JRG College of Pharmacy

JRG COLLEGE OF PHARMACY

UNIVERSITY SOLVED QUESTION WITH ANSWER

Year	:	**2021-22**
Subject	:	**Ph. Organic Chemistry-II**
Subject Code	:	**BP301T**
Subject In-Charge	:	**Mr. Biswajit Biswal**

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

Total Number of Pages : 02

B.Pharm
BP301T

3rd Semester Regular / Back Examination: 2021-22
PHARMACEUTICAL ORGANIC CHEMISTRY - II
BRANCH(S): B.Pharma
Time : 3 Hour
Max Marks : 75
Q.Code : OF577

Answer Question No.1 (Part-1) which is compulsory, any eight 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 :** **(2×10)**

a) What is Reichert- Meissl value?
b) Structure and uses of DDT and BHC.
c) What is Huckel's rule of aromaticity?
d) Write any two Qualitative tests for Phenol.
e) Brief out on reduction reaction of phenanthrene.
f) Describe about Coulson and Moffitt's modification.
g) Explain why benzoic acid is stronger acid than acetic acid?
h) Write the structure and uses of Saccharin and Chloramine.
i) What do you mean Essential fatty acid? Give the examples.
j) What happens when sodium benzoate is heated with sodalime?

Part-II

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

a) Write a note on Sachse Mohr's theory.
b) Explain the Haworth synthesis for Naphthalene.
c) Determination of acid value & Iodine value with its significance.
d) What are lipids? Write their classification in detail.
e) Give reason why ammonia is stronger base than aniline?
f) What are the methods used for the synthesis of phenanthrene.
g) Discuss the reaction and mechanism of Friedel-craft alkylation and Friedel-craft acylation reaction.
h) Explain the preparation and effect of substituents on the acidic character of Aromatic acids.
i) Write the general method of preparations and reactions of aromatic amines.

Part-III

Long Answer Type Questions (Answer Any Two)

Q3 Outline any three preparations and three reactions of Phenol. Explain the acidity of Phenol. **(10)**

Q4 Explain the Hydrolysis and Hydrogenation reactions of Fatty acids. Write a note on the types of rancidity and the methods for prevention of rancidity. **(10)**

Q5 Explain the stability of cycloalkanes on the basis of Bayer strain theory. Mention the general two method of preparation and two Chemical reaction of cycloalkanes. **(10)**

Q6 Write about the aromatic characters of Benzene and Discuss the reaction & mechanism of Aromatic electrophilic substitution reactions with suitable example. **(10)**

3rd Sem Regular / Back Examination :- 2021-22

Part-1 Pharmaceutical Organic chemistry - II

1/ (a) What is Reichert - Meissl value?

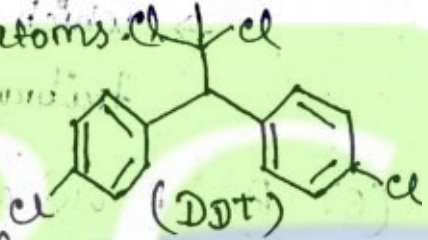
Ans:- It is the number of milliliters of 0.1N KOH required to neutralize the volatile water - soluble fatty acids distilled from 5g of fat.

→ It is used to check adulteration of butter/ghee with vegetable oils.

(b) Structure and uses of DDT and BHC?

Ans:- ★ DDT (Dichloro diphenyl trichloroethane) :-

Str:- A complex str. consisting of two benzene rings connected by a central c-atom, which also bears two chlorine atoms.



(DDT)

→ Chemical formula:- $C_{14}H_9Cl_5$.

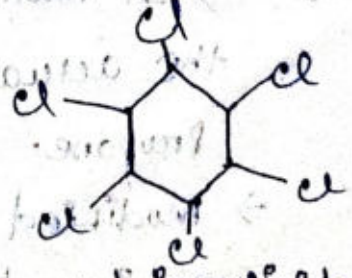
Uses:-

→ widely used as an insecticide for controlling mosquitoes & other diseases vectors.

→ It also used in agriculture to protect crops from insect damage.

★ BHC (Benzene Hexachloride) :-

Str:- A simple str. with a cyclohexane ring where each of the six c-atoms is bonded to a chlorine atoms.



→ Chemical formula:- $C_6H_6Cl_6$.

Uses:-

→ Primarily used as an agricultural Insecticide & in forestry & seed treatment.

→ Applied medicinary to treat lice & Scabies through topical prep's & Shampoos.

(e) What is Huckel's rule of aromaticity?

Ans:- A monocyclic planner conjugated system is aromatic if it contains $(4n+2)$ π-e⁻ ($n = 0, 1, 2 \ldots$).

(g) write any two Qualitative tests for phenol?

Ans:- (1) ferric chloride test:-
→ which forms a colored complex (often violet or blue).

(2) Bromine water Test:-
→ which produces a white ppt of 2,4,6-tribromophenol.

(e) Brief out on reduction reaction of Phenanthrene?

Ans:- → Catalytic hydrogenation (CH_2/Ni or Pt) reduces at 9,10-pos's.
→ 9,10-dihydrophenanthrene further hydrogenation gives perhydrophenanthrene.

(f) Describe about Coulson and Moffitt's modification?

Ans:- → It modify Baeyer strain theory to show the actual pos of C-C bonds in cyclopropane.
→ Modified resonance theory of benzene:- It introduced molecular orbital treatment with sp^2 hybrid orbitals & ~~electrolized~~

delocalized π-e⁻.

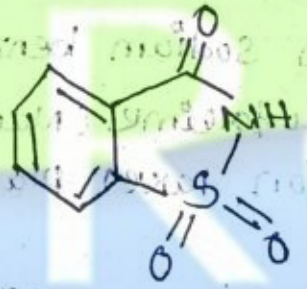
(g) Explain why benzoic acid is stronger acid than acetic acid?

Ans:- Phenyl ring has electron withdrawing effect, stabilizes $-COO^-$ ion more effectively than $-CH_3$. Hence Benzoic acid is - Stronger.

(h) write the str. & uses of Saccharin & Chloramine?

Ans:- (★) Saccharin:-

Str:- A cyclic sulfinide classified as 1,2-benzisothiazole with a keto group & a Sulfonyl group.



uses:-

→ It used in diet soft drinks, candies & low-calorie foods.

