(POC-II) Pharmaceutical Organic Chemistry - IInd

MOST IMPORTANT QUESTIONS

Unit-I

① Write analytic, synthetic & other evidence in the derivations of structure of benzene

OR

Write brief note on structure of benzene [Kekule, Chemical and Resosance].

② Write electrophilic substitution reaction of benzene

OR

Write mechanism of friedal craft alkylation or acylation / sulphonation.

③ Molecular orbital structure of benzene

④ Huckel's rule of Aromaticity.

⑤ Write a note on effect of Substituent on reactivity of benzene

⑥ Write structure and uses of DDT, Saccharin.

Unit-IInd

• Phenols :-

① Describe in details the synthesis and chemical reaction of phenol.

② Why phenol is acidic in nature and what is the effect of substituent on acidity of phenol.

OR

Discuss about Acidity of phenol.

③ Discuss various qualitative test to detect phenols in given sample and chemical rxn.

④ Write structure and uses of phenol, cresol

• Aromatic amines :-

① Write all the method of preparation (synthesis) and chemical reaction of Aromatic amines.

② Why amines are basic in nature and what is the effect of substituents on its basicity.

③ Describe in details the synthesis and chemical reaction of aryl diazonium salts.

- Aromatic Acids :-

① Describe in details the synthesis and chemical reaction of Benzoic acid (Aromatic acids).

UNIT - 3

① Write reaction of fats and oils.

- Hydrolysis
- Hydrogenation
- Saponification ✓ Imp.
- Racidity of Oils ✓ Imp.
- Drying oils

② Write different methods of analysis of fats and oils.

- Acid Value
- Saponification Value
- Ester Value — V. Imp.
- Iodine Value — V. Imp.
- Acetyl Value
- RM Value

③ Write the difference b/w fats and oils.

UNIT - 4

① Describe in details about the synthesis and chemical reaction of
- Naphthalene
- Phenanthrene
- Anthracene

② Structure, chemical synthesis and medicinal use of
- Diphenylmethane
- Triphenylmethane

Unit - 5

① Define Cycloalkanes, write down difference theory of stability of cycloalkanes in details. (10).

② Give Baeyer's strain theory with its limitation.

③ Write a note on theory of strainless ring (Sachse's Mohr theory).

2 Marks Questions very short

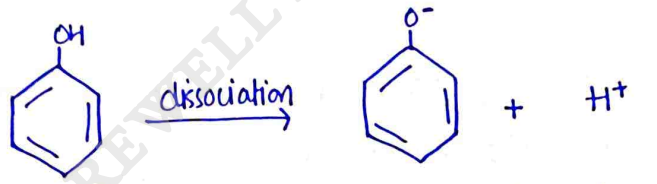
1. Why phenol is acidic in nature
2. Write the reduction reaction of naphthalene
3. Name two reducing agent
4. Write the oxidation reaction of phenanthracene
5. Write the reaction of cyclopropane
6. Name the product formed by friedal craft acylation of benzene
7. What is the mechanism of esterification reaction.
8. Write the use of Resorcinol.
9. Write the structure of ortho-cresol.
10. What is Saponification.
11. What is Ester value.
12. What is Acid Value
13. What is basic of Sachs-Mohr's theory
14. Arrange in order of increasing acidity :- phenol, 4-Nitrophenol, 2,4-Nitrophenol, 2,4,6-Trinitrophenol.
15. Name the product of nitration of toluene
16. Name the product of sulphonation of naphthalene under thermal condition.
17. Name the electrophilic produced in nitration reaction of benzene
18. Give molecular orbital picture of benzene
19. Give structure and use of DDT
20. What is friedal craft acylation. explain with suitable reaction.
21. Give structure and use of Naphthols.
22. Give ~~phenant~~ Haworth Synthesis of phenanthrene
23. Give stability order of cycloalkanes.
24. Draw any four aromatic structures.
25. Give structure and use of diphenylmethane
26. Define and classify polynuclear hydrocarbons.
27. Write Huckel's rule of aromaticity.
28. What is Resonance? Give their suitable example
29. What do you understand by Ring deactivating and ring activating group.
30. Write any on reaction:-
    i) Kolbe reaction of phenol.
    ii) Reimer-Tiemann reaction.

PHARMACEUTICAL ORGANIC CHEMISTRY - II

2 Marks Q & A ANSWERS / SOLUTIONS

① Why phenol is acidic in nature

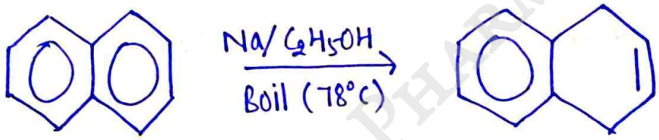
⇒ Phenol gives H^+ ion on dissociation, so it is acidic in nature because According to Arrhenius concept, Acid are those substances which gives H^+ ion on dissociation.



(phenol) (phenoxide ion) (H^+ ion).

② Write the reduction reaction of Naphthalene

⇒ Naphthalene on reduction give 1,4-dihydronaphthalene in the presence/react of sodium and ethyl alcohol.



(Naphthalene) (1,4-dihydronaphthalene).

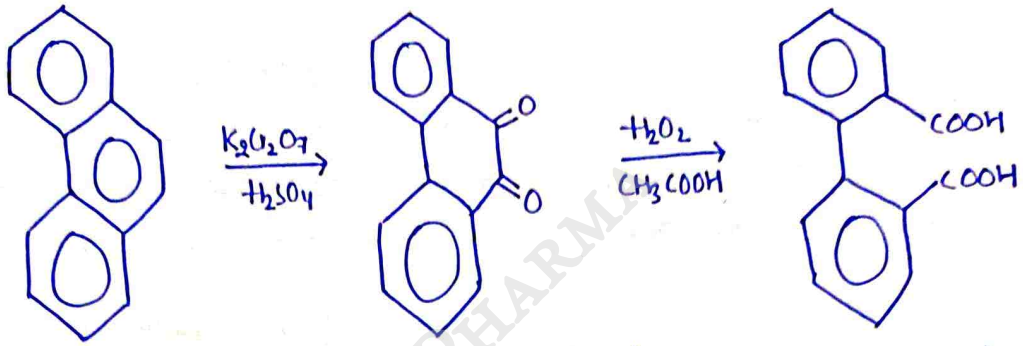
③ Name any two reducing agent

⇒ Lithium, Magnesium

④ Write the oxidation reaction of phenanthrene?

⇒ Phenanthrene undergoes oxidation with potassium dichromate and sulfuric acid in acetic acid to form 9,10-phenanthraquinone

and further oxidation of this with hydrogen peroxide in acetic acid give diphenic acid.



(phenanthrene) (9,10-phenanthraquinone) (Diphenic acid)

⑤ Write the reaction of cyclopropane ? (any one)

⇒ When cyclopropane react with bromine (Br_2) in dark to give 1,3-dibromopropane (CCl_4 used as solvent). [Addition Reaction].

(cyclopropane) (1,3-dibromopropane)

⑥ Name the product formed by friedal craft acylation of benzene

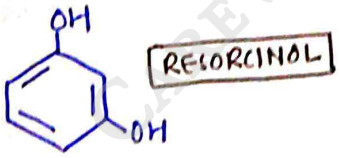
⇒ Acetophenone.

⑦ What is the mechanism of esterification reaction.

⇒ It is the process of combining an organic acid (RCOOH) with an alcohol (ROH) to form an ester. (RCOOR) and water.

(Carboxylic acid) (Alcohol) (Ester)

⑨ Write the use of Resorcinol ?



RESORCINOL

⇉ • Used in manufacturing of resins.
• Used as a disinfectant.

⑩ What is Saponification ?

⇉ The formation of soap and salts from fats and oil (triglycerides) with alkali (NaOH & KOH) is known as saponification.
• The soap is termed as sodium salt of fatty acids.

⑪ What is Ester Value ?

⇉ It is the number of milligram (mg) of KOH required to saponify the ester present in 1gm of the substance

Ester Value = Saponification value - Acid Value

⑫ What is Acid Value ?

⇉ It is used to measure the free fatty acid present in fats and oils. (free fatty acid are harmful for humans).
• Also called as Neutralization number.

⑬ What is Basic of Sachse-Mohr's theory

⇉ This theory explain the stability of cyclohexane and higher cycloalkanes.
Acc. to this, cycloalkanes are not in plane so there is no strain on cycloalkanes.
• Also called as theory of strainless ring.

⑭ Arrange in order of increasing Acidity.

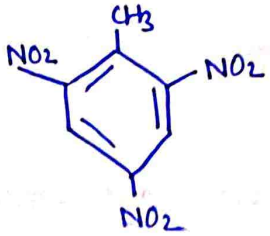
(i) Phenol (ii) 4-Nitrophenol (iii) 2,4-Dinitrophenol (iv) 2,4,6-Trinitrophenol

⇉ Phenol < 4-Nitrophenol < 2,4-Dinitrophenol < 2,4,6-Trinitrophenol

→→ Acidity →→

(15) Name of the product of nitration of toluene?

⇒ 2,4,6-Trinitrotoluene



(16) Name the product of sulphonation of naphthalene under thermal condition.

⇒ Naphthalene on sulphonation under thermal condition give Naphthalene-2-Sulphonic acid.

(17) Name the electrophilic product in nitration reaction of benzene

⇒ In nitration reaction, Nitric acid (HNO_3) dissociate into NO_2^+ and OH^-, and NO_2^+ attached on benzene

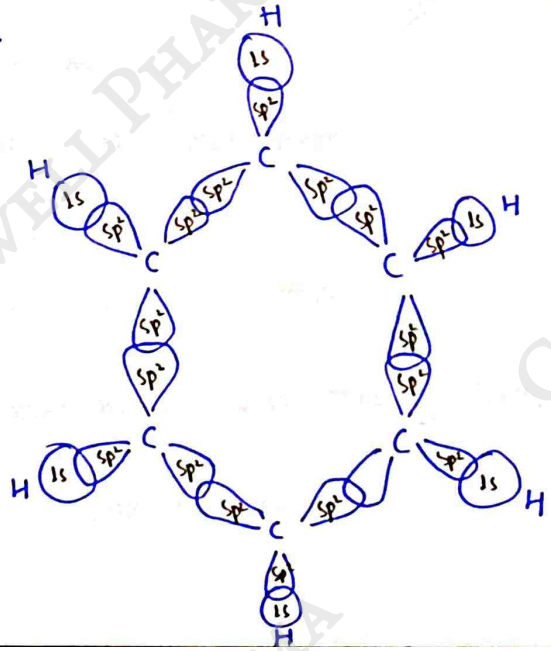
So, Electrophilic produced in nitration reaction of benzene is NO_2^+.

$HNO_3 \longrightarrow NO_2^+ + OH^-$

(18) Give the molecular orbital picture of benzene

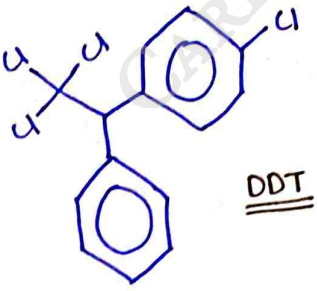
⇒ Mol. formula ⇒ C_6H_6.

Bond Angle ⇒ 120°C



(19) Give structure and uses of DDT

⇒ DDT [Dichlorodiphenyl trichloroethane]



DDT

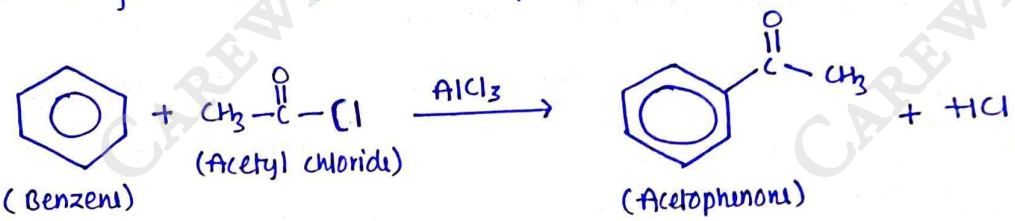
Uses :—

- Used in pesticide control
- Used for control of mosquitoes that spread malaria

(20) What is friedal craft acylation. Explain with suitable reaction.

⇒ It involves the addition of an acyl group to an aromatic ring.

eg. Benzene react with acetyl chloride (CH_3COCl) in the presence of lewis acid catalyst ($AlCl_3$) formed Acetophenone

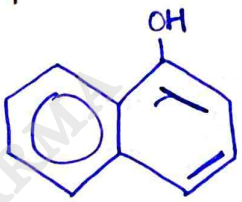


(Benzene) (Acetyl chloride) (Acetophenone)

(21) Give structure and uses of Naphthols.

