	:	**BP301T**
Subject In-Charge	:	**Mr. Biswajit Biswal**

Registration No : | | | | | | | | | | |

Total Number of Pages : 02

Course: B.Pharm
Sub_Code: BP301T

3rd Semester Regular/Back Examination: 2022-23
PHARMACEUTICAL ORGANIC CHEMISTRY II
BRANCH(S): B.Pharma
Time : 3 Hour
Max Marks : 75
Q.Code : L697

Answer Question No.1 (Part-1) which is compulsory, any Seven from Part-II and any two from Part-III.
The figures in the right hand margin indicate marks.

Part-I

Q1 **Answer the following questions :** **(2 x 10)**

a) What is drying of oil?
b) What is Reichert- Meissl value?
c) Write the structure and uses of DDT and BHC.
d) Write any two Qualitative tests for Phenol.
e) Give an account on Huckel's rule of aromaticity.
f) Which one is more acidic Salicylic acid and Nitro benzoic acid?
g) What do you mean Rancidity of oils?
h) Brief out on reduction reaction of phenanthrene.
i) Explain why the Electron donating group acts as an ortho para director?
j) Difference between an oil and fat.

Part-II

Q2 **Focused-Short Answer Type Questions- (Answer Any Seven)** **(5 × 7)**

a) Explain the Friedel crafts alkylation of benzene.
b) Discuss two different methods of synthesis of Anthracene.
c) Write a note on Sachse Mohr's theory.
d) Write a note on diazonium salts.
e) Brief out on the hydrolysis and hydrogenation of fats and oils.
f) Give any five chemical reactions of Benzoic acid.
g) Explain any two reactions of each of Cyclopropane and Cyclobutane.
h) Brief out the tests to differentiate primary, secondary and tertiary amines.
i) Define Saponification value. Give the principle involved in the determination of Saponification value and give its significance.

Part-III

Long Answer Type Questions (Answer Any Two)

Q3 Discuss the reaction & mechanism of Aromatic electrophlic substitution reactions. Give account on Nitration & Halogenations of Benzene. **(10)**

Q4 Explain the stability of cyclo alkanes on the basis of Bayer strain theory and brief out its limitations. **(10)**

Q5 Define & classify Polynuclear hydrocarbons. Enumerate the synthesis and reactions of naphthalene. **(10)**

Q6 Outline any two preparations and three reactions of Phenol. Explain the acidity of Phenol. **(10)**

PYQ – 2022-23

Part-I (2 marks)

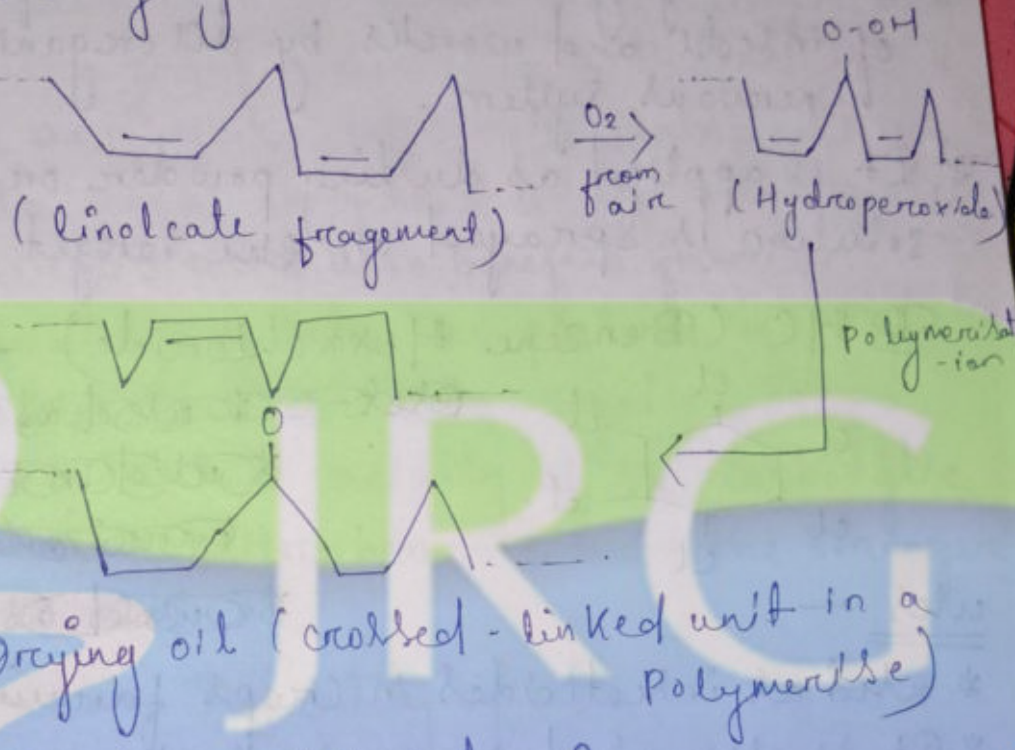
Q1.

a) What is drying of oil?

Ans- When highly unsaturated oil are exposed to air, they undergoes oxidation and polymerisation to form a thin waterproof film.

=> These oils are called drying oils and reaction is termed as drying.

Reaction



b) What is Reichert-Meissl value?

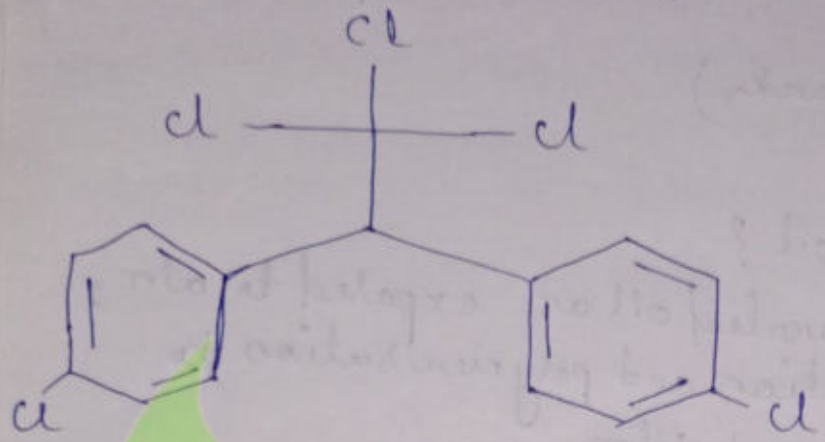
Ans => It is a measure of the amount of volatile fatty acid in a fat or oil.

=> It is defined as it is the no. of ml of 0.1N KOH required to neutralise the soluble, volatile fatty acid derived from 5 gm of fat or oil.

=> It is useful in testing the purity of butter, since it contain the good concentration of volatile fatty acids

c) Write the structure and uses of DDT and BHC.

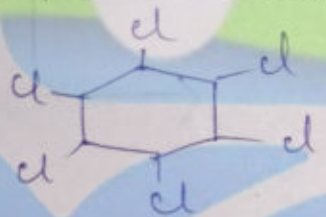
Ans DDT (Dichloro phe Diphenyl Trichloro Ethane)



uses —

* It is a highly toxic contact poison for wide variety of insects and works by disorganizing their nervous system.
* It is applied as dusting powder or its aqueous solution is sprayed on the target site.

BHC (Benzene Hexachloride) —



uses —

* used as insecticides in crops farming.
* It is also used in various pharmaceuticals.

d) Write any two Qualitative tests for phenol?

Ans - (1) litmus paper test —

=> Since, phenols are acidic in nature, hence they turns blue litmus paper into red.

(2) Solubility test — phenols are weak acidic in nature hence they are soluble in Sodium hydroxide but insoluble in Sodium Carbonate or Sodium Bicarbonate.

e) Give an account on Huckel's rule of aromaticity:

Ans In 1931, a German Scientist Huckel gave certain rules for defining aromaticity of organic compounds as follows:

* Compound should by cyclic.
* There should be a conjugation (delocalised electrons).
* Compound should be planner.
* Total number of π electrons should be $(4n+n)$, where $n = 0, 1, 2 \ldots$

f) which one is more acidic salicylic acid and Nitro benzoic acid?