→ Sweetens medications & toothpastes.

(★) Chloramine:-

Str:- NH_2Cl a derivative of ammonia where one hydrogen is replaced by a chlorine atom.

uses :-

→ Primary disinfectant in municipal water systems for ongoing disinfection in pipes.

→ It is used to kill bacteria, fungi and algae in water.

(i) what do you mean Essential fatty acid? Give the Examples.

Ans :- → It can't be synthesized by body, must be supplied in diet.

→ Example :- Linoleic acid, Linolenic acid, Arachidonic acid.

(j) what happens when Sodium benzoate is heated with Sodalime?

Ans :- when Sodium benzoate (C_6H_5COONa) is heated with sodalime ($NaOH + CaO$), a decarboxylation reaction takes place.

Rea :-

$$C_6H_5COONa + NaOH \xrightarrow[\Delta]{CaO} C_6H_6 + Na_2CO_3$$

→ So, heating Sodium benzoate with sodalime gives benzene as the main product.

Part-II

2//(a) write a note on Sachse Mohr's theory?

Ans:- Sachse Mohr's theory:-

→ It is known as theory of Strainless Rings.

→ Baeyer's theory failed to Explain the stability of higher cycloalkanes because he assumed that all the cycloalkanes are planer in nature.

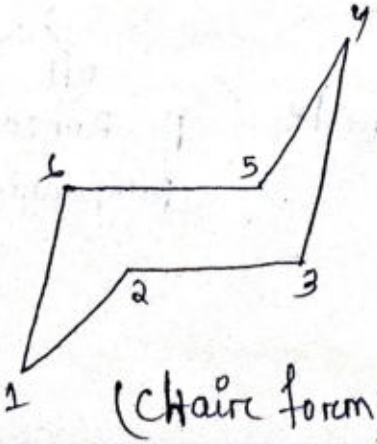
→ Sachse and Mohr in 1918 proposed a theory to Explain the stability of higher cycloalkanes.

→ A/Q to Sachse Mohr's theory the higher cycloalkanes are free from any kind of strain and very stable if they aren't forced into a plane.

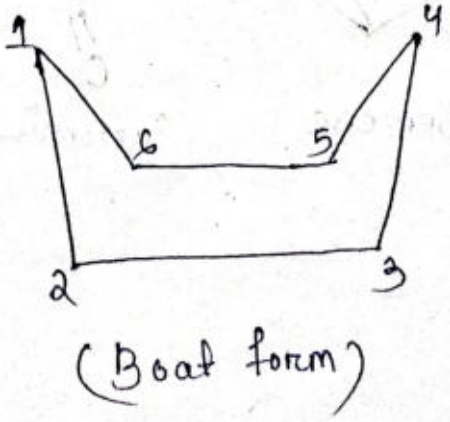
→ He assumed that ring are folded or in puckered conf & that's why they retained their normal tetrahedral angle (109°28') & as a result they become free from any kind of strain.

Chair & Boat from of Cyclohexane:-

→ A/Q to Sachse Mohr's theory cyclohexane exist in two non-planner from i.e. chair form & Boat from.



(Chair form)



(Boat form)

→ In the Boat from, Carbon no. 2, 3, 5 & 6 lie in the same plane & carbons 1 & 4 above the plane.

→ In the chain from, Carbon no. 2, 3, 5, 6 lie in the same plane and carbon 4 is above the plane & Carbon 1 below it.

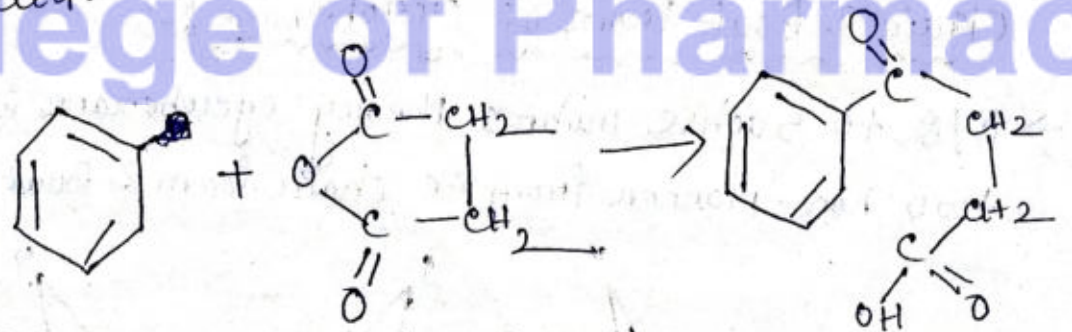
(b) Explain the Haworth Synthesis for Naphthalene?

Ans:- Haworth synthesis for Naphthalene is a five step chemical reaction.

① Friedl Craft Acylation.
② Clemmensen Reduction - I.
③ Ring closure Reaction.
④ Clemmensen Reduction - II.
⑤ Aromatization.

① Friedl Craft Acylation:-

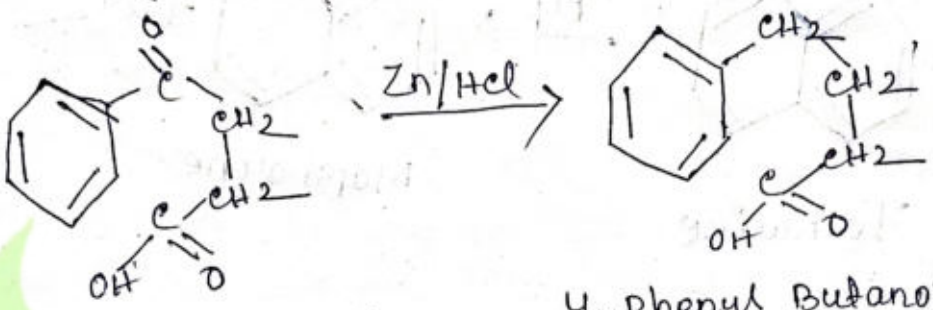
→ Benzene and Succinic Anhydride are heated in the presence of $AlCl_3$ to form 3-benzoyl propanoic acid.



Benzene Succinic Anhydride β - Benzoyl propanoic acid.

(2) Clemmensen Reduction-I :-

→ β-Benzoyl Propanoic acid is treated with Amalgamated Zinc in the presence of HCl to give 4-phenyl Butanoic acid.