⇒ Uses :—

- Used as insecticides
- Used in perfumery
- Also used for making dyes.



(Naphthols)

(22) Give Haworth synthesis of phenanthrene

⇒ In 5 marks section

(23) Give stability order of cycloalkanes.

⇒ Cyclohexane > Cyclopentane > Cyclobutane > Cyclopropane.

⟵⟵ STABILITY ⟵⟵

(24) Draw any four aromatic structures.

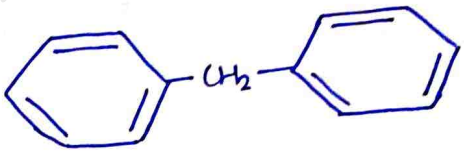
⇒

(Benzene) (Phenol) (Aniline) (Naphthalene)

(25) Give structure and uses of diphenylmethane

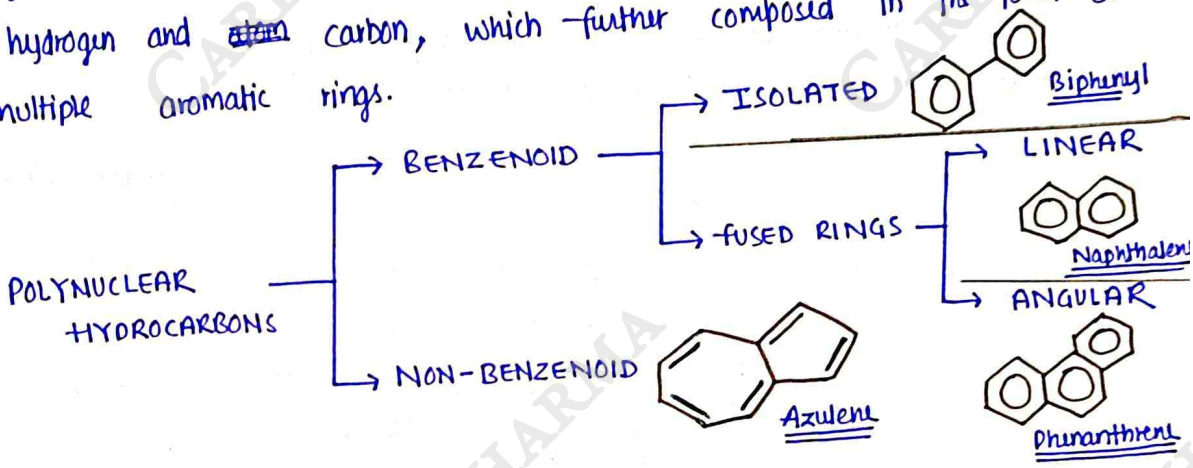
⇒ Uses:-

- Used in the synthesis of methylene diphenyl diisocynate, which is used in the manufacture of polyurethane



(26) Define and classify polynuclear hydrocarbons.

⇒ Polynuclear hydrocarbons are organic compounds which contain only hydrogen and carbon, which further composed in the form of multiple aromatic rings.



(27) Write Huckel's Rule of aromaticity

⇒ That rule which helps in identification of aromatic compound.

$4n+2 = \pi e^-$, where πe = π bond in compound

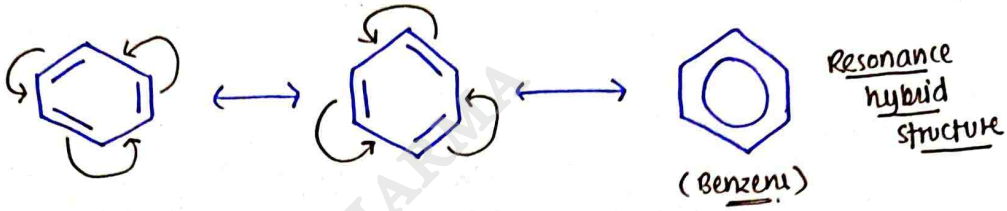
(1 π bond = 2e-)

n = 0, 1, 2, 3, 4 ....

(28) What is Resonance? Give their suitable example

⇒ When a compound can be represented by more than one lewis structure and actual structure is hybrid of all these structure

eg: In Benzene, their are continuously delocalisation of π bond.



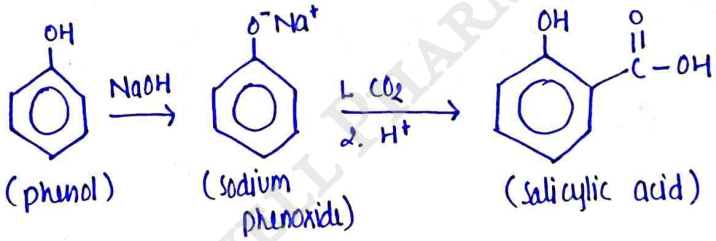
(29) What do you understand by Ring deactivating and Ring activating group.

⇒ Activating group :- Which increase the rate of reaction in electrophilic aromatic substitution reaction, relative to H. eg. OH group.

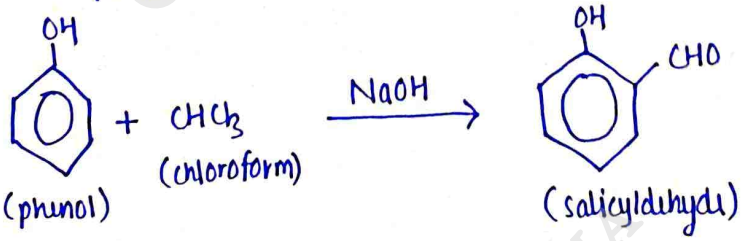
Deactivating group :- Which decrease the rate of reaction in electrophilic aromatic substitution reaction, relative to H. eg. f, Cl etc.

(30) Write reaction :-

i) Kolbe reaction of phenol ⇒ Phenol react with sodium hydroxide to form sodium phenoxide which react with carbon dioxide to form salicylic acid.



ii) Reimer-tiemann reaction ⇒ Phenol is treated with chloroform ($CHCl_3$) in the presence of sodium hydroxide (NaOH), salicyldehyde formed.



Short Answer (5/10 Marks)

Unit-1

Star
Date 15-12-20
Page No.

Q1- Write analytic, synthetic & other evidence in the derivations of structure of Benzene.

Or

Write brief note on structure of benzene [Kekule, Chemical & Resonance].

Ans- Benzene is an organic compound which contain 6 Carbon atom attached with 6 hydrogen atoms.

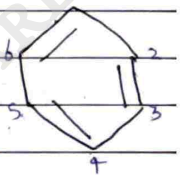
- It contain resonance.

- Structure of Benzene :- There are 3 types :

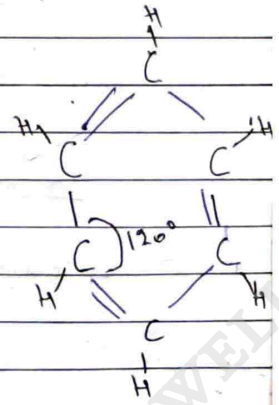
1- Kekule Structure → Benzene is a cyclic compound.

- First carbon is connect with 6 carbon.

- So, benzene is six carbon compound & it follow Huckle rule, so it is aromatic.

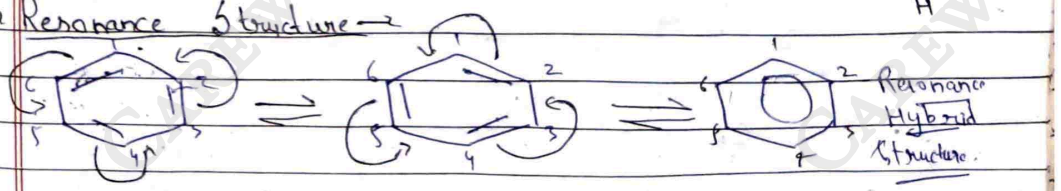


2- Chemical Structure → It contain double bond, π bond & single bond (σ) both.



- Molecular formula → C_6H_6
- Molecular weight → 78
- It have sp^2 hybridisation.
- Bond Angle → 120°
- Bond length → 1.5° A [Carbon to Hydrogen]
  1.3° A [Carbon to Carbon].

3- Resonance Structure →



- Continously delocalisation of π-bond.
- So, it show Resonance hybrid Structure.

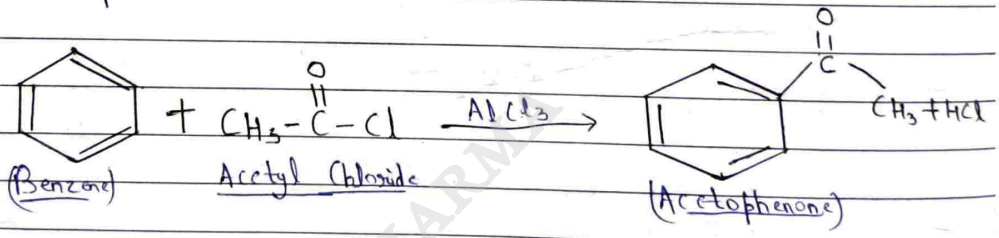
Star
Date
Page No.

Q-2- Write electrophilic substitution rⁿ of benzene?
Or
Write mechanism of friedal craft alkylation or acylation/ Sulphonation?.

Ans-2 Both rⁿ belongs to electrophilic substitution rⁿ of benzene. In both rⁿ hydrogen replaced with an electrophile.

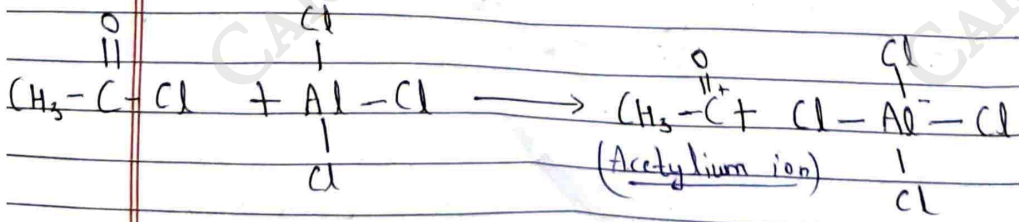
(i) Friedal craft acylation → It involves the addition of an acyl grp to an aromatic ring.

In which benzene react with acetyl chloride (CH_3COCl) in the presence of lewis acid catalyst ($AlCl_3$) anhydrous aluminium chloride which further formed Acetophenone.

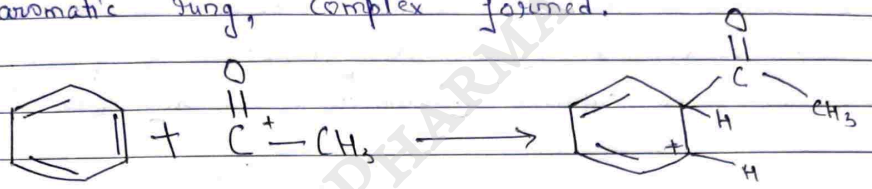


- Mechanism : [Four steps]:

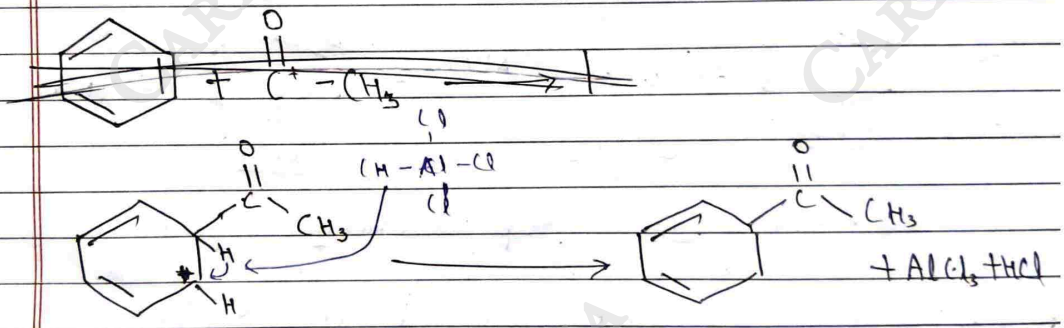
i-2 Rⁿ occur b/w $AlCl_3$ & CH_3COCl, complex is formed & Acetyl Chloride [CH_3COCl] loses its one chloride ion.



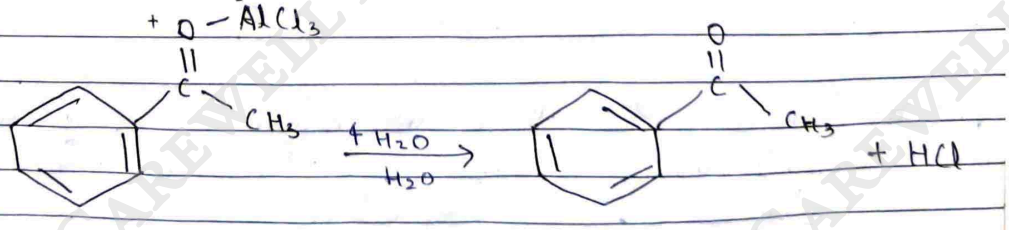
Step ii) Now, Acylium ion [RCO^+] or Acetylium ion [CH_3CO^+] goes on to execute an electrophilic attack on aromatic ring, complex formed.