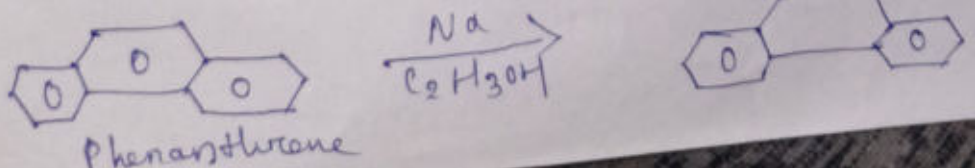
Ans Nitrobenzoic acid is more acidic than salicylic acid because the nitro group's electron-withdrawing effect is stronger and more effectively stabilizes the nitrobenzoate anion compared to the salicylate anion. while salicylic acid also benefits from an electron-withdrawing effect, the presence of a nitro group on the benzene ring significantly increases the acidity of the carboxylic acid group, making nitrobenzoic acid the stronger acid.

g) What do you mean Rancidity of oils?

Ans Rancidity is a process that occurs in fats and oils in which fats and oils are spoiled and degraded due to oxidation, hydrolysis or other chemical reactions.

h) Brief out on reduction reaction of Phenanthrene.

Ans Phenanthrene undergoes reduction in the presence of Sodium and ethanol to form 9, 10 Dihydrophenanthrene.



i) Explain why the Electron donating group acts as an ortho para director?

Ans Because they increase electron density at their positions, making them more nucleophilic and thus attractive to electrophiles.

j) Difference between an oil and fat.

Ans

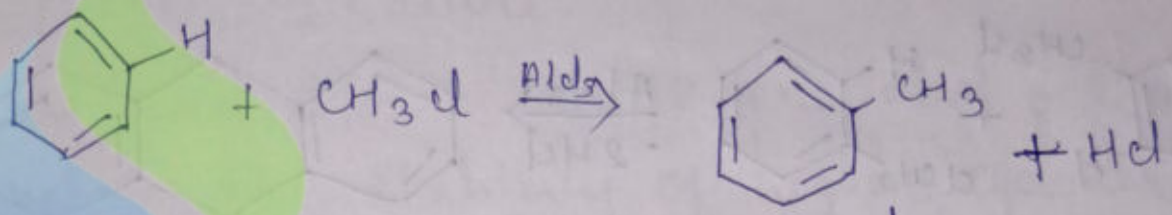
Fats	oils
* Solid or Semi-solid at room temperature	* Generally liquids at room temperature.
* Higher melting point.	* lower melting point.
* less Soluble in water	* more Soluble in water than fats.
* they are typically Saturated.	* they are typically unsaturated
* Mostly Contains Single bond	* ~~Not~~ Contains one or more double bond.

PART-II

Q2

a) Explain the Friedel crafts alkylation of benzene.

Sol In friedel-Crafts Alkylation (named after a french chemist, charles friedel and an american chemist James Crafts) Benzene reacts with Alkyl Group to form Alkyl Benzene.



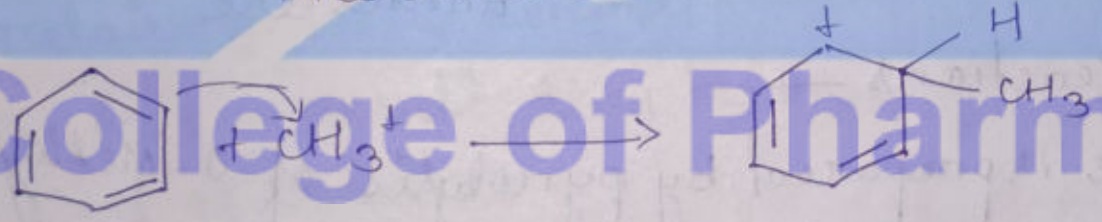
methyl Benzene

Mechanism

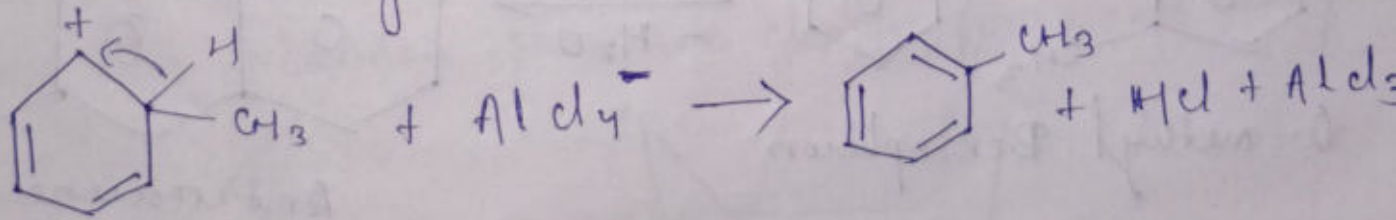
Step-I formation of Electrophile

$CH_3Cl + AlCl_3 \longrightarrow CH_3^+ + AlCl_4^-$

Step-II Attack of Electrophile to form Carbcation intermediate.



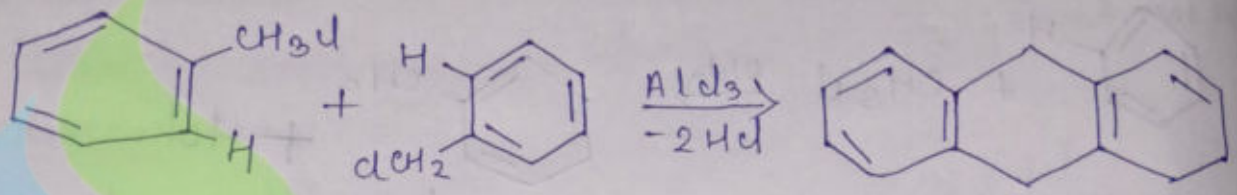
Step-III loss of proton leads to the formation of methyl Benzene (product).



b) Discuss two different methods of Synthesis of Anthracene.

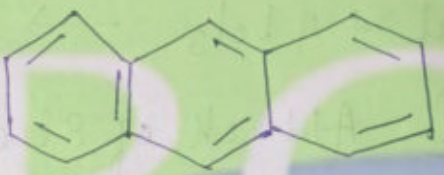
Ans (1) Friedel Crafts Reaction —

Two molecules of Benzyl chloride reacts to form 9,10 Dihydro anthracene which on further reaction ~~loses~~ loses two Hydrogen to form Anthracene.



Benzyl chloride

9,10 Dihydroanthracene

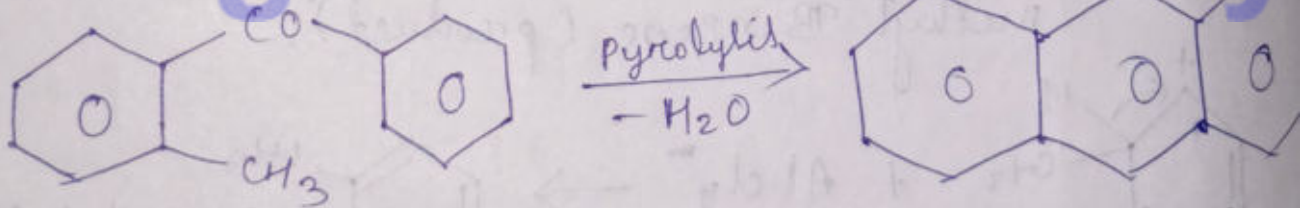


-2H

Anthracene

(2) ELBS Reactions —

Anthracene is prepared by pyrolysis of O-Methyl benzophenone.



O-methyl Benzopheron

Anthracene

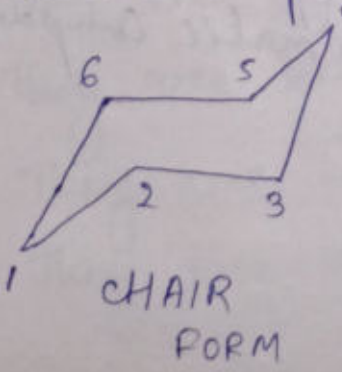
c) Write a note on Sachse Mohr's theory.