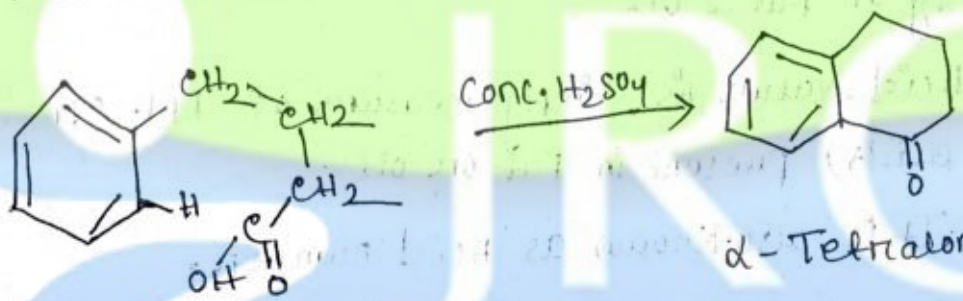


β-Benzoyl Propanoic acid

4-phenyl Butanoic acid

(3) Ring closure Reaction :-

→ 4-phenyl Butanoic acid is heated with conc. H_2SO_4 to form α-tetralone.

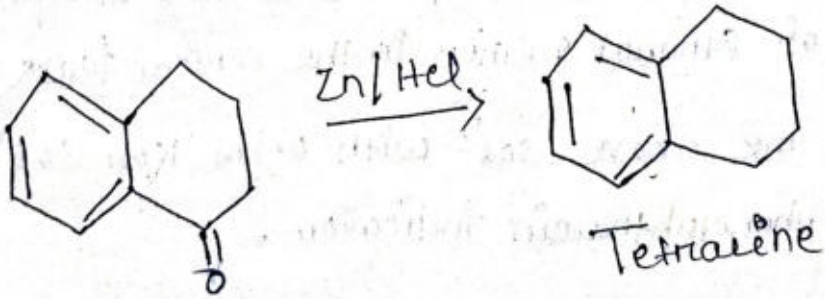


4-phenyl Butanoic acid

α-Tetralone

(4) Clemmenson Reduction-II :-

→ α-Tetralone heated with Zinc & HCl to give tetraline.

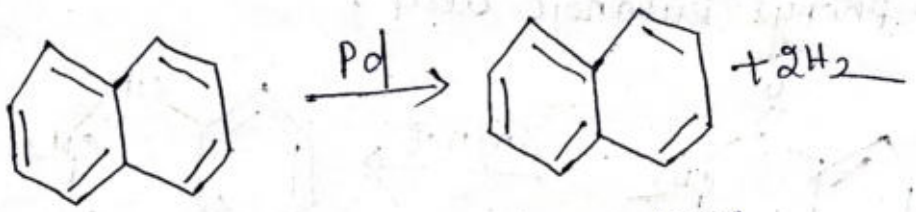


α-Tetralone

Tetraline

⑤ Aromatization :-

→ Tetralin is heated with Palladium to give Napthalene



Tetraline

Napthalene

(C) Determination of acid value & Iodine value with its significance?

Ans:- Acid value :-

→ It is defined as no. of mg of KOH required to completely neutralize free fatty acids present in 1g of fat & oil.

→ Acid value is simply measure of FFA (Free fatty acids) present in fat or oils.

→ It is also known as Acid number.

Principle :-

→ The Acid value is determined by titrating the fat/oil against KOH/NaOH sol^{n} using phenolpthalein as an indicator.

→ 1g. of sample is dissolved in 50ml mix. of equal volumes of Ethanol & Ether in the conical flask.

→ Titrate the above sol^{n} with 0.1M KOH sol^{n} using phenolphthalein indicator.

Calculation:-

Acid value can be calculated using following Eq^n

$$\text{Acid value} = \frac{V_{NaOH} \times N \times 56.1}{W}$$

Here, V_{NaOH} = Vol. of NaOH used

N = Normality of NaOH sol^n.

W = weight of sample (g)

Significance:-

→ Acid value measures the amount of free fatty acids which have been liberated by hydrolysis due to air, moisture etc.

→ Pharmaceutical oils should be free from acidity.

Iodine Value:-

→ It is simply defined as no. of grams of iodine absorbed by 100gm of fat or oil.

→ Each oil has its Specific Iodine Number.

→ It measures the degree of unsaturation of oil/fat.

Principle:-

→ Iodine no. is defined by wijs Method.

→ Now, the remaining iodine monochloride is treated with potassium Iodide.

→ The liberated Iodide in then titrated with sodium Thiosulphate Solution.

→ The same process is again repeated for blank Titration without Sample.

→ Starch sol^n is used as indicator.

Calculation :-

$$\text{Iodine value} = \frac{(B-S) \times N \times 12.69}{W}$$

Here, B = vol. of thiosulphate for Blank Titration.

S = vol. of thiosulphate for sample Titration.

N = Normality of thiosulphate sol?.

W = weight of sample (g)

Significance :-

→ Iodine value measures the degree of unsaturation of oils.

→ Low iodine no. is desirable in oils.

(d) what are lipids? write their classification in details?

Ans:- Lipids :-

→ Lipids are a large and diverse group of naturally occurring organic compounds that are insoluble in water but soluble in non-polar organic solvents.

→ They are hydrophobic or amphipathic in nature.

→ It play essential roles in energy storage, structural components of cell memb, insulation, signaling.

Classification of lipids :-

→ Lipids can be classified into three main categories.

(1) Simple lipids.

(2) Compound lipids.

(3) Derived lipids.

(1) Simple lipids :-

→ These are esters of fatty acids with various alcohols.

(a) Fats and oils :-

→ Esters of fatty acids with glycerol.

→ Fats are solid at room temp^{n}, while oils are liquid.

→ Ex :- Tristearin, Triolein.

(b) Waxes :-

→ Esters of long-chain fatty acids with long-chain monohydric alcohols.

→ Insoluble in water.

→ Ex :- Beeswax, Lanolin

(2) Compound lipids :-

→ These are esters of fatty acids with alcohol, but in add^{n}, they contain other groups like phosphate, carbohydrate, protein etc.

(a) Phospholipids :-

→ It contain phosphoric acid in add^{n} to fatty acids & alcohol.

→ Important in cell membranes.