Step iii) Now, Complex is deprotonated for restoring aromaticity Proton attached with chloride ion [from $AlCl_4^-$ complex] form HCl, & $AlCl_3$ again regenerated.

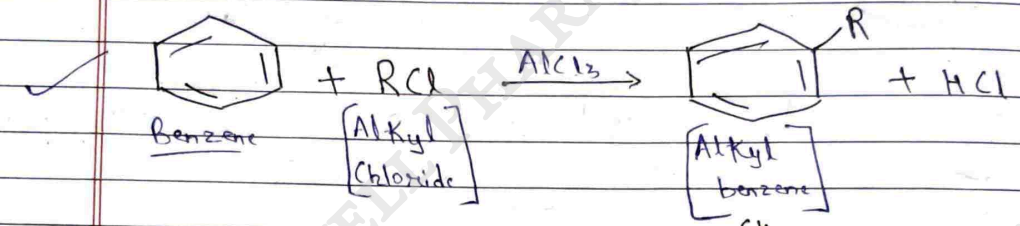


Step iv) Now, regenerated catalyst $AlCl_3$ attacks on carbonyl oxygen, which further liberated by adding water in excess amount.

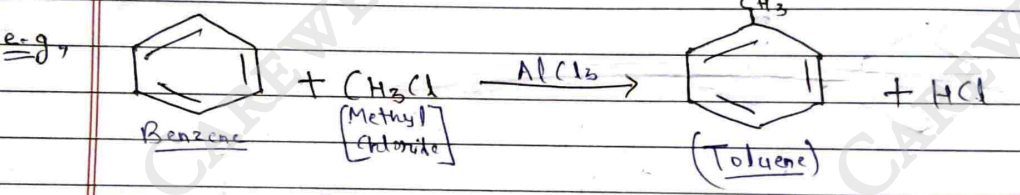


Required Acyl benzene [Acetophenone] product obtained.

(iii) Friedal - Craft Alkylation → It involves the addition of alkyl grp to an aromating proton. In which benzene react with alkyl halides & form alkylbenzenes in presence of Lewis acid catalyst [Aluminium chloride] $AlCl_3$

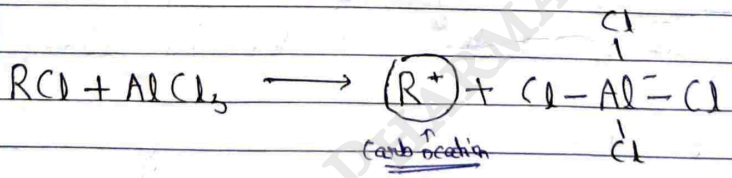


e.g.,

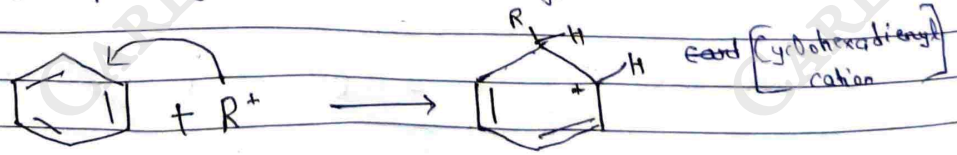


- Mechanism → [Three step mechanism] :

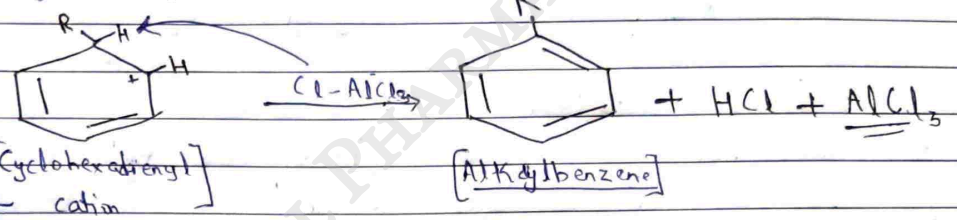
Step 1 → $AlCl_3$ react with alkyl chloride, resulting formation of an electrophilic carbocation.



Step 2 → Carbocation R^+ attack an aromatic ring, forming cyclohexadienyl cation as intermediate complex [temporary lost aromaticity].



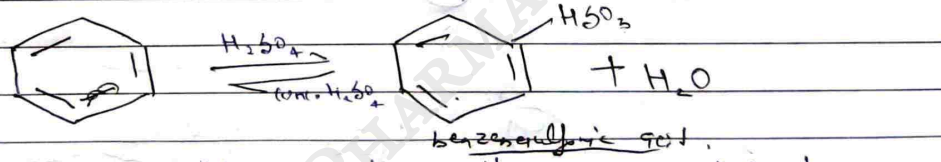
Step 3 → The complex deprotonated for restoring aromaticity, Proton goes on to form hydrochloric acid, regenerating the $AlCl_3$ catalyst.



[Cyclohexadienyl cation] [Alkylbenzene]

- Required [Alkylbenzene] (toluene) product obtained & HCl & $AlCl_3$ formed.

(iii) Sulphonation of Benzene → It belong to electrophilic substitution of benzene, In which, benzene react with H_2SO_4 [Sulphuric acid] in the presence of conc. H_2SO_4, it formed benzenesulfonic acid.

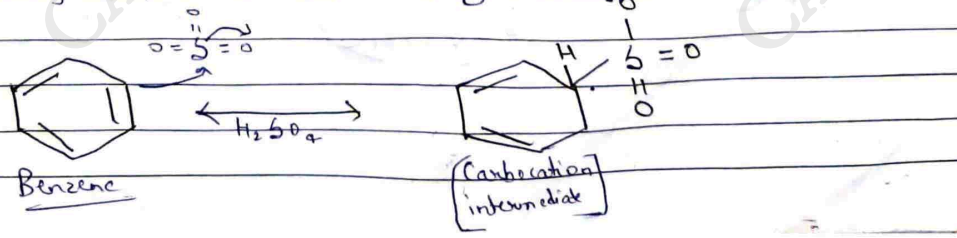


benzenesulfonic acid.

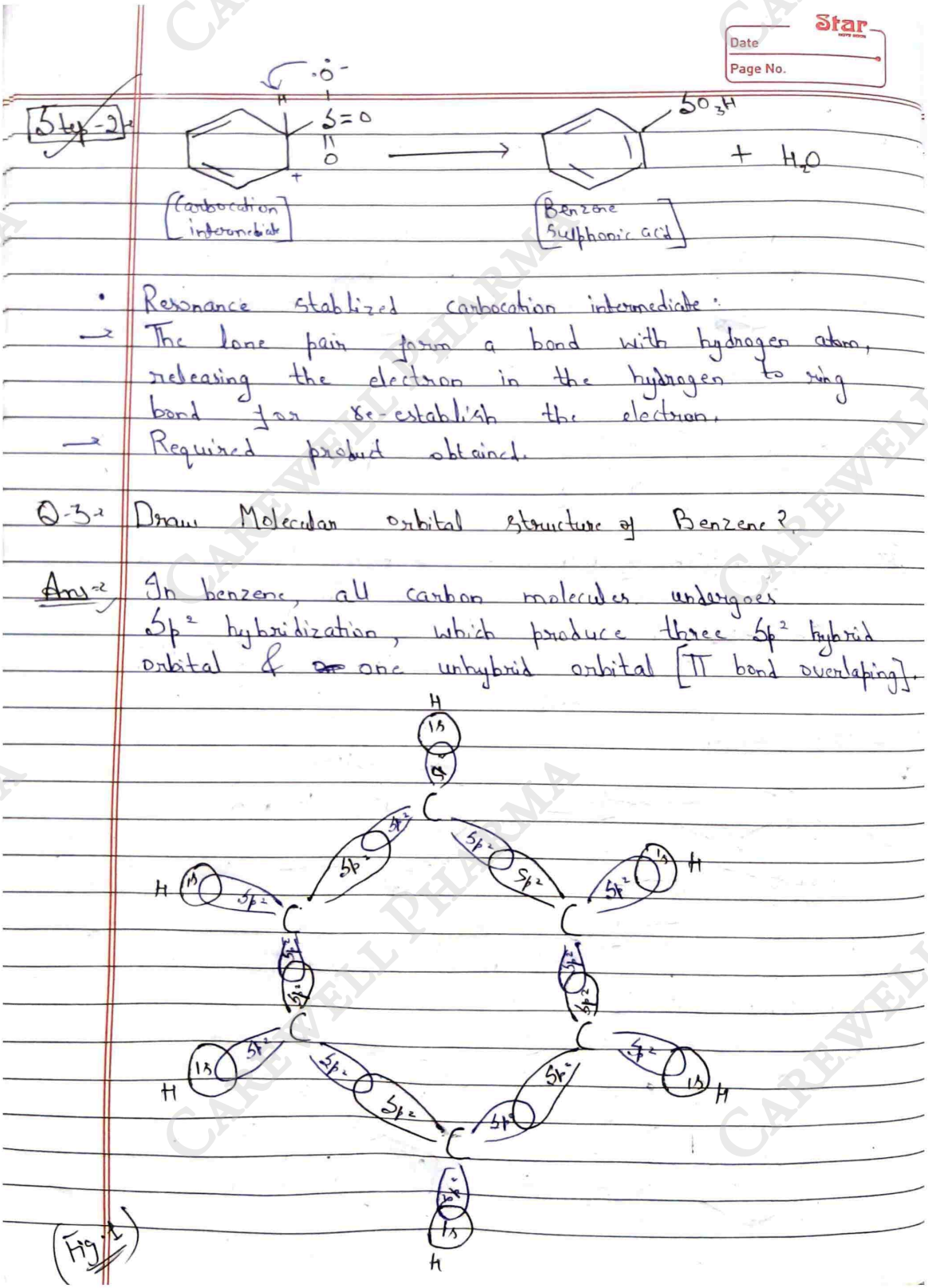
It is reversible reaction, it forms which benzene is heated with fuming Sulphuric acid or concentrated Sulphuric acid, it yield benzenesulphonic acid.

- Mechanism → 2 steps.

Step 1 → In which, carbocation formed in benzene, SO_3 attached with benzene.



Benzene [Carbocation intermediate]



• Resonance stablized carbocation intermediate :

→ The lone pair form a bond with hydrogen atom, releasing the electron in the hydrogen to ring bond for re-establish the electron.

→ Required product obtained.

Q-3- Draw Molecular orbital structure of Benzene ?

Ans- In benzene, all carbon molecules undergoes Sp^2 hybridization, which produce three Sp^2 hybrid orbital & one unhybrid orbital [π bond overlaping].