Ans- Sachse Mohr's Theory

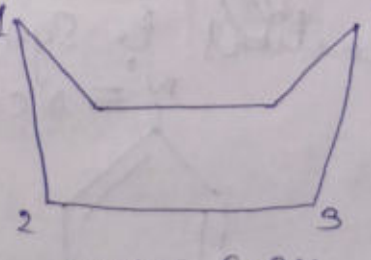
* It is also known as theory of stainless Rings.
* Baeyer's theory failed to explain the stability of higher cycloalkanes (i.e, cyclohexane, cycloheptane) because he assumed that all the cycloalkanes are planer in nature.
* Sachse and Mohr in 1918 proposed a theory to explain the stability of higher cycloalkanes.
* According to Sachse Mohr's theory the higher cycloalkanes are free any kind of strain and very stable if they are not forced into a plane.
* He assumed that ring are folded or in puckered condition and that's why they retained their normal tetrahedral angle (109°28') and as a result they become free from any kind of strain.

Chair and Boat form of cyclohexane

According to Sachse Mohr's theory cyclohexane exist in two non-planner form i.e chair form and Boat form.



CHAIR FORM



BOAT FORM

* In the Boat form, Carbon no. 2, 3, 5 and 6 lie in the same plane and carbons 1 and 4 above the plane.
* In the chair form carbon no. 2, 3, 5, 6 lie in the same plane and carbon 4 is above the plane and carbon 1 below it.
* Between Both chair form of cyclohexane is more stable than its boat form because boat form has unfavourable non-bonded interaction between hydrogen atoms.
* The chair and Boat form of cyclohexane rapidly interconverted into each other and that's why can not be isolated individually.

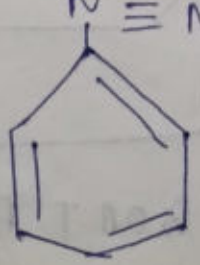
d) Write a note on diazonium salts.

Ans Aryl Diazonium Salt.

=> The word Diazo made from two words ('Di' means 'two' and 'Azo' means 'Nitrogen'.

=> Aryl Diazonium Salt is an organic compound that contains a diazo group ($-N_2^+$) attached to an aromatic ring.

=> These salts are important intermediates in organic chemistry and are commonly used in various reactions to synthesize Aromatic Compounds.



Preparation

Aryl Diazonium Salt prepared in following two steps:

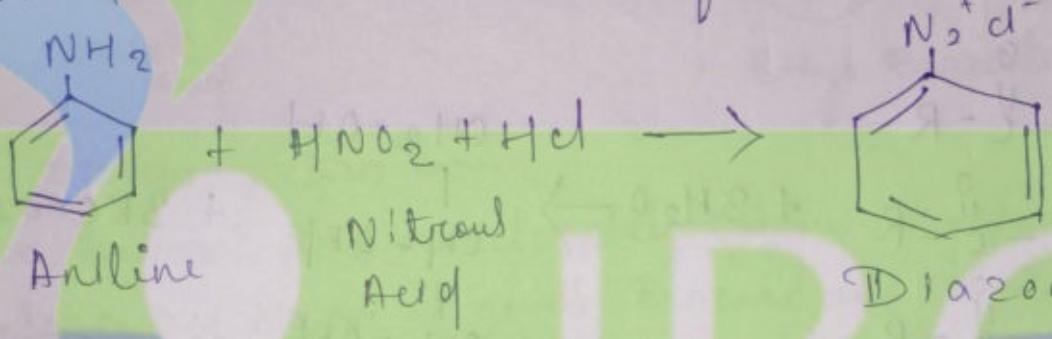
Step - I

In step I Sodium Nitrate ($NaNO_3$) react with Hcl to form Nitrous Acid (HNO_2) and Sodium chloride (Nacl)

$$NaNO_2 \longrightarrow Hcl \longrightarrow HNO_2 + Nacl$$

Step - II

In the Second Step the formed Nitrous Acid reacts with Aromatic Amines to form Diazonium Salt.



Aniline — Nitrous Acid — Diazonium Salt.

Synthetic uses

* They are used for manufacturing of various dyes.
* They are used in various industries for preparing significant organic compounds.

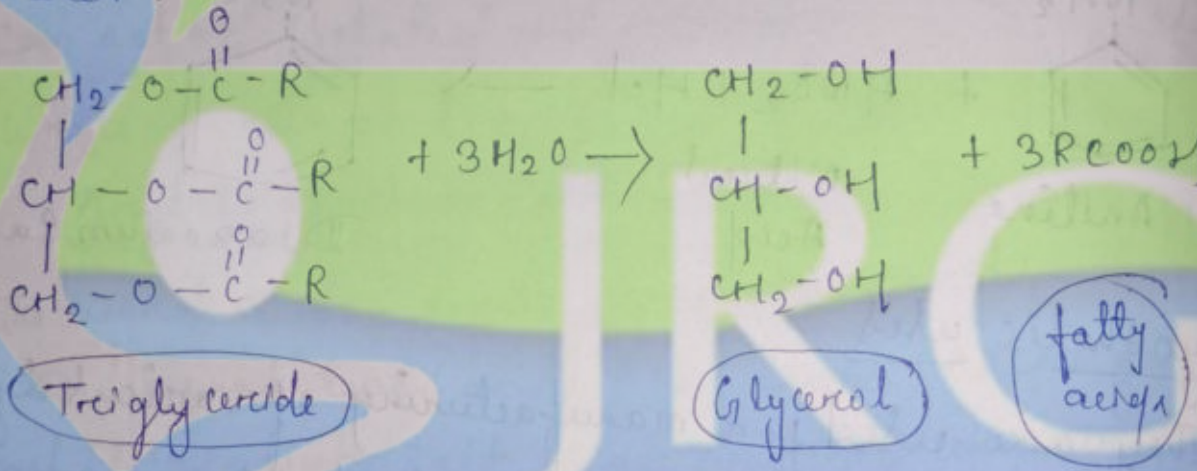
Physical properties of Aryl Diazonium Salt.

* They are colourless crystalline solids.
* They are highly water - Soluble
* They are ionic in nature.
* They are darken when exposed to air.

e) Brief out on the hydrolytic and hydrogenation of fats and oils.

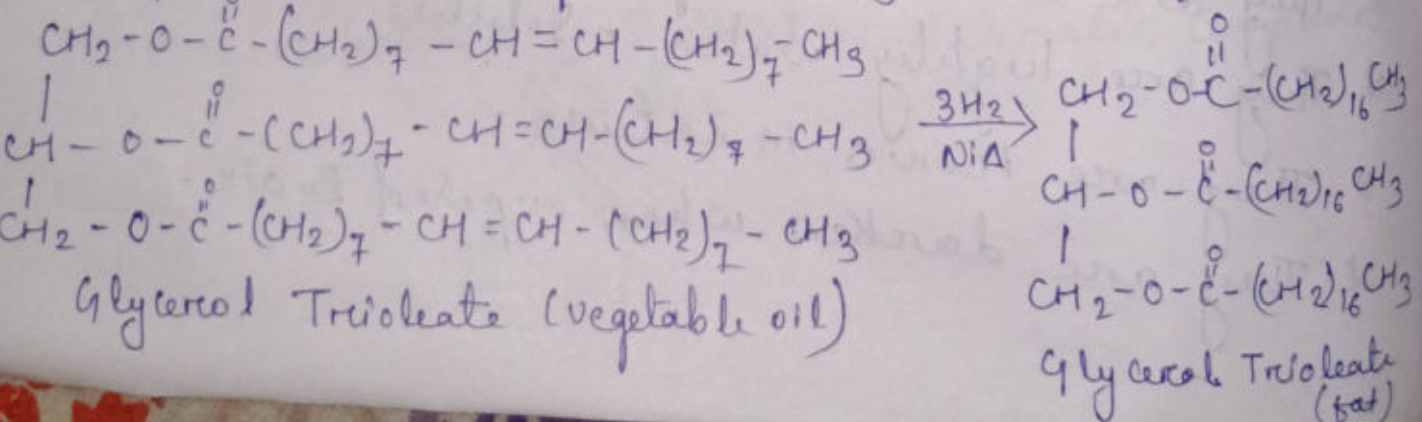
Ans ① Hydrolytic ~~

* Hydrolytic of fats and oils involves breakdown of triglycerides into Glycerol and fatty acids through the addition of water.
* In human body, they are hydrolyzed by enzyme called lipase, found in digestive tract of body.
* The Glycerol and fatty Acids produced are further Metabolized for energy through various biological Process.