→ Ex :- phosphoglycerides, Sphingomyelins.

(b) Glycolipids :-

→ It contain carbohydrate group in add to fatty acids & alcohol.

→ Found abundantly in brain and nervous tissue.

→ Ex:- Cerebrosides, Ganglio sides.

(c) Lipoproteins :-

→ Lipids combined with proteins.

→ Transport of lipids in blood & Lymph.

(3) Derived lipids :-

→ These are substances obtained by hydrolysis of simple & compound lipids which still possess the general characteristics of lipids.

→ Ex:- fatty acids, Glycerol, Steroids.

(e) Give reason why ammonia is stronger base than aniline?

Ans:- (•) In ammonia (NH_3) :-

→ The lone pair on nitrogen is freely available because there is no delocalization.

→ This makes it easy for NH_3 to accept a proton (H^+).

(•) In Aniline ($C_6H_5-NH_2$) :-

→ The nitrogen atom is directly attached to a benzene ring.

→ The lone pair of nitrogen undergoes resonance with the aromatic ring.

→ This delocalization reduce the electron density on nitrogen, so its lone pair is less available for bonding with H^+.

Conclusion:-

→ Ammonia is a stronger base than aniline because in ammonia the lone pair on nitrogen is completely available for protonation, where as in aniline it is partially delocalized into the benzene ring, decreasing availability.

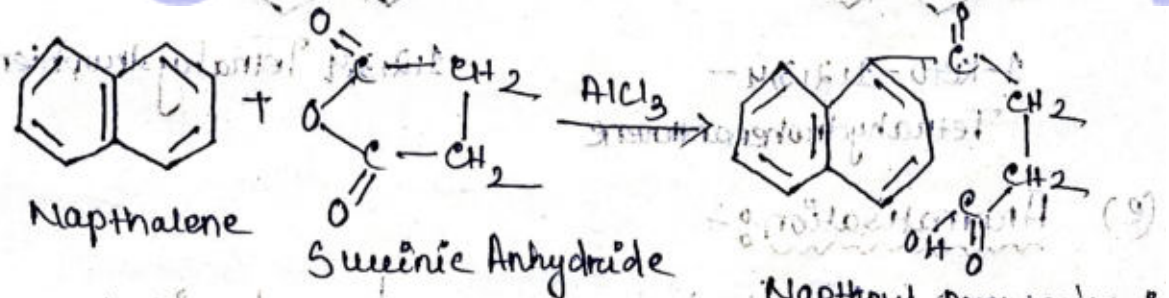
(f): What are the Methods used for the Synthesis of phenanthrene?

Ans:- Phenanthrene can be synthesized by following reactions:-

(1) Haworth Synthesis:-

(a) Friedel Craft Acylation:-

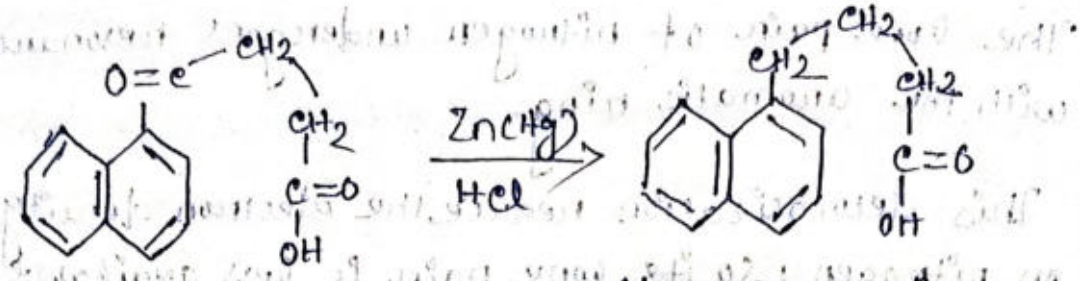
→ Napthalene reacts with Succinic anhydride in the presence of $AlCl_3$ to from Napthoyl Propanoic acid.



Napthalene + Succinic Anhydride → Napthoyl Propanoic acid

(b) Clemmensen Reduction:-

→ Napthyl Propanoic acid reacts with amalgated Zinc in the presence of HCl to form Napthyl Butanoic acid.

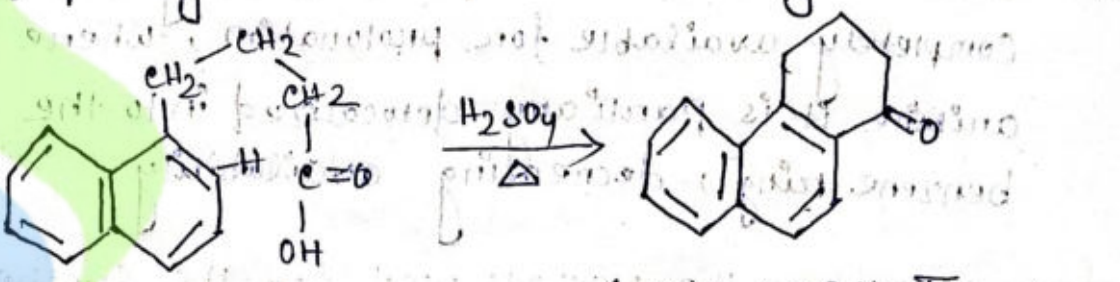


Napthoyl Propanoic acid

Napthyl Butanoic acid

(C) Cyclisation :-

→ Napthyl Butanoic acid heated in the presence of H_2SO_4 to give 1-Keto-1,2,3,4-Tetrahydrophenanthrene.

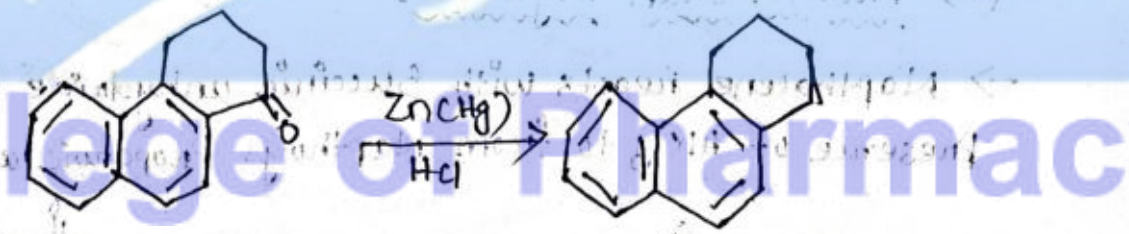


Napthyl Butanoic acid

1-Keto-1,2,3,4-Tetrahydrophenanthrene

(d) Clemmensen Reduction :-

→ 1-Keto-1,2,3,4 Tetrahydrophenanthrene reacts with Amalgamated Zinc in the presence of HCl to give 1,2,3,4 Tetrahydrophenanthrene.