(Fig. 1)

→ sp^2 hybrid orbital overlap with sp^2 hybrid orbital of adjacent C atom to form σ bond (sigma) & remaining one sp^2 hybrid orbital of each carbon atom are overlap with its atomic orbital of H-bond to form C-H bond (sigma) ~~of each~~ (See in fig. 1)

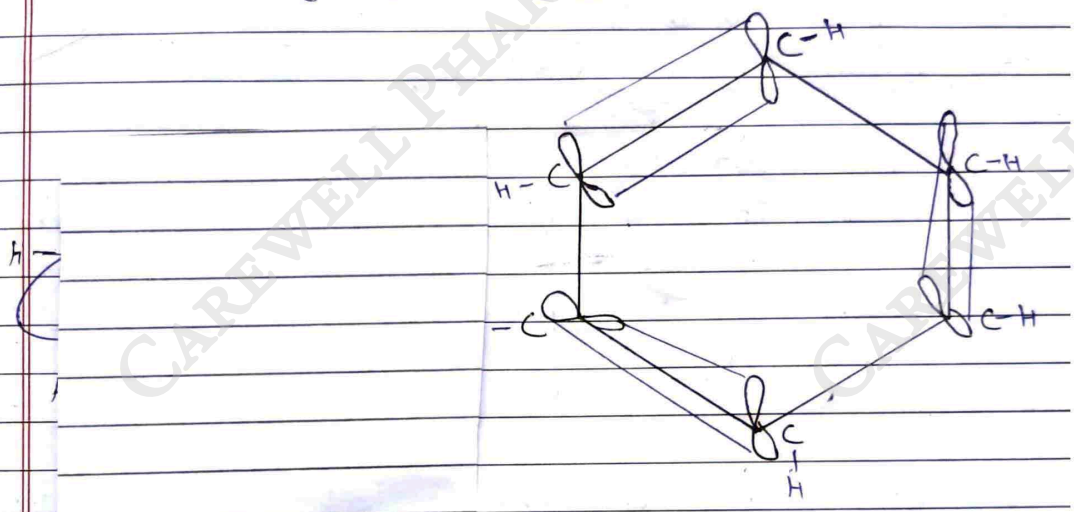
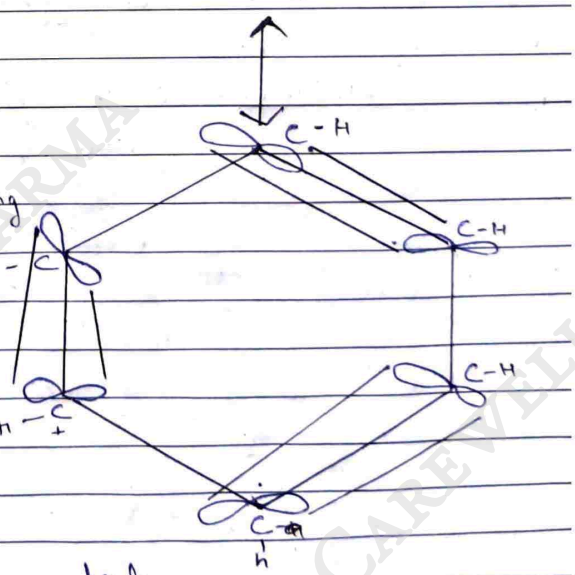


Fig. 2

→ Each carbon atom containing one unhybrid orbital, which overlap with unhybrid orbital of adjacent carbon atom [side ways overlaping] to form π-bond.
(See fig. 2)



→ These ~~are~~ is our complete molecular orbital of benzene.

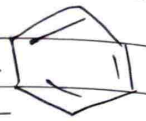
Q-4 Huckel's rule of Aromaticity.

Ans = That rule which helps in identification of Aromatic Compounds, or Aromatic compounds are those which follow huckel rule.

→ It should be cyclic

→ Compound should be in conjugation. (resonance).

→ Huckle rule ⇒ $4n + 2 = \pi e$



$4n + 2 = 6$

$4n = 6 - 2$

$n = \frac{4}{4}$

$n = 1$

Where,

πe = π bond in compound (1π bond = $2e^-$)

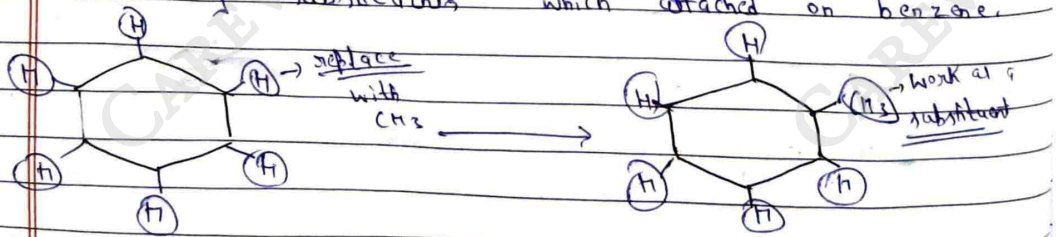
n = integer no. 0, 1, 2, 3...

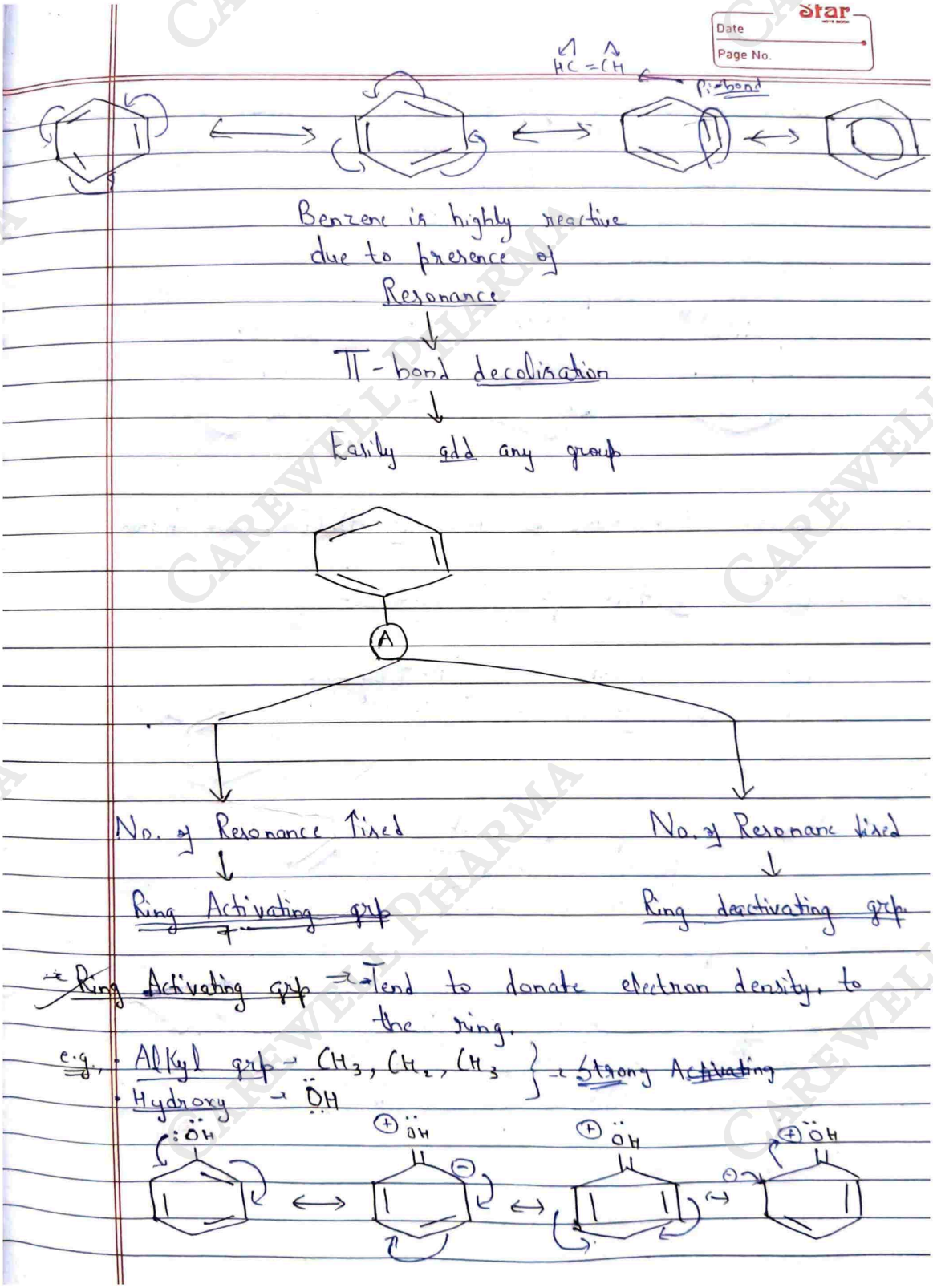
Q-5 Write a note on effect of Substituent on reactivity of benzene?

Ans = Substituent → In benzene ring, when any grp replace H-atom & attached himself at this place. this process is known as Substituent.

→ Benzene is highly reactive ring due to presence of resonance [π bond delocalisation] & more active (stable).

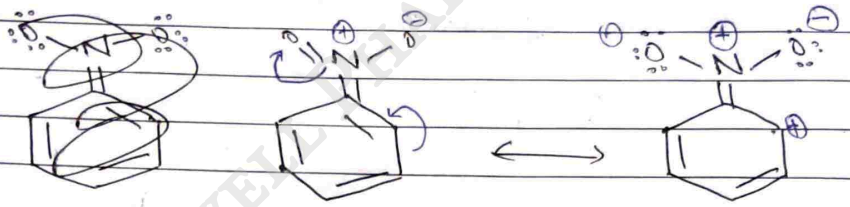
→ When any substitution attached on the ring it change the activity of the ring & this is depend on the nature of substituents which attached on benzene.





Ring deactivating grp → Tend to withdraw electron density to the ring.

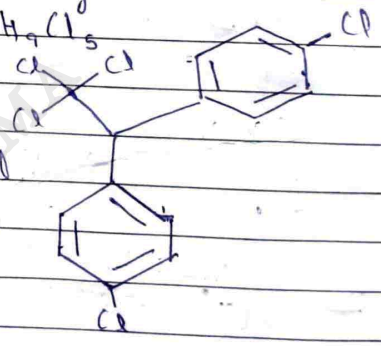
e.g., Halogens → :Cl:, :F:
Nitro → NO_2
→ Strong deactivating



Q-6 → Write structure & uses of DDT, Saccharin.

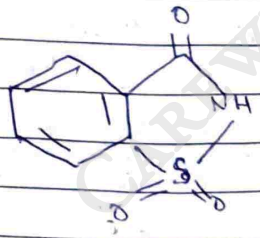
Ans-6 → DDT → [Dichlorodiphenyltrichloroethane]

Molecular weight → 354.48 g mol⁻¹
Molecular formula → $C_{14}H_9Cl_5$



Uses:
→ It's used in pesticide control
→ In some place it is used for the control of mosquitoes that spread malaria.

Saccharin → [Benzoic Sulfimide]
Molecular formula → $C_7H_5NO_3S$
Molecular weight → 183.18 g/mol.



→ It is used for an artificial sweatner, with no food energy. So, it is very helpful for diabitics patients.

→ It's about 300 to 400 sweat as sucrose & 600 times more than sugar.

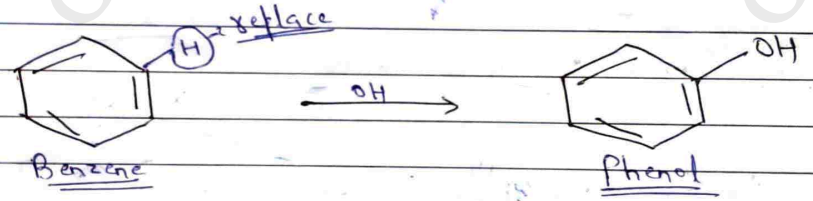
→ Used in Colldrinks, Cookies, Medicines etc.

Unit-2

- Phenols

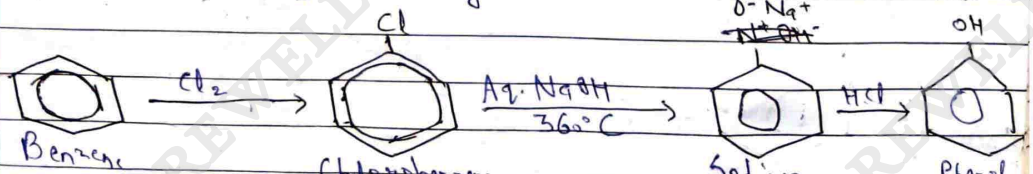
Q1→ Describe in details the synthesis & chemical rⁿ of Phenol. → (10)

Ans→ Phenol is an aromatic organic compounds in which one hydroxyl group [-OH] replace one-hydrogen in Benzene.

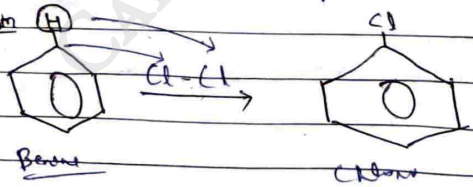


- Synthesis [method of prep^{n} of Phenols]:

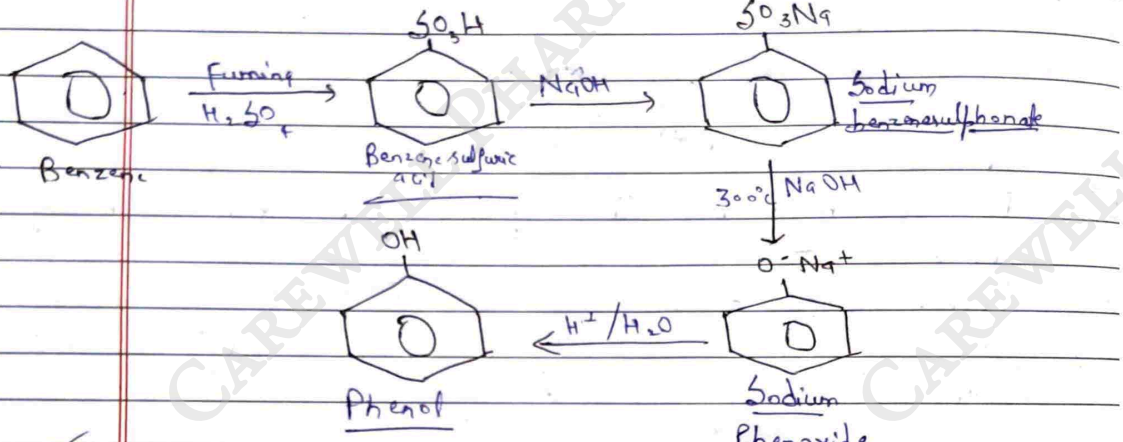
Dows process / Chlorobenzene → This involves the hydrolysis of chlorobenzene with aq. NaOH at high temp. & pressure followed by treatment with dilute HCl.