② Hydrogenation ~~

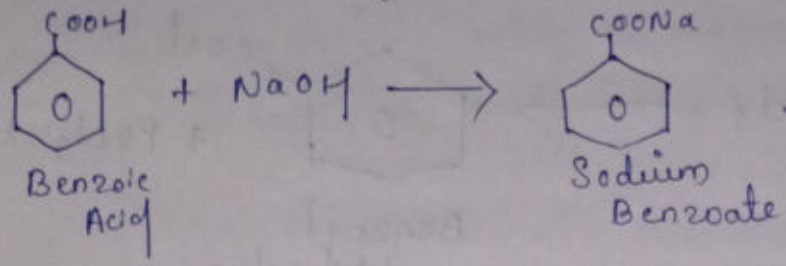
* Hydrogenation is the process of converting Unsaturated triglycerides to Saturated one by adding hydrogen in the presence of metal Catalyst (Ni).
* The process is used for converting oils into fats.



(f) Give any five chemical reactions of Benzoic acid.

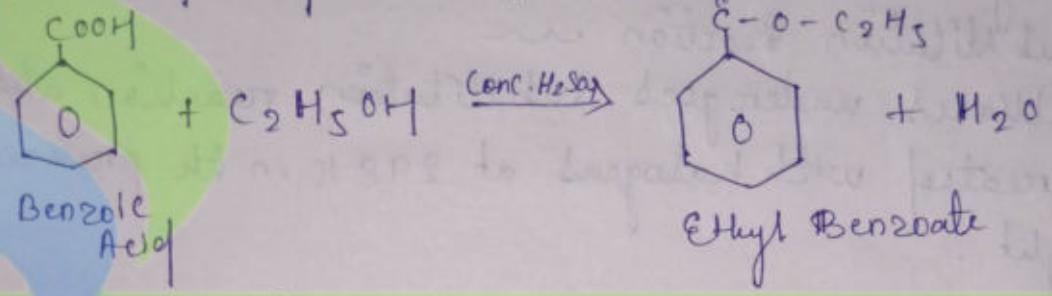
Ans (i) Salt formation :-

* When Benzoic Acid reacts with base it forms salt.



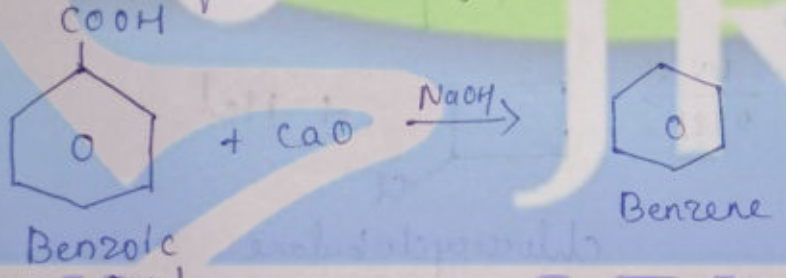
(ii) Esterification :-

* Benzoic Acid reacts with Alcohols in the prelence of Concentrated Sulphuric Acid to form Ester.



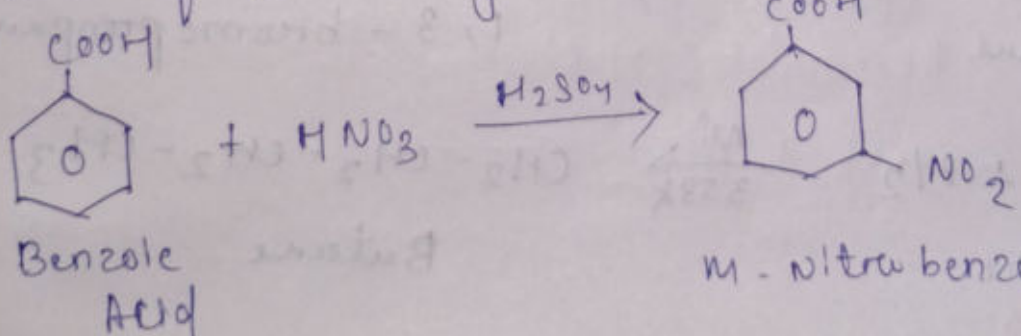
(iii) Decarboxylation :-

* When Benzoic Acid reacts with Calcium oxide in the Prelence of NaOH it gives Benzene and Calcium Carbonate



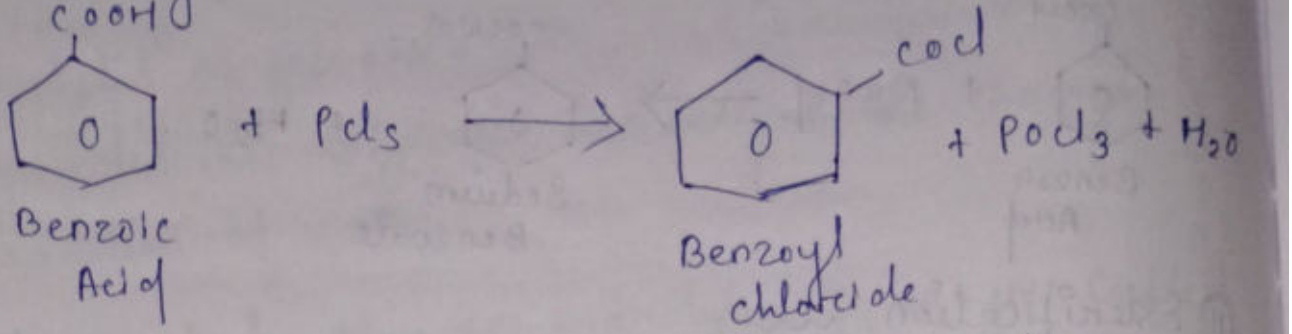
(iv) Nitration :-

* When Benzoic Acid reacts with Concentrated HNO_3 in the Prelence of H_2SO_4 it gives Nitro benzoic Acid.



(v) Formation of Benzoyl chloride :-

* Benzoic Acid reacts with phosphorus pentachloride to form Benzoyl chloride.



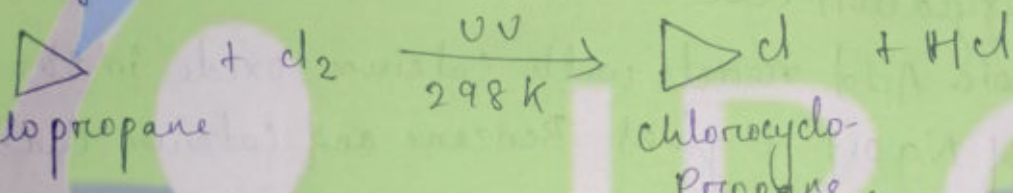
Benzoic Acid

Benzoyl chloride

g) Explain any two reactions of each of cyclopropane and cyclobutane.

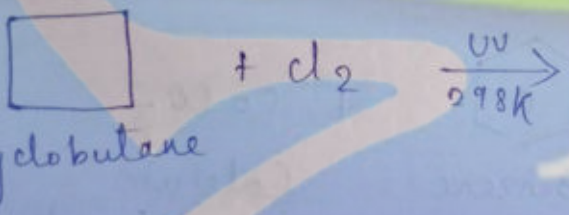
Ans (i) Substitution Reaction :-

=> Cycloalkanes undergoes substitution reaction when they treated with halogens at 298 K in the presence of UV light.



Cyclopropane

Chlorocyclo-Propane.