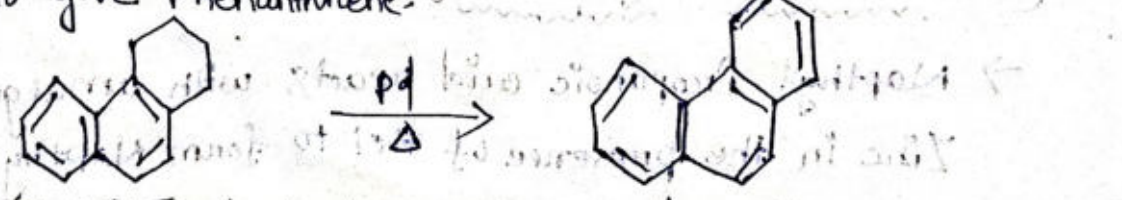


1-Keto-1,2,3,4-Tetrahydrophenanthrene

1,2,3,4 Tetrahydrophienanthrene

(e) Aromatisation :-

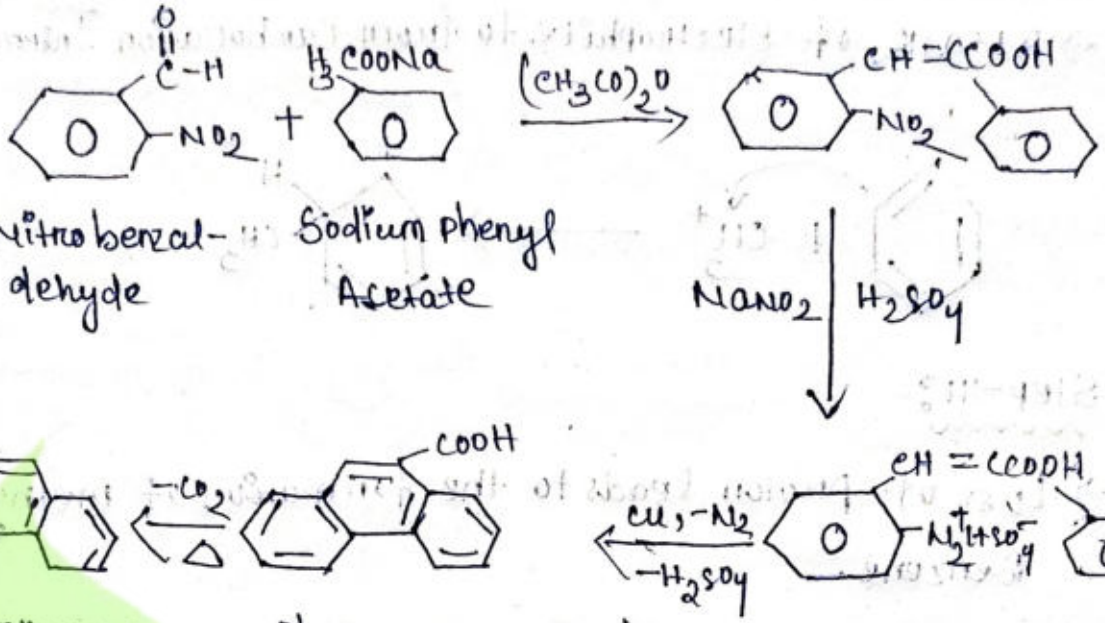
→ 1,2,3,4 Tetrahydrophenanthrene heated with Palladium to give Phenanthrene.



1,2,3,4 Tetrahydrophenanthrene

Phenanthrene

(2) P Schorn Synthesis :-



O-Nitrobenzaldehyde

Sodium phenyl Acetate

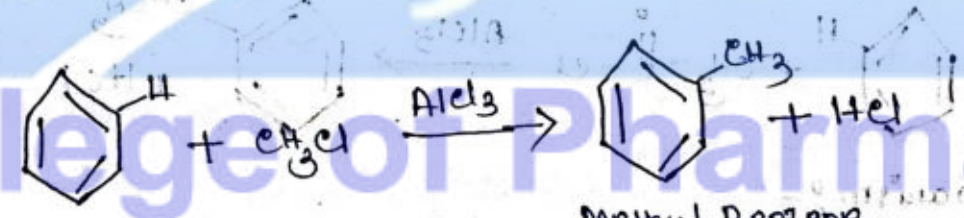
Phenanthrene

Phenanthrene-9-carboxylic acid

(9) ① Discuss the reaction and mechanism of Friedel-Craft alkylation and friedel-Craft acylation reaction ?

Ans :- Friedel crafts alkylation :-

→ In Friedel Crafts alkylation Benzene reacts with Alkyl group to form Alkyl Benzene.



Methyl Benzene

Mechanism :-

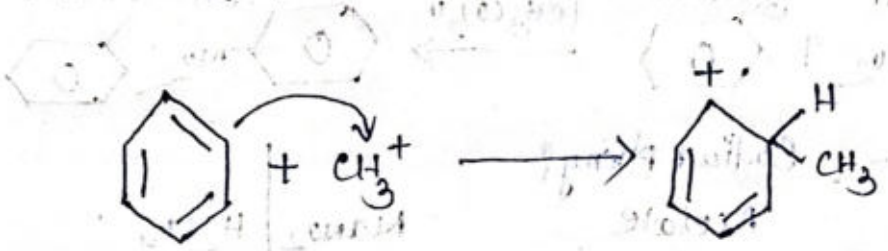
Step-1 :-

formation of Electrophile-

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

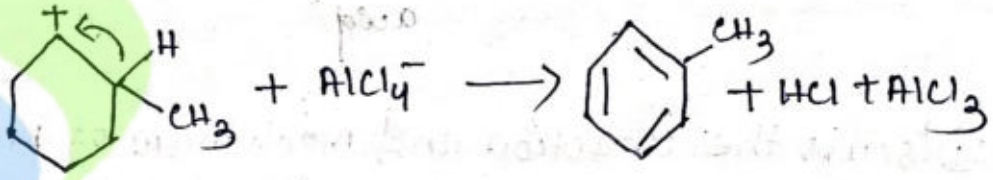
Step-II :-

→ Attack of Electrophile to from Carbocation Intermediate



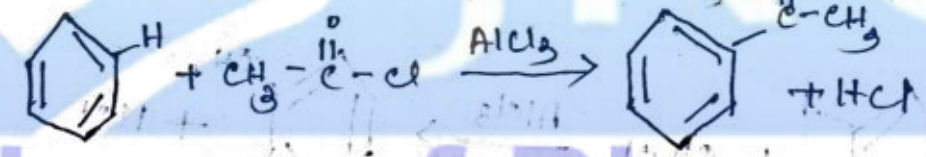
Step-III :-

→ Loss of proton leads to the formation of methyl Benzene.