Mechanism

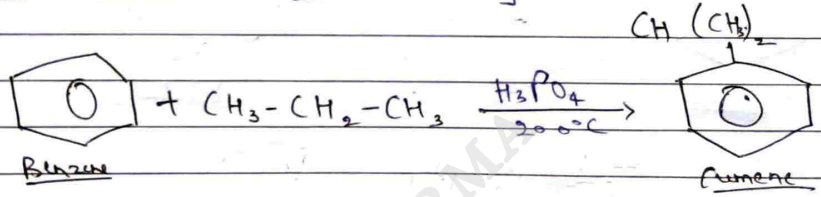


2. From Sodium Benzenesulphonate → This involves fusion of Sodium benzenesulphonate with solid NaOH at 300°C followed by treatment with dilute HCl.



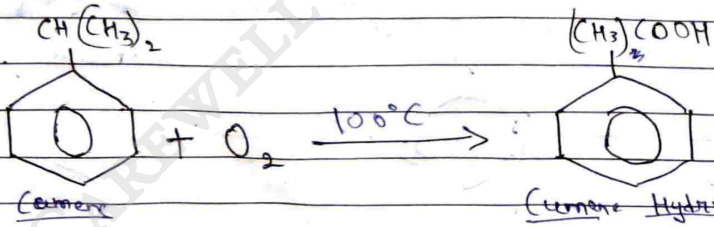
3. From Cumene : [Cumene Process] :

Step 1 →

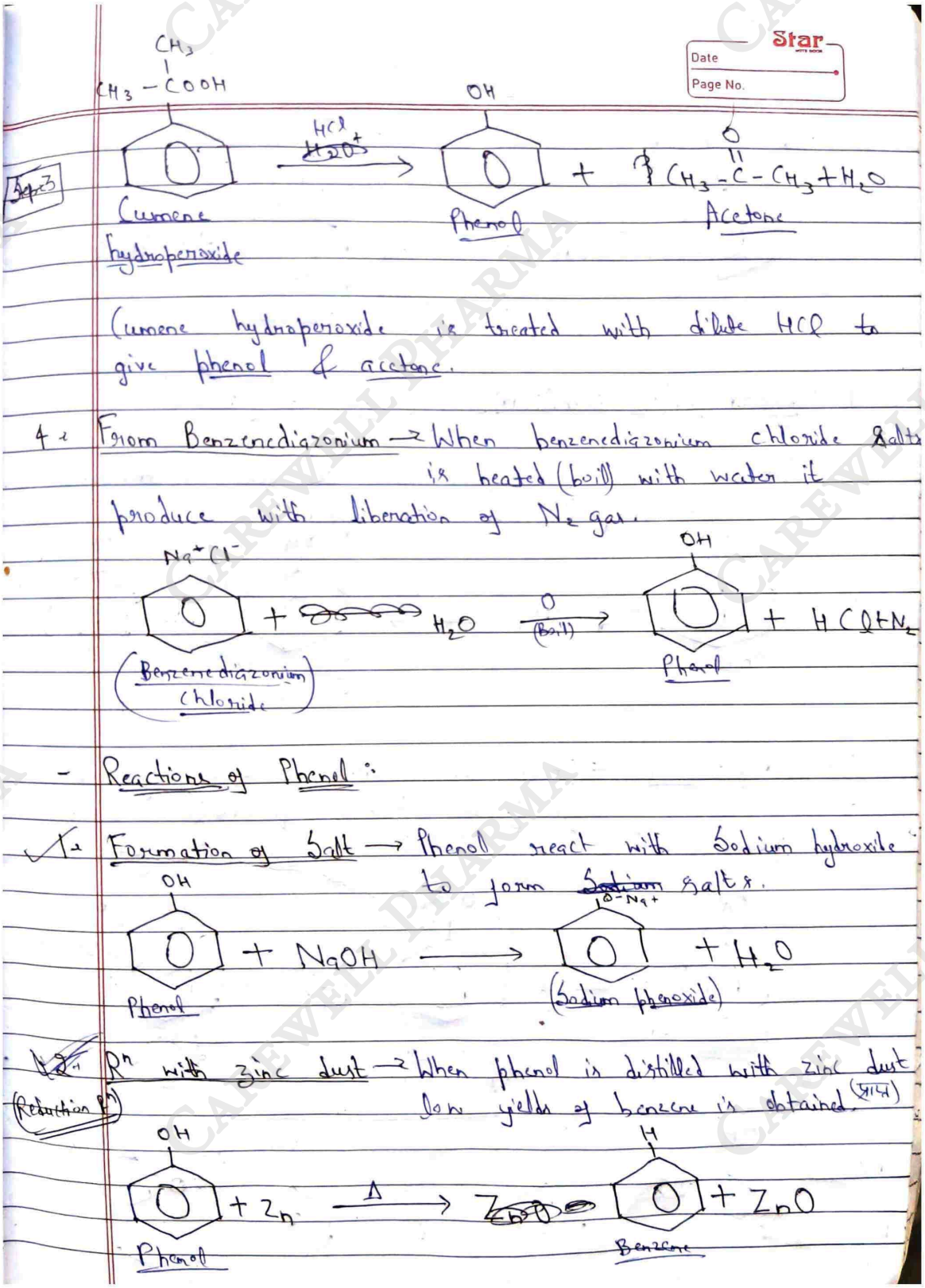


Benzene is treated with propane in the presence of H_3PO_4 [Phosphoric acid] to form Cumene.

Step 2 →

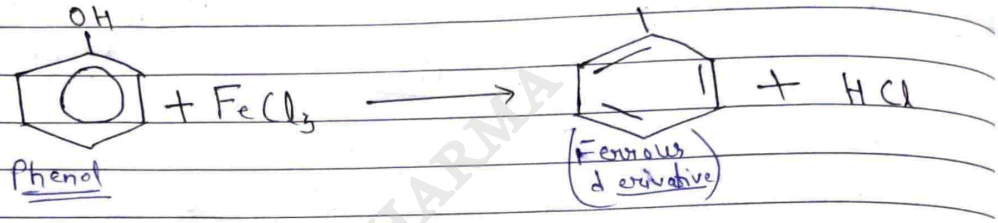


Cumene is oxidized using air to form Cumene hydroperoxide.



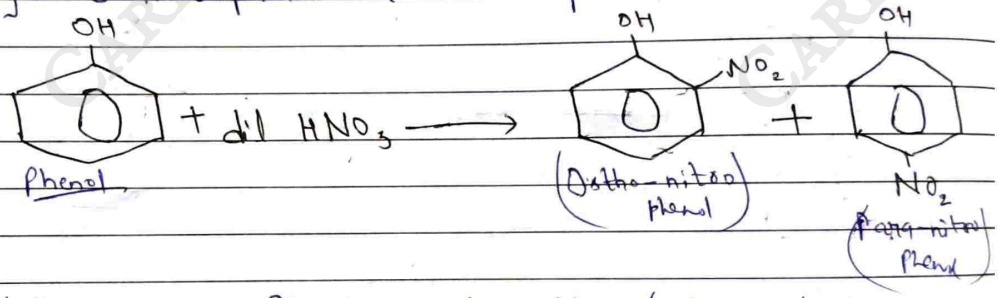
Star
Date
Page No.

3. Rn with $FeCl_3$ → Phenol react with ferric chloride to give intermediate derivatives.

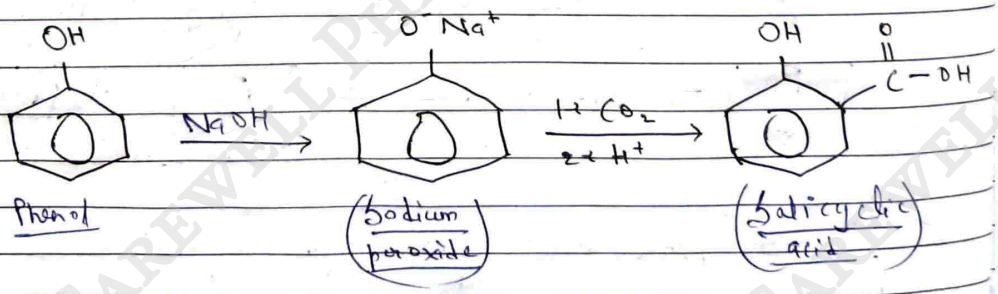


4. Electrophilic Substitution rn [Nitration]:

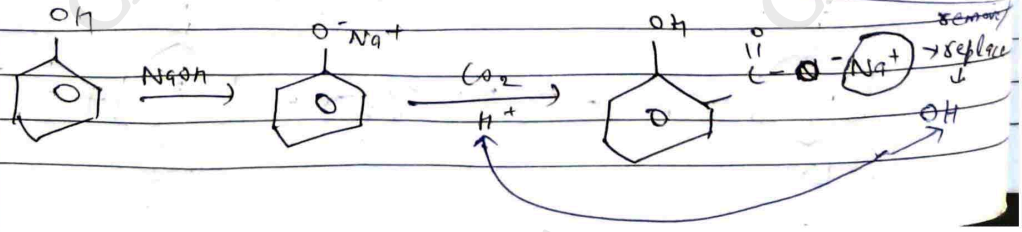
Phenol react with dil. HNO_3 to give a mixture of O-nitrophenol & P-nitrophenol.



5. Kolbe's rn → Phenol react with Sodium hydroxide to form Sodium phenoxide, which react with Carbon dioxide to form Salicylic acid.



Mechanism

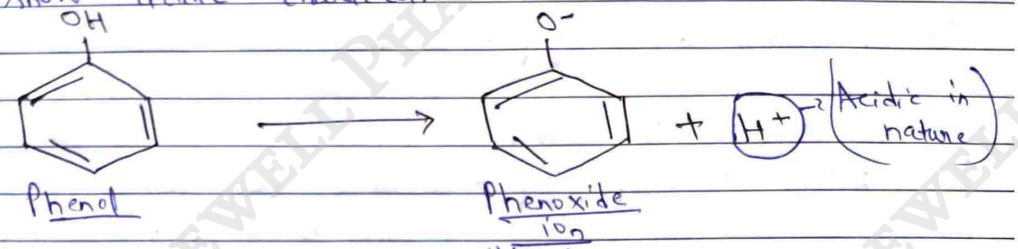


Q-2) Discuss about the Acidity of Phenol?

OH

Why Phenol is acidic in nature & What's the effect of substituent on acidity of Phenol?

Ans:- When any compound dissociated into H^+ ion. Then it show acidic character.



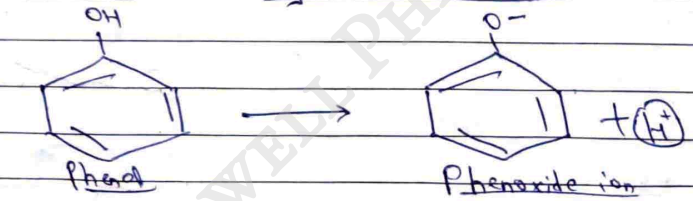
So, When phenol dissociated it break into two in which one is H^+. So, phenol acidic in nature.

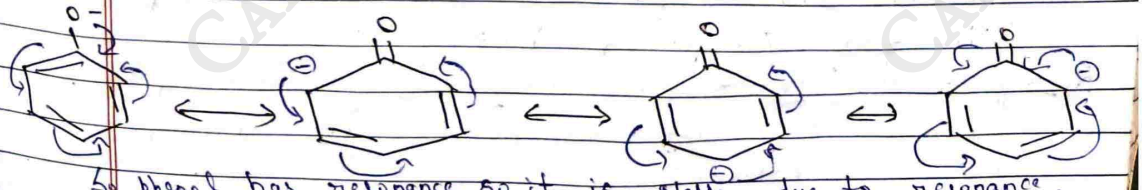
→ The compound which release H^+ more or quick have more acidic.

→ The compound which is more stable after release of H^+ has more acidic.

→ The condition, which show acidity or stability is
- Resonance
- I-character.

- Resonance: After dissociation





So, phenol has resonance, so it is stable due to resonance, So, it's Acidic in nature.

Star
Date
Page No.