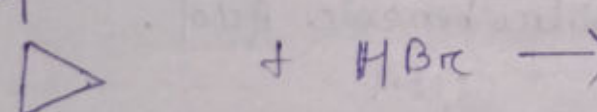


Cyclobutane

Chlorocyclobutane

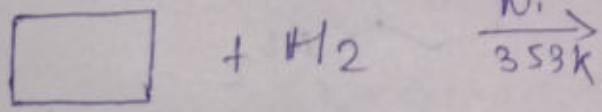
(ii) Addition Reactions :-

* Cycloalkanes undergoes addition reaction to gives open chain compounds :



cyclopropane

1, 3 – bromopropane



cyclobutane

Butane

PART-III

Long Answer type ~

3) Discuss the reaction and mechanism of Aromatic electrophilic Substitution reactions. Give account on nitration and Halogenations of Benzene.

Ans Chemical Reactions of Benzene ~

=> Most commonly benzene undergoes electrophilic Substitution reaction (Electrophilic Aromatic Substitution reaction).

=> In these reactions hydrogen atom of the aromatic ring is replaced by an electrophile.

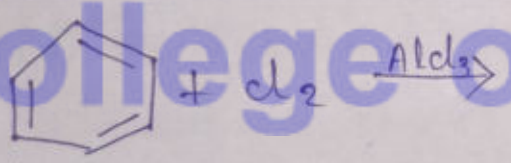
=> Benzene mainly undergoes Electrophilic Aromatic Substitution Reaction.

(1) Halogenations

(2) Nitration.

(1) Halogenation of Benzene ~

In Halogenation, benzene reacts with Halogens (Br_2, Cl_2, I_2) in the presence of lewis acid catalyst ($AlCl_3$) to give Bromobenzene or chlorobenzene or Iodobenzene.



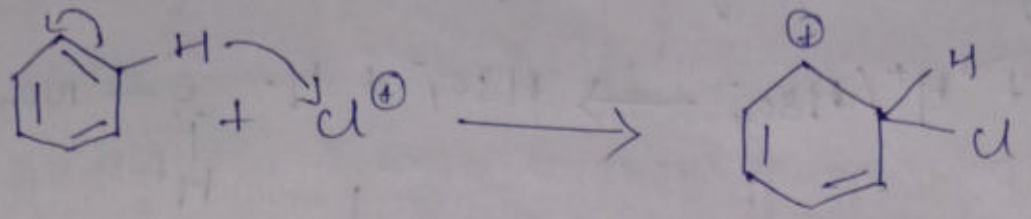
Benzene — Chlorobenzene

Mechanism of Halogenation (chlorination)

Step-I ~ Formation of Electrophile (chloronium Ion)

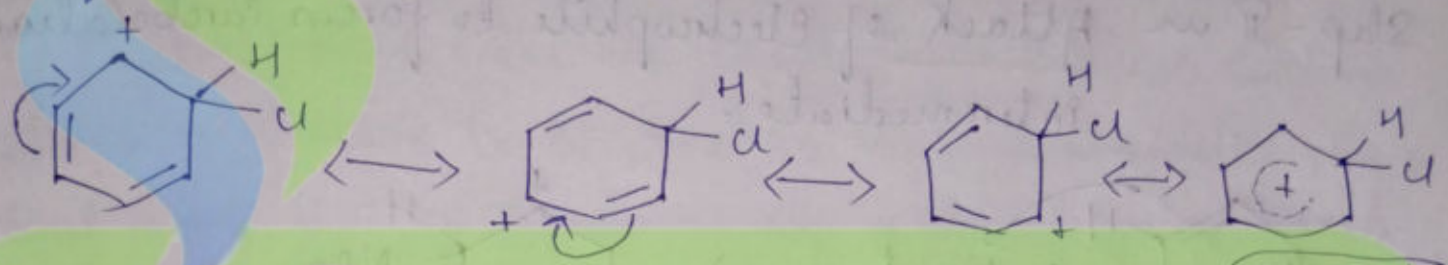
$$Cl - Cl + AlCl_3 \longrightarrow Cl^+ + AlCl_4^-$$

Step - II :- Attack of Electrophile on Benzene to form Carbonium Ion



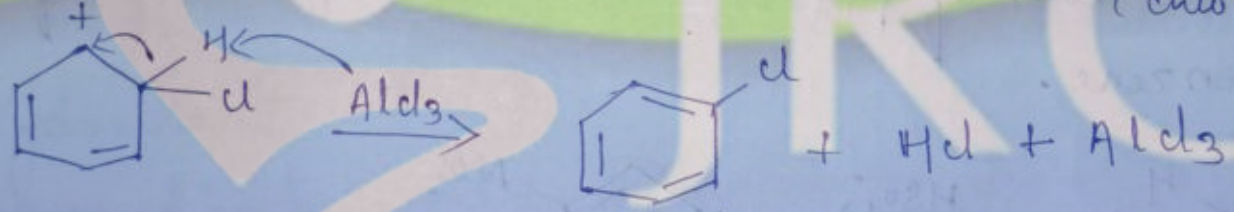
Carbonium Ion

Now the above Carbonium ion is resonance stabilized and forms σ complex.



(σ - complex)

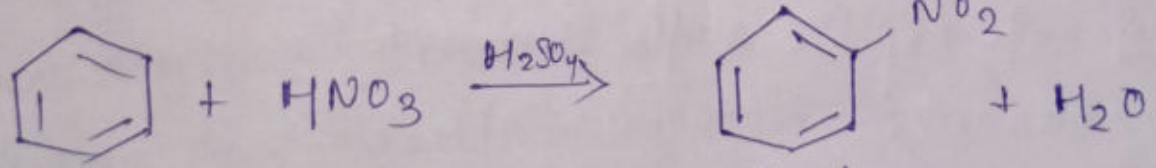
Step - III :- Loss of proton and formation of product (chlorobenzene)



Chlorobenzene

(2) Nitration :-

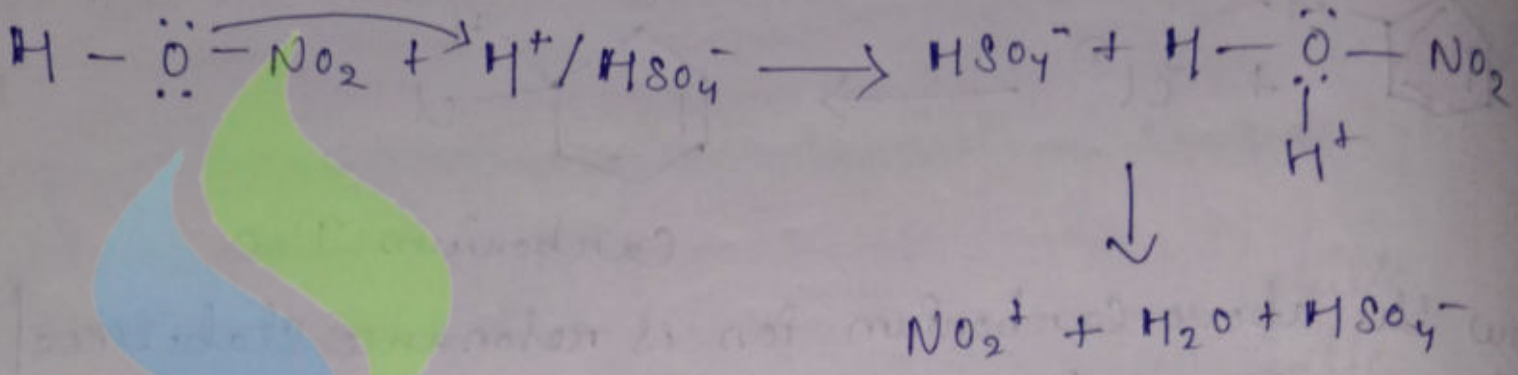
In Nitration, Benzene reacts with concentrated HNO_3 in the presence of concentrated H_2SO_4 to form Nitro benzene.