Friedel Crafts Acylation :-

→ In friedel crafts Acylation benzene reacts with Acyl group to form Aromatic ketones in the Presence of $AlCl_3$.



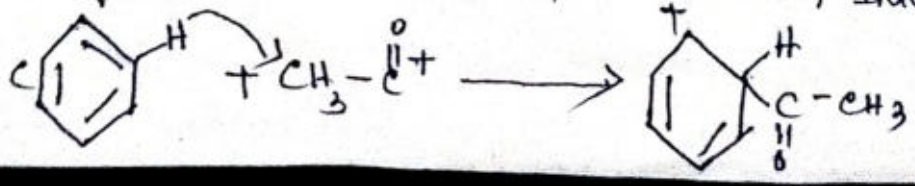
Mechanism :-

Step-1 :-

formation of Electrophile.

Step-2 :-

Attack of Electrophile to form Carbocation Intermediate.



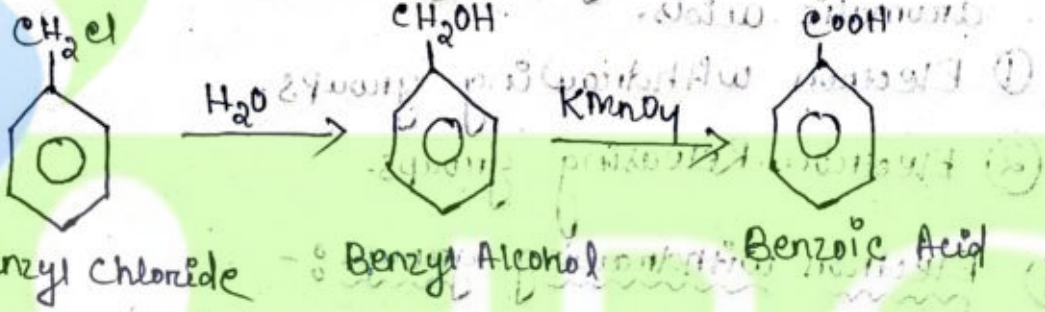
(h) Explain the prep & effect of substituents on the acidic character of Aromatic acids?

Ans:- → Aromatic Acids are the derivative of aromatic Hydrocarbons in which 1° Hydrogen of aromatic ring is replaced by carboxylic functional group (-COOH)

Method of Preparation:-

① Oxidation:-

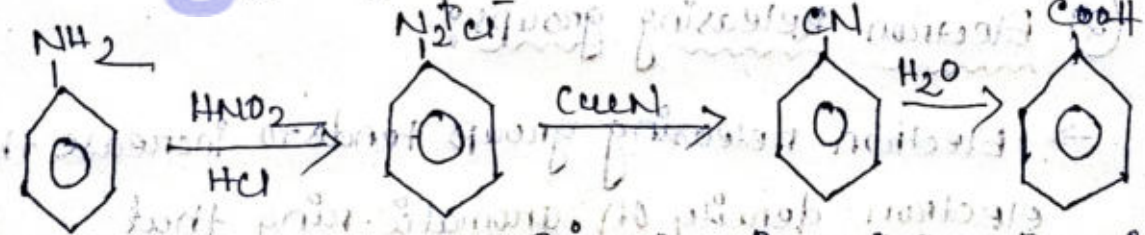
→ oxidation of benzyl chloride with acidic potassium permanganate yeilds the formation of Benzoic acid.



Benzyl Chloride — Benzyl Alcohol — Benzoic Acid

② From Diazonium Salt:-

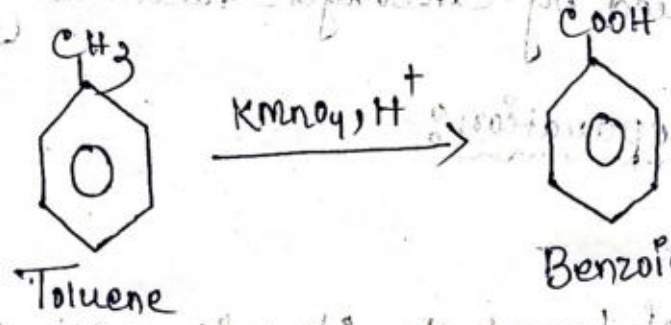
→ Aniline on reacting with nitrous acid ($CHNO_2$ / HCl) gives Benzene diazonium chloride which on reaction with CuCN produce Benzonitrile which on further hydrolysis gives Benzoic acid.



Aniline — Benzene Diazonium Chloride — Benzonitrile — Benzoic acid

③ By oxidation of alkyl Benzenes :-

→ Alkyl Benzenes are oxidized by dilute Nitric acid or potassium permangarate to give benzoic acid.



Toluene — Benzoic acid

Effect of Substituents ON Acidity :-

→ There are mainly two types of group present on aromatic acids.

① Electron withdrawing groups.

② Electron Releasing groups.

① Electron withdrawing groups :-

→ Electron withdrawing groups tends to decrease the electron density on aromatic ring that ultimately increase the stability of ring & hence Acidity increases.

→ Ex :- $-NO_2$, $-CHO$ etc.

② Electron Releasing groups :-

→ Electron releasing groups tends to increase the electron density on aromatic ring that ultimately decreases the stability of ring & hence Acidity decreases.