• Percentage of s- Character:

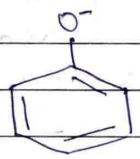
So, Phenol has 3 sigma (σ) bond, So it has sp^2 hybridization
In which, % s-character is = 33.33%.
This is acidic more than alcohol.

• Effect of substituent on Acidity of Phenol: There are two types of substituent [group] which will add or attached on phenol.

1) Electron donate grp → In which, has ability to donate electron.
e.g., CH_3, Cl, OH etc.

2) Electron accept grp → In which has ability to accept [gain] electron.
e.g., NO_2, NH_2 etc.

- After dissociation:



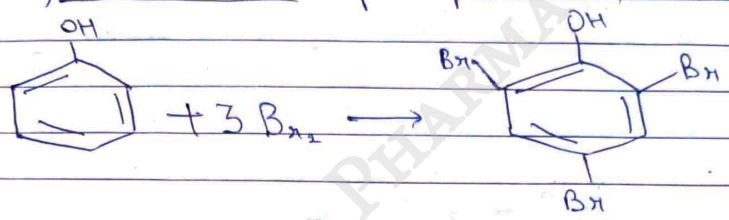
Electron donate → It electron density Increased → Unstable → Acidity decreased

Electron accept → It electron density increased → Stable Increased → Acidity Increased

Q-3 → Discuss various qualitative test to detect phenols in given sample & chemical rxn.

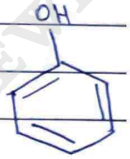
Ans → Litmus Test → Phenol turns blue litmus paper into red, this show that phenol acidic in nature.

2→ Bromine Water Test → Take aq. soln of phenol & add excess of bromine water.
A yellowish white precipitate is obtained.



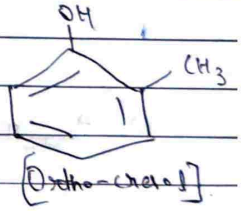
(2,4,6-tribromophenol)

Q.4→ Write structures & uses of Phenol, Cresol:



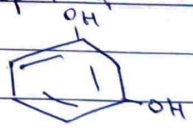
Ans → Phenol → Uses:
→ Use as raw material for drug such as Aspirin, Salol.
→ Used in preservatives, antiseptic [Dettol] etc.
→ Earlier it was used as soap, known as [Carbolic soap].

Cresol: Uses:
→ They are strong germicides, so they are used in disinfectant & antiseptics in low conc.
→ Use as Wood preservatives.
→ Use as making photographic developer & explosives.



(Ortho-cresol)

3. Resorcinol: → Used in manufacturing of resins.



→ It's topical used to treat acne, eczema, & other skin disorders.
→ Used as a disinfectants or an antiseptic in p'ceutical products.
→ Used in hair dyes.

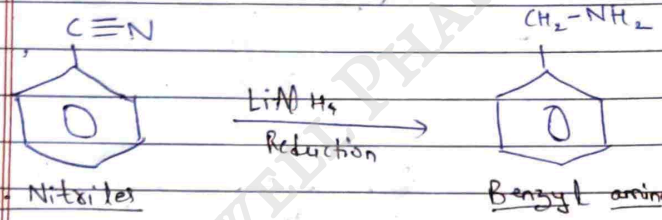
Star
Date
Page No.

Aromatic amines :

Q1 → Write all the method of prep [Synthesis] & chemical rⁿ of Aromatic amines.

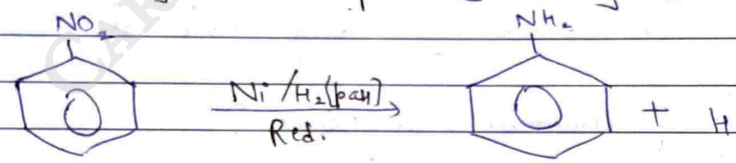
Ans → Method of Prep :

1 → Reduction of Nitriles : [Removal of O_2 & Addition of H_2]



Ar- Nitriles — Benzyl amine

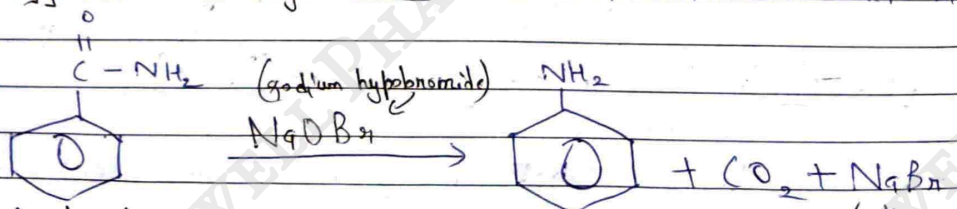
2 → Reduction of Nitro compound : [Removal of O_2 & Add. of H_2]



Nitrobenzene — Aniline

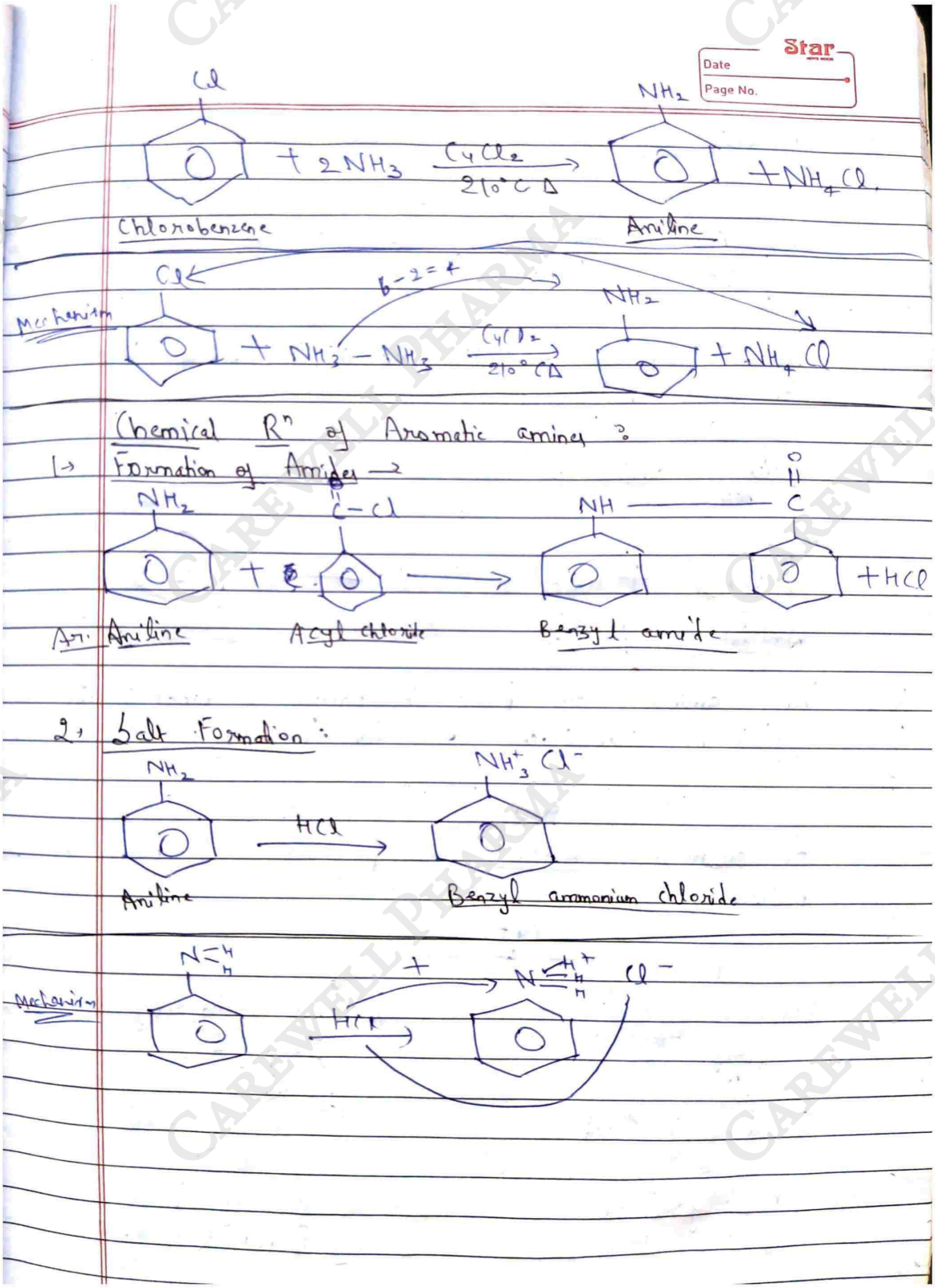
When nitrobenzene is react with H_2 in the presence of catalyst Ni it gives Aniline.

3 → Hoffmann Rearrangement Rⁿ : ~~When Acetamide is react with~~

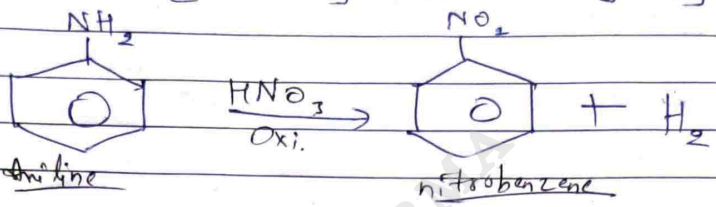


Acetamide — Aniline — Sodium bromide

4 → By Ammonolysis of Chlorobenzene :- When chlorobenzene undergoes [react with ammonia] in the presence of copper chloride at high temp. it gives aniline.

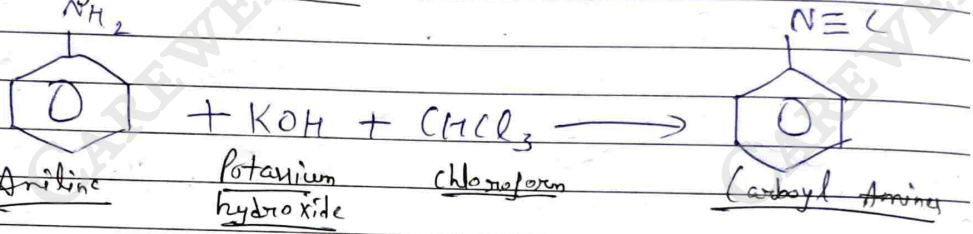


3- Oxidation → [Removal of H_2 & Add. of O_2]



Aniline undergoes oxidation in the presence of HNO_3 to gives Nitrobenzene.

4- Carbyl amine rn →



Q-2- Why amines are basic in nature & what is the effect of substituents on its basicity.

Ans=

So, Ammonia contain lone pair so it is basic in nature.

NH_3

Electron releasing group (I^+)
↓↓
E^- density ↑ised
↓
Basicity ↑ised
e.g., CH_3, CH_2 etc.

Electron withdrawing group [I^-]
↓↓
E^- density ↓ised
↓
Basicity ↓ised
e.g., $R-\ddot{N}H_2 < R-\ddot{N}H-R$ < $R-\ddot{N}-R$ (R')

Star
Date
Page No.

- Effect of substituent on its Basicity :- → In aromatic amines, benzene has resonance so, it is less basic but it is more stable.

Stability ↑ised ⟶ Acidity ↑ised ⟶ Basicity ↓ised

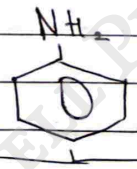
Substitute → Stability ↑ised ⟶ Basicity ↓ised.
Substitute → Stability ↓ised ⟶ Basicity ↑ised.

- Electron donating group → In this group, attached with aromatic amines as a substituent it ↑ised the electron density, which further ↑ised the basicity.

e.g. CH_3, C_2H_5

- Electron withdrawing group → In this group, attached with aromatic amines as a substituent it ↓ised the electron density, which further ↓ised the basicity.

e.g. Cl, Br, F, OH etc.



Electron donating grp
↓
Density ↑ised
↓
Stability ↓ised
&
Basicity ↑ised

Electron withdrawing grp
↓
Density ↓ised
↓
Stability ↑ised
↓
Basicity ↓ised.

Q-3:- Describe in details the synthesis & rxn of aryl diazonium salts?

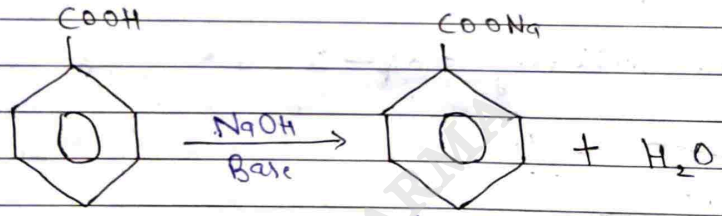
Aromatic Acids:

Q-1:- Describe in details chemical reaction of Benzoic acid [Aromatic acids].