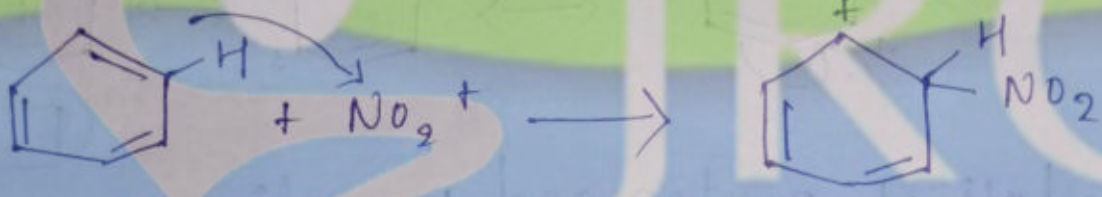
Nitrobenzene

Mechanism :-

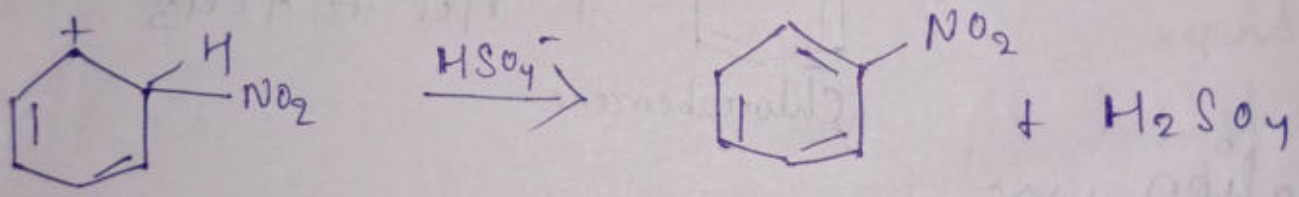
Step-I :- formation of Electrophile (Nitronium Ion)



Step-II :- Attack of Electrophile to form carbocation intermediate.



Step-III :- Loss of proton leads to the formation of Nitrobenzene.



Q4) Explain the stability of cyclo alkanes on the basis of Bayer Strain theory and brief out its limitations.

Ans Bayer's Strain theory :-

=> Adolf Von Bayer in 1885 proposed a theory to explain the relative stability of cycloalkanes.

=> He proposed the theory of Angle Strain on the fact that since all the Carbons of cycloalkanes are Sp^3 hybridized, hence the bond angle between Carbon atoms will have to be 109°28' in cycloalkanes.

=> But when Baeyer measures the angle of cycloalkanes he found different bond angle in different cyclo alkanes

=> On this balis, he proposed the theory of Angle Strain.

=> The theory explains reactivity and stability of Cycloalkane.

=> According to him the distortion or deviation from Normal tetrahedral angle (109°28') causes a Strain in the ring that leads to the instability of cycloalkane

Angle Strain :-

=> The deviation in ideal bond angle from the real bond angle is called Angle Strain.

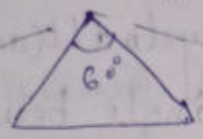
=> Higher the angle Strain, lesser will be the Stability and higher the reactivity of cycloalkanes.

$$\text{Angle Strain} = \frac{1}{2}(109°28' - \text{Bond Angle})$$

Angle Strain In Cyclopropane :-

=> Since all the Carbon atoms of cyclopropane are sp^3 hybridised hence bond angle should be 109°28'.

=> But since the ring of cyclopropane is a triangle, hence all the angle are of 60° instead of 109°28', that leads to angle strain in cyclopropane.



Angle strain $= \frac{1}{2}(109°28' - 60°)' = \frac{49°28'}{2} = 24°44'$

Angle strain $\propto \frac{1}{\text{stability}}$

=> The angle strain is maximum in cyclopropane compare to other cycloalkanes hence it is very unstable and highly reactive easily undergoes Ring opening reaction.

limitations :-

=> Baeyer's ~~theo~~ strain theory is applicable only for upto first 3 members of cycloalkanes family.

=> He assumed that all the cycloalkanes are planer in nature.

=> He did not explain angle strain in larger cycloalkanes.

=> According to Baeyer, cyclopentane should be more stable than cyclohexane but actually it is reversed.

cyclopentane > cyclohexane > cyclobutane > cyclopropane

05

Polynuclear hydrocarbon — Unit-IV

* polynuclear hydrocarbons are belongs to the class of Aromatic hydrocarbons that contains multiple Aromatic rings made up of hydrocarbon compounds.
* Two or more benzene rings fused together to form these compounds.
* These compounds are also known as Polycyclic Aromatic Hydrocarbons.

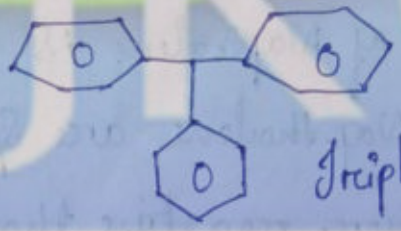
Types —

Polynuclear hydrocarbons are mainly divided into two types:

1. Isolated Ring Compounds.
2. Fused Ring Compounds.

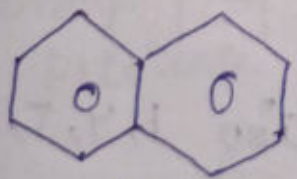
1. Isolated Ring Compounds — In these compounds, Aromatic rings are isolated.

Diphenyl Methane

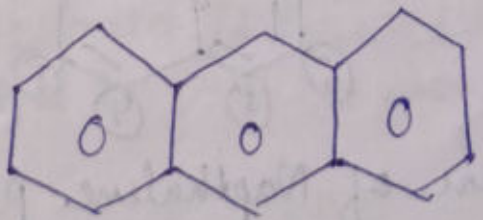


Triphenyl Methane

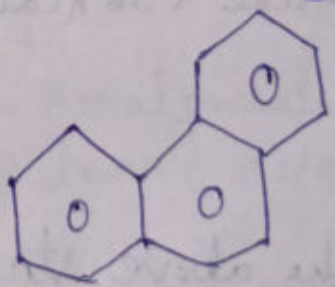
2. Fused Ring Compounds — In these compounds Aromatic Rings are fused.



Napthalene



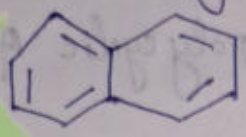
Anthracene



Phenanthrene

NAPTHALENE

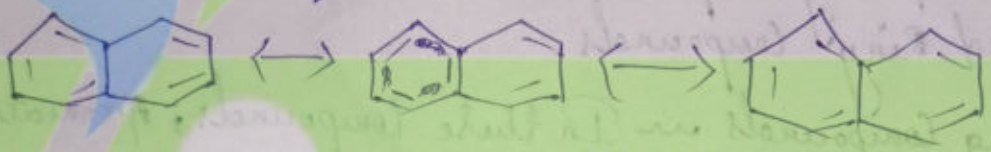
* A Napthalene molecule is derived from fusion of pair of benzene Ring.
* It is a member of fused ring hydrocarbons under the class of polynuclear hydrocarbons.
* Napthalene is a crystalline, aromatic, white solid hydrocarbon.



π = double bonds

Resonance in Napthalene —

* Napthalene forms 3 resonating structure.
* Delocalization of π bonds makes Napthalene stable.

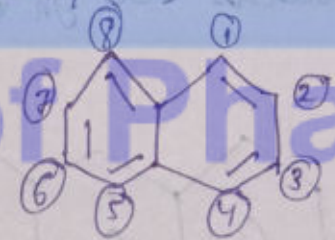


Chemical properties —

i) Chemical formula of Napthalene is $C_{10}H_8$

ii) All Carbons in Napthalene are Sp^2 hybridized.

iii) Napthalene are more reactive than benzene because resonance energy in napthalene (61 Kcal/mol) is less than twice to that of benzene (36 Kcal/mol).



iv) In the above structure of Napthalene position 1, 4, 5, 8 → α and position 2, 3, 6 7 → β.

v) Also unlike the Benzene C–C bond length in napthalene are not same.

vi) C_1–C_2 bond length in napthalene is shorter (1.36 Å) than C_2–C_3 bond length (1.40 Å) due to more double bond character on C_1–C_2 bond.