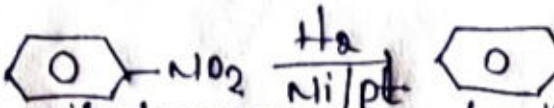
→ Ex :- $-CH_3$, $-OH$ etc.

i/ Write the general method of preparations & Reaction of Aromatic amines?

Ans:- Method of preparations:-

(i) By Reduction of nitrocompound -

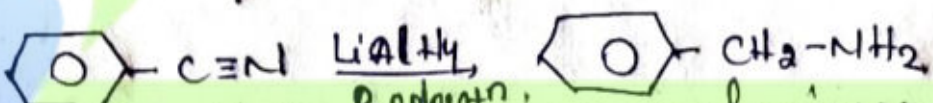
When nitrobenzene is react with H_2 in the presence of catalyst Ni/pt it gives Aniline.



(Nitrobenzene) (Aniline)

ii) By reduction of nitriles -

When aromatic nitriles undergoes reduction reaction with reducing agent like $LiAlH_4$ it produce aromatic amins.

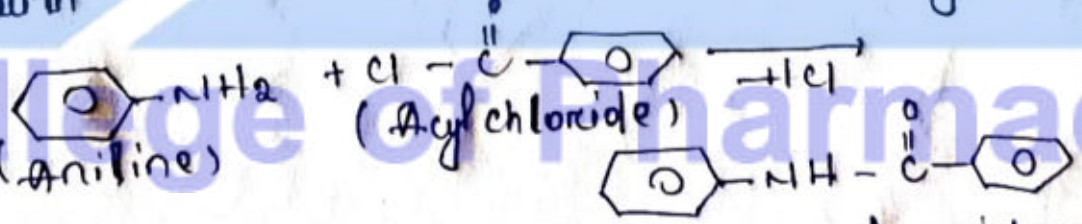


(Aromatic Nitriles) (Benzyl amines)

Chemical Reactn of Aromatic Amine:-

i/ forming of Amides:-

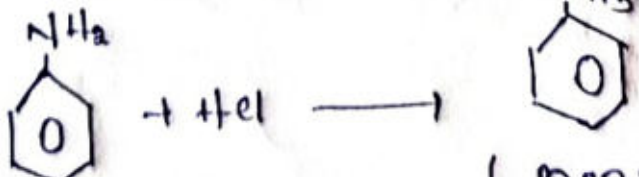
When aromatic amine (Aniline) react with acyl chloride it produced benzyl amide with the formation of Amide linkage.



(Aniline) (Acyl chloride) (benzyl amide)

ii/ formation of salt:-

When aromatic amine treated with HCl it produced benzenaminium chloride.



(Aniline) (benzaminium chloride)

Part - III

3- Outline any three preparation and three reaction of phenol. Explain the acidity of phenol ?

Ans :- **Preparation of phenol :-**

1. From Haloarenes (Dow's process) :-

Chlorobenzene is fused with NaOH at 623K and 300 atm pressure.

→ The product is sodium phenoxide, which on acidification gives phenol.

$$C_6H_5Cl + NaOH \xrightarrow{623K,\ 300\,atm} C_6H_5ONa \xrightarrow{HCl} C_6H_5OH$$

2. From Benzene Sulphonic Acid :-

Benzene is sulphonated with conc. H_2SO_4 to give benzene sulphonic acid.

→ On fusion with NaOH at high temperature, sodium phenoxide forms.

→ Acidification yields phenol.

$$C_6H_5SO_3H \xrightarrow{NaOH} C_6H_5ONa \xrightarrow{HCl} C_6H_5OH$$

3. From Diazonium salts :-

Aniline is diazotized with $NaNO_2$ and HCl at 273 - 278 K to give benzene diazonium chloride.

→ On hydrolysis, its produces phenol.

$$C_6H_5N_2^+Cl^- + H_2O \xrightarrow{Warm} C_6H_5OH + N_2 + HCl$$

Reaction of phenols :-

1. Electrophilic substitution :- (Bromination)

phenol react with bromine water to give 2,4,6-tribromophenol (white precipitate).

$C_6H_5OH + 3Br_2 \longrightarrow 2,4,6\text{-}C_6H_2Br_3OH + 3HBr$

2. Nitration :-

phenol react with dilute nitric acid to form a mixture of o-nitrophenol and p-nitrophenol with concentrated nitric acid.

→ It forms 2,4,6-trinitrophenol (picric acid)

3- Reimer-Tiemann Reaction :-

→ phenol react with chloroform and NaOH to form salicylaldehyde (o-hydroxybenzaldehyde).

$C_6H_5OH + CHCl_3 + 3NaOH \longrightarrow o\text{-}HOC_6H_4CHO + 3NaCl + 2H_2O$

Acidity of phenols :-

phenol is more acidic than alcohols but less acidic than carboxylic acids.

→ In phenol, after losing H^+, the phenoxide ion ($C_6H_5O^-$) is stabilized by resonance.

→ The negative charge on oxygen delocalizes into the aromatic ring making the ion stable.

→ In alcohols, the alkoxide ion is not stabilized by resonance, hence alcohols are less acidic.

→ Electron - withdrawing group ($-NO_2$, $-CN$, $-X$) increase acidity (stabilize phenoxide ion).

→ Electron - donating groups ($-CH_3$, $-OCH_3$) decrease acidity (destabilize phenoxide ion).

4. Explain the Hydrolysis and Hydrogenation reaction of fatty acid. Write a note on the types of rancidity and the methods for prevention of rancidity ?

Ans :- Hydrolysis of Fatty acid :-

Hydrolysis is the breaking down of fats (triglycerides) into glycerol and free fatty acid by the action of water.

→ It can be catalyzed by enzymes like lipase or by acids / alkalis.

Example :-

$$\text{Triglyceride} + 3H_2O \xrightarrow{\text{Lipase}} \text{Glycerol} + 3 \text{ fatty acid}.$$

Hydrogenation of Fatty Acid :-

→ Hydrogenation is the addition of hydrogen (H_2) to unsaturated fatty acids (with double bonds) in the presence of a catalyst like Ni, Pd or Pt.

→ It converts liquid oils (unsaturated) into semi-solid or solid fats

Example :-

$$R-CH=CH-R + H_2 \xrightarrow{Ni} R-CH_2-CH_2-R$$

Types of Rancidity :-

Rancidity is the spoilage of fats and oils due to undesirable chemical changes, leading to foul odor and taste.