Ans:- In which, we formed other compounds, with the help of benzoic acid.

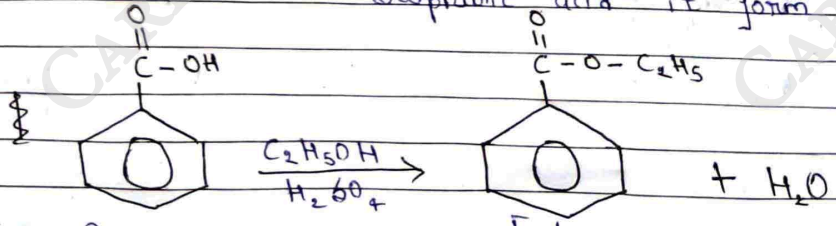
① :- **Sodium Benzoate Salt formation:**

When benzoic acid, react with any base it form salts, react with NaOH.



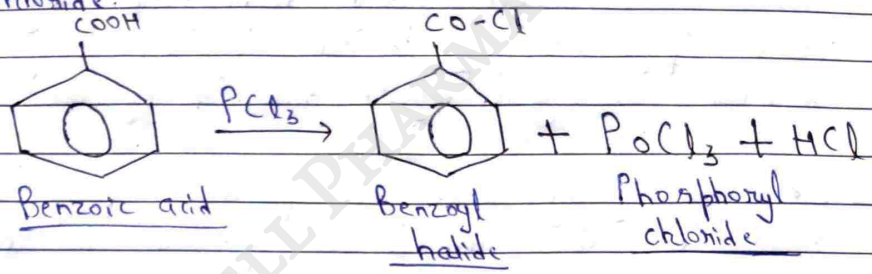
Benzoic acid — Sodium Benzoate / salt

② :- **Ester formation** :- It reacts with alcohols, in the presence of concentrated Sulphuric acid it form ester.



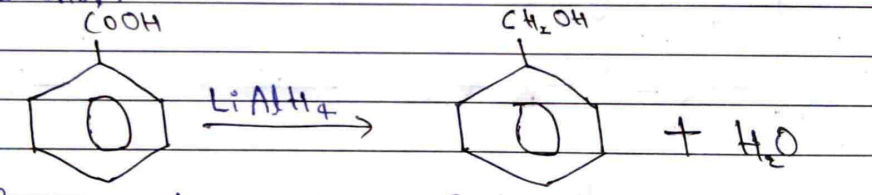
Benzoic acid — Ester

③ → Formation of Acyl Halids → When it react with phosphorus pentachloride it form benzoyl halides & give phosphoryl chloride.



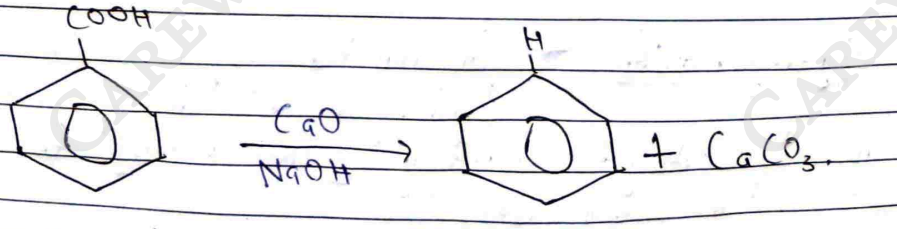
Benzoic acid — Benzoyl halide — Phosphoryl chloride

④ → Reduction to Benzyl chloride → When it react with Lithium aluminium hybride & undergoes reduction it give Benzyl alcohol.



Benzoic acid — Benzyl alcohol

⑤ → Decarboxylation → When it react with Calcium oxide in the presence of NaOH then after decarboxylation it give benzene & release $CaCO_3$.



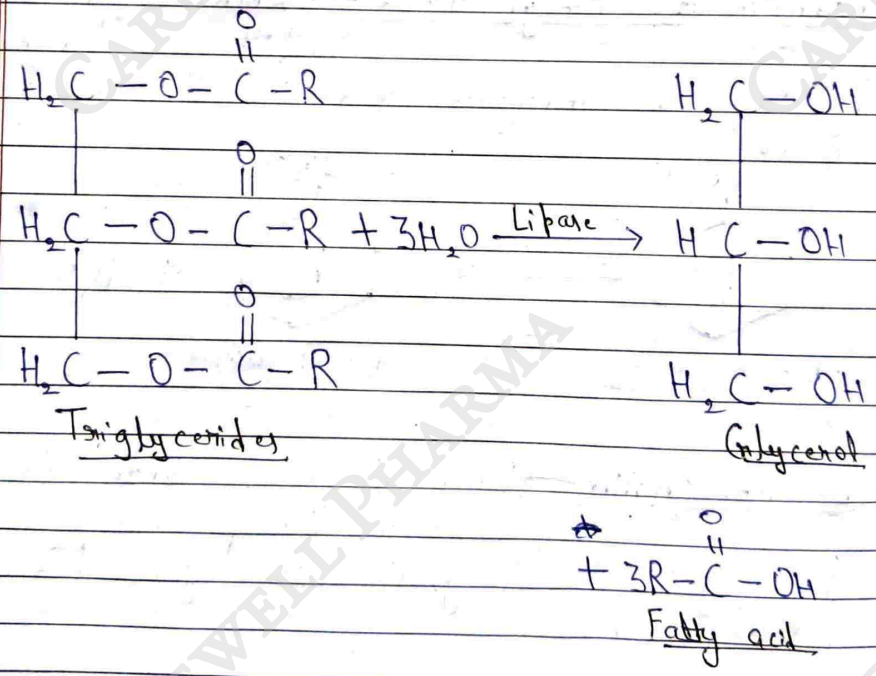
Benzoic acid — Benzene

Unit-3

Q-1 → Write reaction of fats & Oils.

- **Hydrolysis** → In this, triglycerides [tri-ester] are easily hydrolysed by enzymes called lipase [catalyst] in the digestive tract of animals to give fatty acid & glycerol.

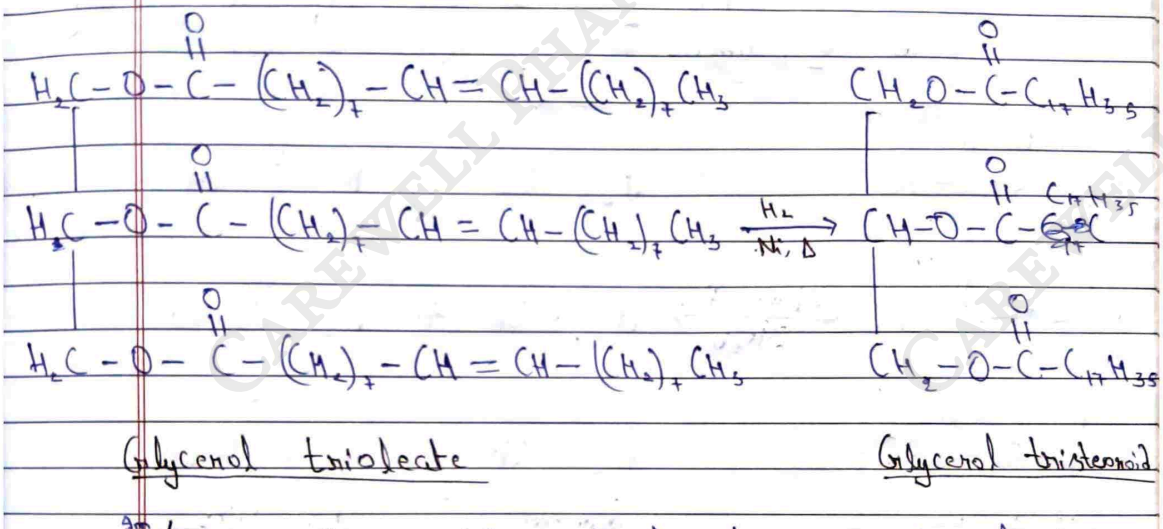
So, the fatty acids are produced play an imp. role in the metabolic process in the animals body.



- **Hydrogenation** → Unsaturated glycerides react with hydrogen in the presence of a metal catalyst usually [nickel nickel] to give saturated glycerides.

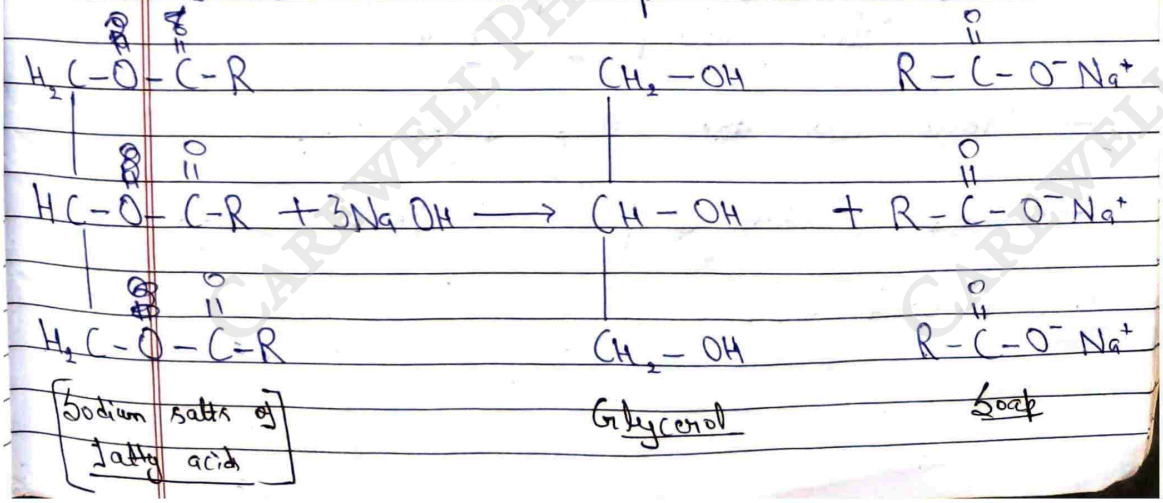
Star
Date
Page No.

Vegetables oils are triglycerides of unsaturated fatty acids such as oleic acid & after reaction it form saturated glycerides with in solid form.



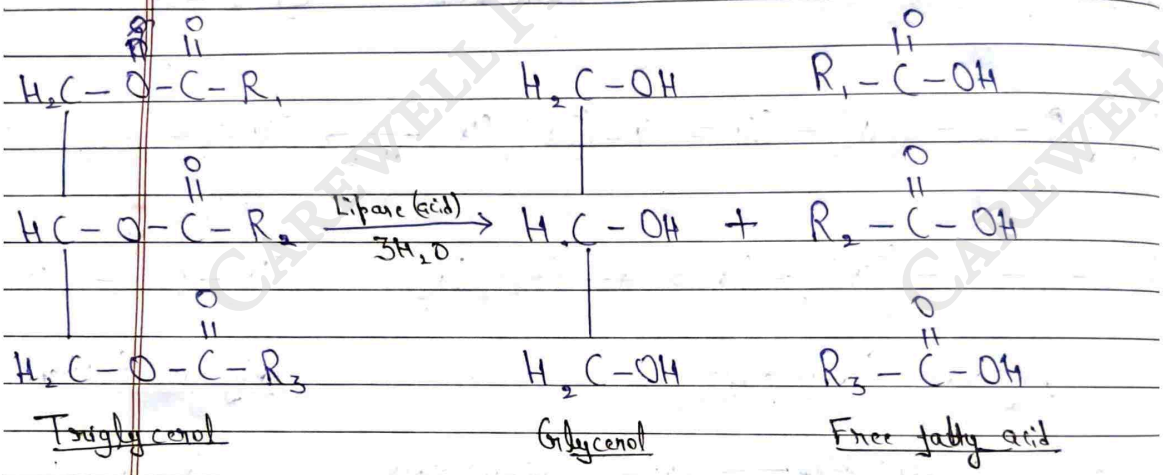
Glycerol trioleate — Glycerol tristearoid

- **Saponification** → When triglycerides are hydrolysed [saponified] by alkalis [NaOH] Glycerol & salts of fatty acids are produced & these Sodium & potassium salts which are obtained termed as soap.



Sodium salts of fatty acid — Glycerol — Soap

- **Rancidity of Oil** → It is also known as Rancidification. When fats & oils are left exposed to moist, air, they develop foul smell & sour taste.
It occured when fats & oils exposed for any length of time.