Physical properties :-

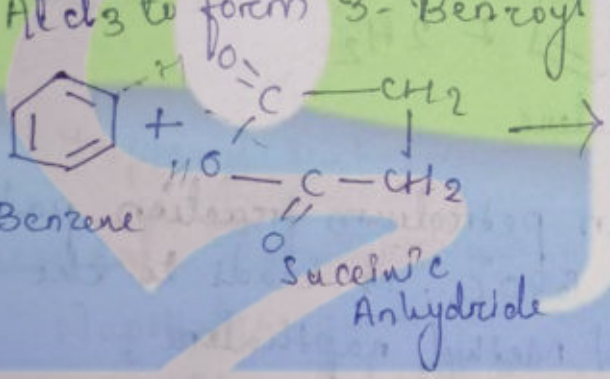
i) Napthalene is a white crystalline Solid.
ii) Its Melting point is 80°C.
iii) Its Boiling point is 217°C.
iv) It is Insoluble in water but Soluble in Organic Solvents.

Synthesis

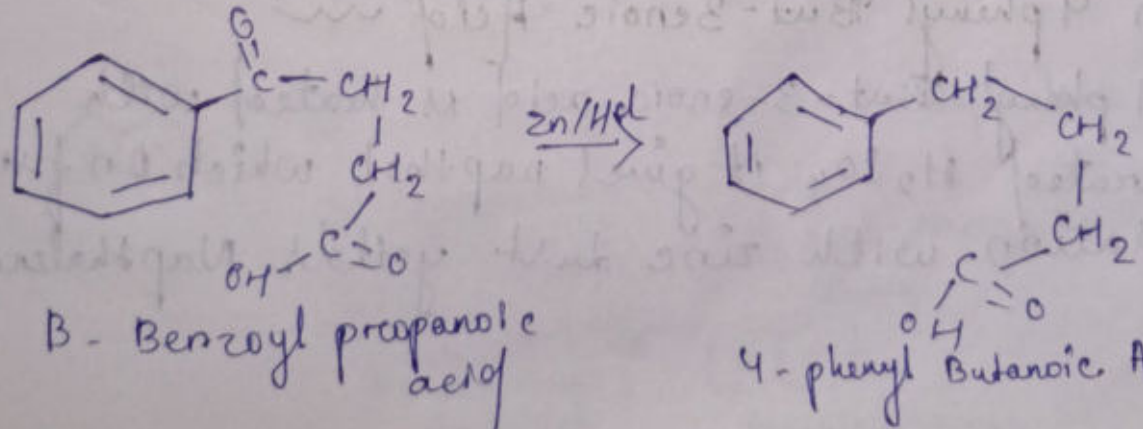
Napthalene can be Synthesized by following various Methods.

① HAWORTH Synthesis —— It is a five Step chemical reaction: ① Friede - Craft Acylation
② clemmensen Reduction - I
③ Ring closure Reaction
④ clemmensen Reduction - II
⑤ Aromatization

① Step - I (Friedel craft Aylation) ——
Benzene and Succinic Anhydride are heated in the prelence of $AlCl_3$ to form 3- Benzoyl propanoic Acid.

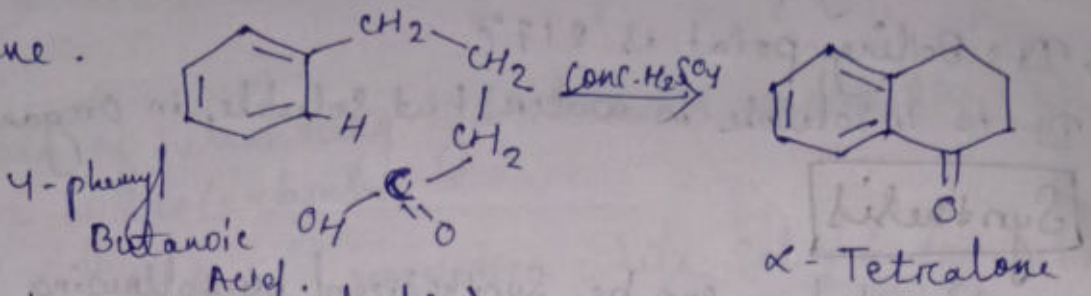


② Step - II (clemmensen Reduction) ——
B - Benzoyl propanoic acid is treated with Amalgamated zinc in the prelence of HCl to give 4- phenyl Butanoic acid.



③ Step - III (Ring closure Reaction) ~~

4-phenyl Butanoic Acid is heated with Conc. H_2SO_4 to form α-tetralone.

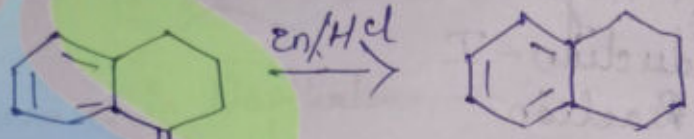


4-phenyl Butanoic Acid.

α-Tetralone

④ Step - IV (clemmenson Reduction) ~~

α Tetralone heated with zinc and HCl to give tetraline

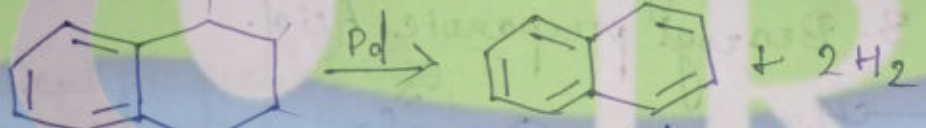


α-Tetralone

Tetraline

⑤ Step - V (Aromatization) ~~

Tetralin is heated with palladium to give Napthalene.



Tetraline

Napthalene

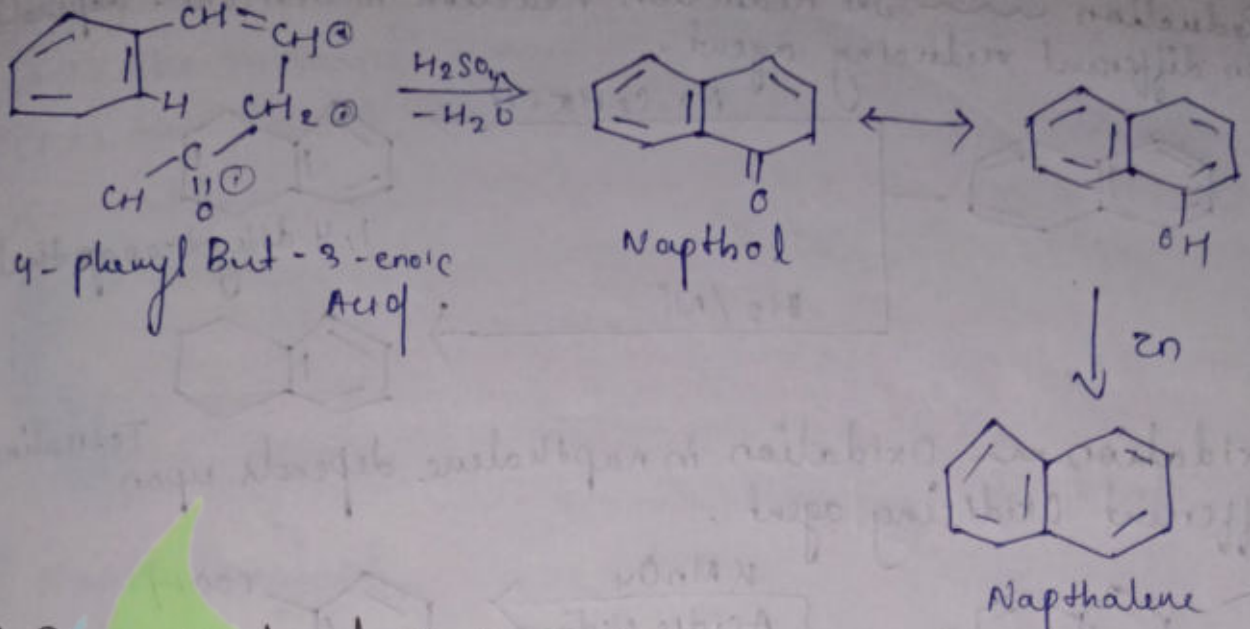
② From petroleum ~~ When petroleum fraction passed over copper (Cu) catalyst at 680°C, it leads to the formation of Napthalene and Methyl napthalene.