Types :-

1- Hydrolytic Rancidity
2- Oxidative Rancidity
3- Microbial Rancidity

1- Hydrolytic Rancidity :-

It is caused by hydrolysis of triglycerides by water or lipase enzymes.

→ Release free fatty acid.

butyric acid in butter ⟶ bad smell

2- Oxidative Rancidity :-

It is caused by oxidation of unsaturated fatty acids in presence of oxygen, light or heat.

→ produces aldehydes, ketones and peroxides with offensive odor.

3- Microbial Rancidity :-

→ It is caused by bacterial or fungal action on fats, producing unpleasant-smelling compounds.

Method for prevention of rancidity :-

1. Use of Antioxidants :-

Adding substances like BHA, BHT, Vitamin E, vitamin C are added to oils and fats to prevent oxidation.

2. proper storage :-

Store fats and oils in airtight containers to limit contact with air (oxygen).

3. protection from Light & Heat :-

Use dark-colored bottles/containers and keep in a cool placed to slow oxidation.

4. Refrigeration :-

Low temperature reduces chemical reaction and microbial activity.

5. Hydrogenation :-

Converting unsaturated oils into more stable saturated fats makes them less prone to rancidity.

6. Hygienic conditions :-

Prevents microbial rancidity by avoiding contamination during handling and storage.

5. Explain the stability of cycloalkanes on the basis of Bayer strain theory. Mention the general two method of preparation and two chemical reaction of Cycloalkanes ?

Ans :- Stability of cycloalkanes on the basis of Bayer strain theory :-

→ Bayer proposed that stability of cycloalkanes depends on the angle strain due to deviation of bond angles from the normal tetrahedral angle (109.5°).

→ In a regular cycloalkane, the C-C-C bond angle is forced to adopt values depending on the ring size.

- Cyclopropane (60°) :-
  → Very strained
  → Highly unstable.
- Cyclobutane (90°) :-
  → Strained but less than cyclopropane.
- Cyclopentane (108°) :-
  Nearly strain-free, most stable.
- Cyclohexane :-
  (120° in a flat form, but actually adopts chair conformation to relieve strain, so very stable)

→ According to Bayer, rings other than five members should be unstable due to angle strain, but later

studies showed that larger rings relive strain by adopting puckered conformation.

Two General Method of preparation of cycloalkanes :-

1. From α, ω- dihalogen compound :- (Wurtz Reacⁿ)

When a dihalogen derivation of an alkane react with sodium metal in dry ether, intramolecul coupling takes place and a ring is formed.

$$Cl-(CH_2)_n-Cl + 2Na \xrightarrow{\text{dry ether}} (CH_2)_n + 2NaCl$$

Example :-

1,4- dichlorobutane → cyclobutane

2. By Dieckmann condensation :- (Intramolecular Claisen condensation)

A diester containing two ester groups undergoes intramolecular condensation in the presenc of sodium ethoxide to form a cyclic β-keto ester. Hydrolysis followed by decarboxylation gives cycloalkane.

Example :-

Diethyl adipate (After condensation, hydrolysis & decarboxylation) ⟶ Cyclopentanone ⟶ cyclopentane.

Two chemical reaction of cycloalkanes :-

1- Halogenation (substitution Reaction) :-

Cycloalkanes (except cyclopropane and cyclobutane which behave like alkenes due to ring strain) undergo

free radical substitution with halogenes in the presence of heat or light.

$$C_6H_{12} + Cl_2 \xrightarrow{h\nu} C_6H_{11}Cl + HCl$$

2. Combustion Reaction :-

Cycloalkanes burn in oxygen to produce carbon dioxide and water, similar to alkanes.

$$C_5H_{10} + 7.5\,O_2 \longrightarrow 5CO_2 + 5H_2O$$

6. Write about the aromatic characters of Benzene and Discuss the reaction & mechanism of Aromatic electrophilic substitution reaction with suitable example ?

Ans :- Aromatic character of Benzene :-

Benzene (C_6H_6) is a cyclic conjugated hydrocarbon that exhibits unique stability due to its aromatic nature.

Features of Aromaticity in Benzene :-

1. Cyclic and planar structure :-

Benzene is a planar hexagonal ring with bond angles of 120°.

2. Conjugation :-

Each carbon atom is sp^2 hybridized and the unhybridized p-orbitals overlap continuously forming a cyclic conjugated π-system.

3. Huckel's Rule :-

Benzene has 6 π-electrons, which fits the formula $(4n+2)\ \pi$ electron $(n=1)$, making it aromatic.

4. Bond Lengths :-

All six C – C bonds are equal ($\approx 1.39\ \text{Å}$), intermediate between single and double bonds.

5. Extra Stability :-

Benzene resists addition reaction and prefers substitution reaction, preserving its aromatic ring.

Aromatic Electrophilic substitution :-

Benzene, being aromatic and highly stable, does not undergo addition reaction like alkenes. Instead, it undergoes substitution reaction, where a hydrogen atom is replaced by an electrophile (E^+) while the aromaticity is retained.

Mechanism of EAS :-

1- Generation of Electrophile (E^+) :-

The attacking species is formed from the reagent in presence of a catalyst.

2. Attack on Benzene (slow step) :-

The π-electron of benzene attack the electrophile, producing a resonance-stabilized carbocation intermediate called the arenium ion.

3. Resonance stabilization :-

The positive charge delocalize over the ortho and para position.

4. Deprotonation (Fast step) :-

A base remove the proton (H^+) from the carbon attached to electrophile. Aromaticity of the ring is restored, giving the substituted product.

Example :-

Nitration of Benzene :-

Reaction :-

$$C_6H_6 + HNO_3 \xrightarrow{H_2SO_4} C_6H_5NO_2 + H_2O$$

Mechanism :-

1. Generation of Electrophile (Nitronium ion) :-

$$HNO_3 + H_2SO_4 \longrightarrow NO_2^+ + HSO_4^- + H_2O$$

2. Attack on Benzene :-

The nitronium ion (NO_2^+) attacks benzene, forming an arenium ion.

3. Resonance stabilization :-

The positive charge delocalizes over the ring carbons.

4. Deprotonation :-

Loss of H^+ restores aromaticity, giving nitrobenzene ($C_6H_5NO_2$).