Napthalene

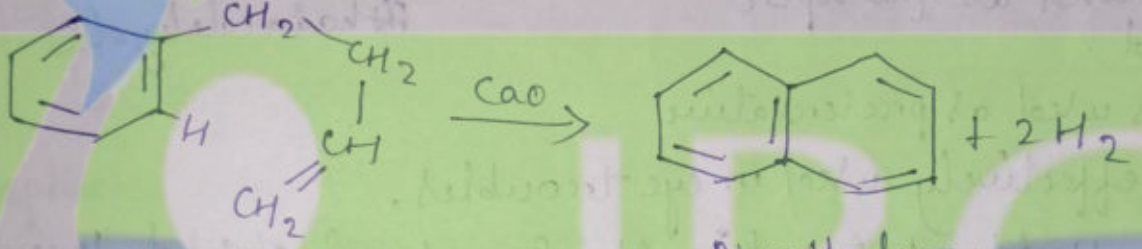
Methyl Napthalene.

③ From 4 phenyl But-3-enoic Acid ~~

When 4 phenyl But-3-enoic acid is heated with concentrated H_2SO_4 it gives napthol which on further distillation with zinc dust yeilds Napthalene.



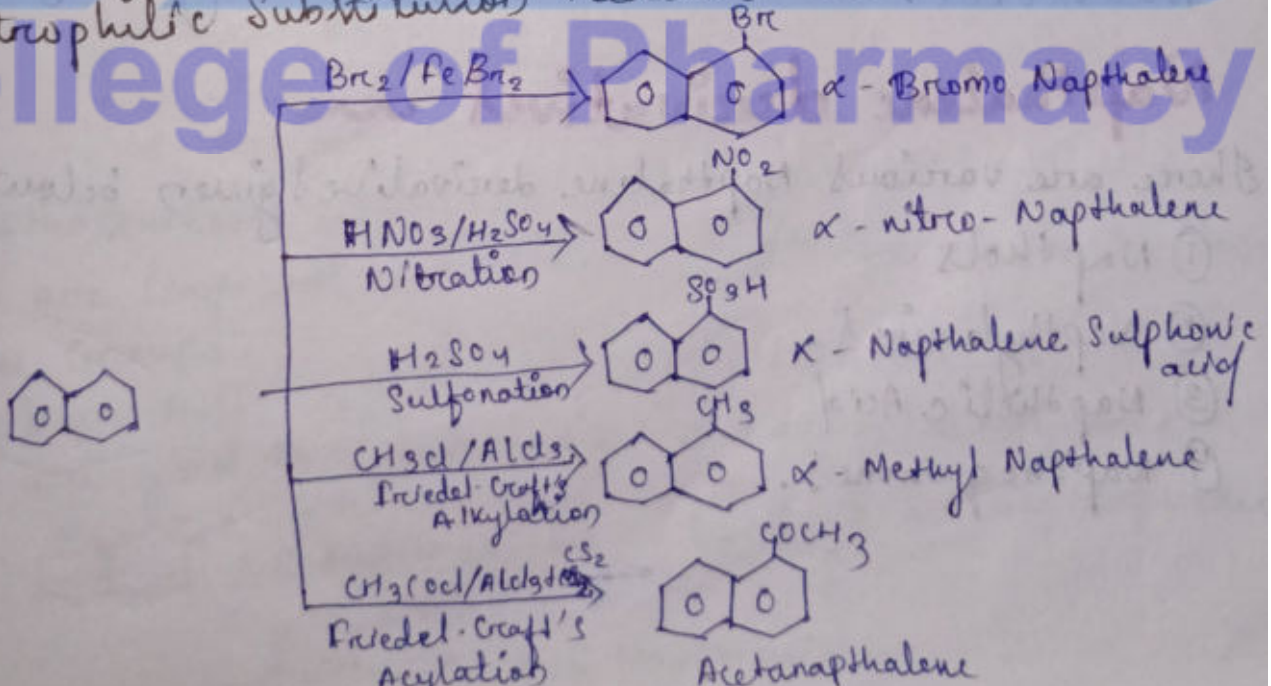
⑨ From 4 phenyl But-1-ene :- When 4-phenyl-But-1-ene is passed over Red Hot Calcium oxide, it yields the formation of Napthalene.



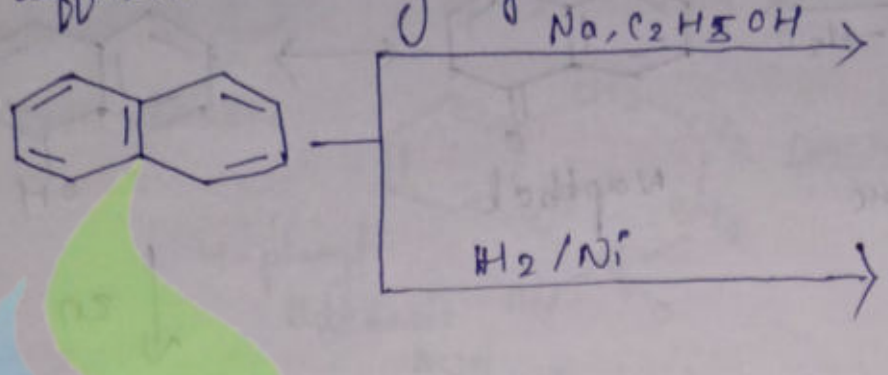
Chemical Reaction :-

Napthalene undergoes the following chemical reactions —

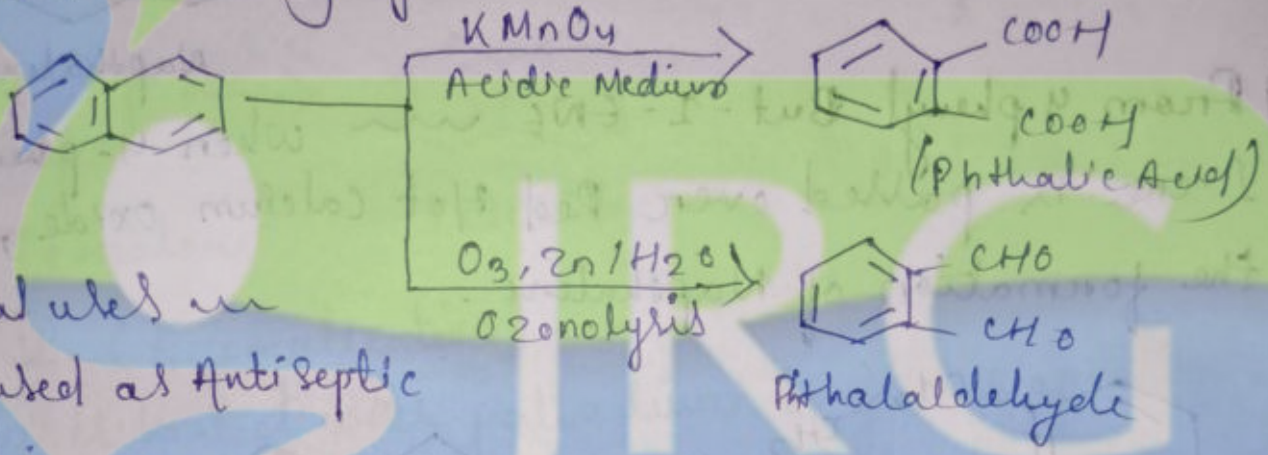
① Electrophilic Substitution reaction :-



(2) Reduction ~~~ The reduction reaction in benzene depends upon different reducing agent.



(3) Oxidation ~~~ Oxidation in napthalene depends upon different oxidizing agent.



Medicinal uses ~~~

* Dt is used as Antiseptic Agent.
* Dt is used as preservative
* Dt is effectively used in eye troubles.
* Dt is effective in treating the Symptoms of cold, fever, Gonorrhoea etc.
* Dt is used in Synthesis of various dyes.
* Dt is also used in Synthesis of various drugs like Nadoxolol.