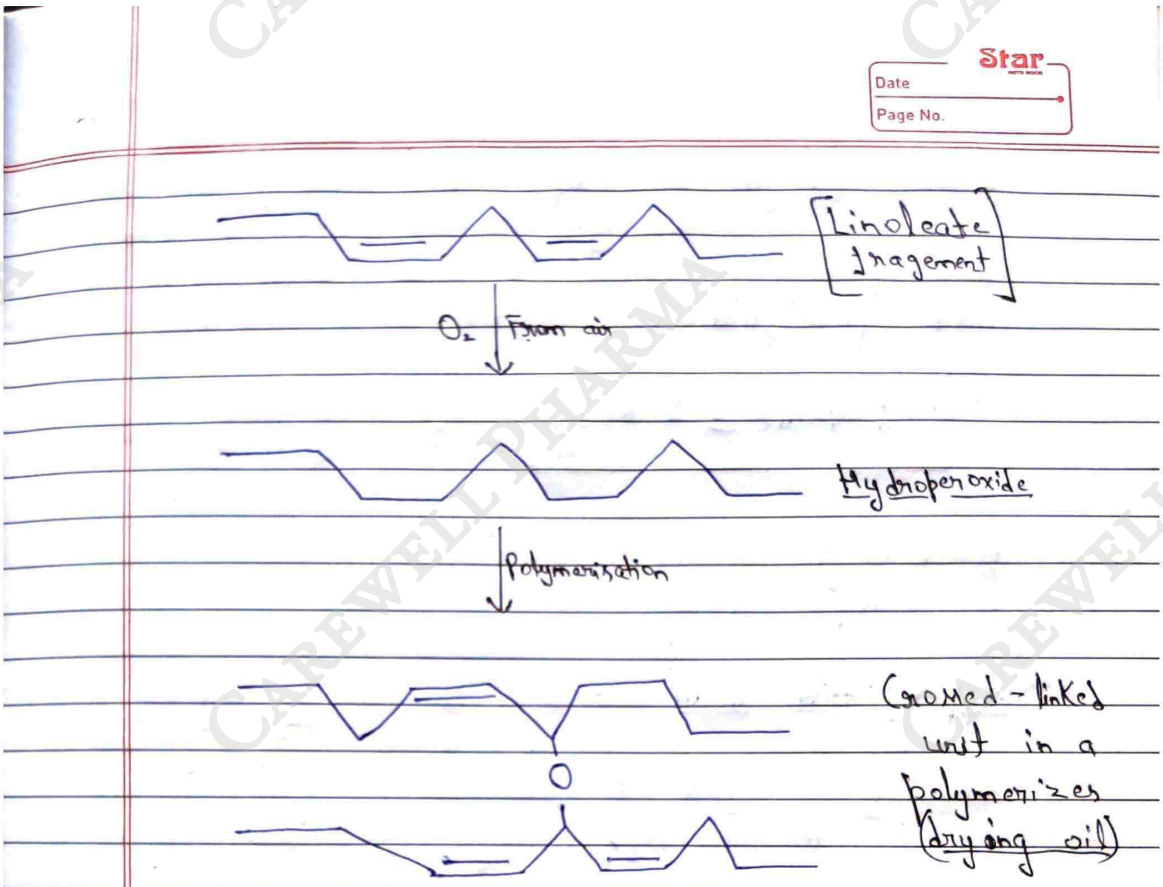


- **Drying Oil** → When highly unsaturated oil are exposed to air, they undergo oxidation & polymerization to form a thin waterproof film.

→ These oils are called drying oil.

→ And reaction & procen is known as drying oil.

e.g., Linseed oil.



Q-2: Write different methods of analysis of fats & oils.

- **Acid Value** → It is also known as Neutrilization no.
  → It's used to measure the free fatty acid present in fats & oils.
  → And free fatty acids in fats & oils are harmful for human body.
  - **Principle** → It's determined by directly titrating the oil/fat in an alcoholic hydroxide solution.

Dissolve 10 gm of sample in 50ml of mixtures of equal volume of ethanol [95%] & ether, then previously neutralised with 0.1M KOH. & add phenolphthalein solution as a indicator.

$$\text{Acid Value} = 5.61 \frac{n}{w}$$

Where, n = Burette reading
w = Sample weight

- Saponification Value → It's the no. of mg of KOH required to saponify one gram of a fats & oils.
→ It is measure of average molecular weight of the fatty acids presents.

- Principle → It is the process by which the fatty acids in the triglycerides or fats are hydrolysed by an alkali to give glycerol & potassium / salts of fatty acids.

→ A known quantity of fats & oil is refluxed with an excess amount of alc. KOH.
→ After saponification, it titrate against a standard acid
→ Sample is titrated with 0.5M HCl.
→ Perform blank titration.
→ The value obtained is used for the determination of saponification value of fats & oils.

→ Phenolphthalein solution used as a indicator.

$$\text{Saponification value} = \frac{28.05}{W}$$

Where, W = weight of sample.

- **Ester Value** → It's the no. of mg of KOH required to saponify the ester present in 1 gm of the substance.

$$\text{Ester Value} = \text{Saponification value} - \text{Acid value}$$

- **Principle** → It is determined by titrated the sample of oil & fat in an alcoholic medium against 0.5M HCl.

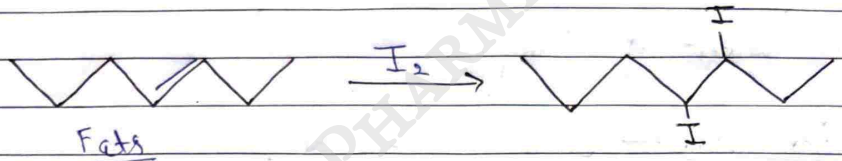
- **Methods:**

→ Weight accurately about 2g of sample. Add 25ml of 0.5M ethanoic KOH.
→ And boiled under reflux condenser on a water bath for 1 hour.
→ Then, add 2ml of water in it.
→ Then, titrate the excess of alkali with 0.5M HCl using a further 0.2ml of phenolphthalein indicator.
→ Repeat the operation without sample.
→ The difference b/w the titrations represents the alkali required to saponify the esters.

Star
Date
Page No.

v.Imp.

Iodine Value → It's the no. of grams of iodine that would add to C=C present in 100g of the fats & oil.



– **Principle :-**

→ The oil/fat sample taken in carbontetrachloride is treated with a known excess of iodine monochloride solution in glacial acetic acid.

→ The excess of iodine monochloride is treated with potassium iodine.

→ Now, this sample is titrate against 0.1M Sodium thiosulphate solution, starch solution used as a indicator for estimation of librated iodine.

→ Then perform a blank titration.

$$\text{Iodine Value} = \frac{1.269}{\text{wt}}$$

• **Acetyl Value** → It's the gram of KOH required to acetic acid librated by the hydrolysis of 1gm of the acetylated substance.

– **Principle** → It is determined through saponification value.

→ Boil the 1gm of sample with 2ml of acetic anhydride for 2 hours.
→ Add 60ml water & boils for 30min.
→ Separate & wash the acetylated product
→ Determined the saponification value of the acetylated substance.
→ Determined the saponification value of the substance.

$$\text{Acetyl Value} = \frac{1335}{1335}$$

- **Reichert-Meissl Value. [RM-Value]:**

→ It is useful in testing the purity of butter, since it contains a good conc. of Volatile fatty acids.

- **Volatile fatty acid** → So, it is defined as the vol of 0.1N KOH required to completely neutralize the volatile fatty acid distilled from 5gm fat.

– **Principle:**

→ Fats is saponified using glycerol – alkali solution & acidified by sulphuric acid to librate free fatty acid.
→ The liberated fatty acids are steam distilled & the steam volatile fatty acids are collected as condensate

→ The cooled condensate of the volatile fatty acids is filtered for separation of water soluble & water insoluble fatty acids.

→ The water soluble fatty acids is titerated with alkali to give RM value.

5gm of fat
↓ distillation (Hydrolysis)
Volatile fatty acids
[water soluble fatty acids]
↓ 0.1 N KOH solution
Neutrilized

e.g. Butter.
↓
RM Value → (25 to 30)

While RM value is less than 1 for more other edible oils.
Thus, adulteration of butter can be easily tested by this sensitive RM number.

Q-3:- Write the difference b/w fats & Oils.

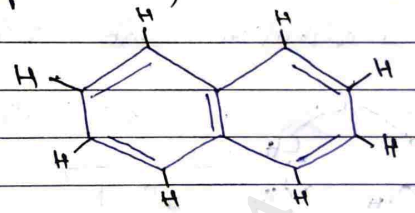
Ans:-

Fats	Oils
Fats are solid at room temperature.	Oils are liquid at room temperature.
Fats are saturated.	Oils are unsaturated.
Fats have high melting & boiling point.	Oils have low boiling points.
Fats are found in animals.	Oils are found in both animals & plants [vegetables].

Unit :- 4

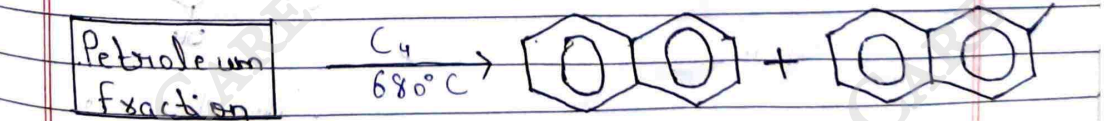
Q.1:- Describe in details about the synthesis & chemical reaction of Naphthalene, Phenanthrene, Anthracene.

Ans:- **Naphthalene** :-



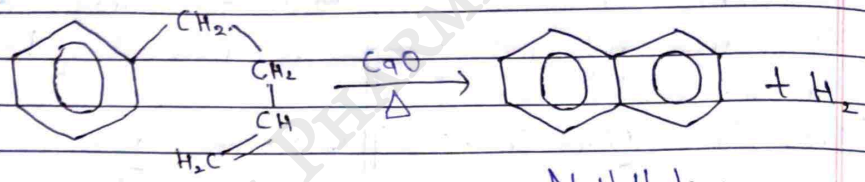
- **Synthesis of Naphthalene:**

1:- **From Petroleum** :- When petroleum fraction are passed over copper catalyst at 680°C, naphthalene & methylnaphthalenes are formed.



Naphthalene Methylnaphthalene

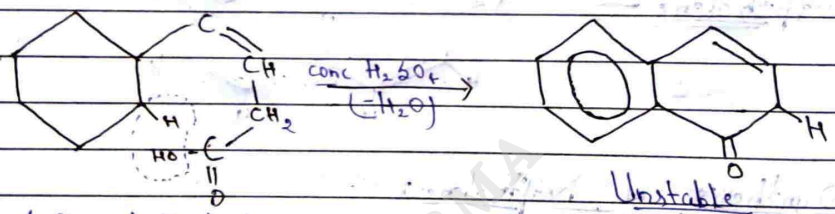
2) :- From 4-phenyl-1-butene → When 4-phenyl-1-butene is passed over red hot calcium oxide, naphthalene is obtained.



4-Phenyl-1-butene

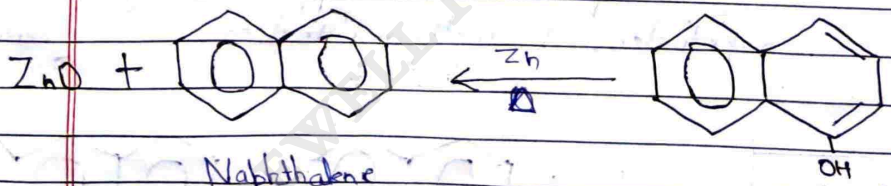
Naphthalene

3) :- From 4-Phenyl-3-butenoic Acid → When 4-phenyl-3-butenoic acid is heated with concentrated sulphuric acid, 1-Naphthol is formed, this on distillation with zinc dust give naphthalene.



4-Phenyl-3-butenoic

Unstable

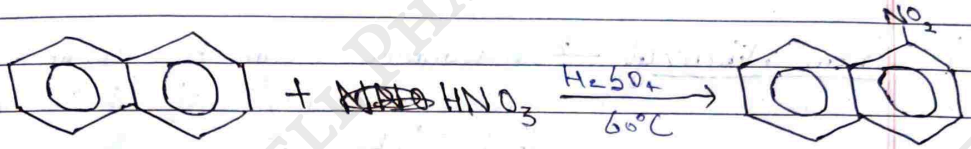


Naphthalene

1-Naphthol

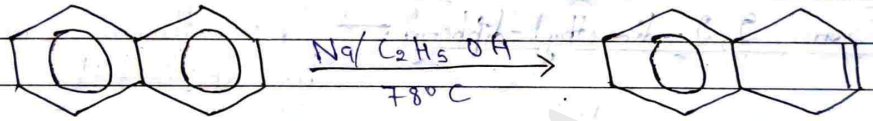
- Reactions of Naphthalene :

1) Nitration → Naphthalene undergoes nitration with concentrated nitric acid in the presence of sulfuric acid at 60°C to produce 1-nitronaphthalene.



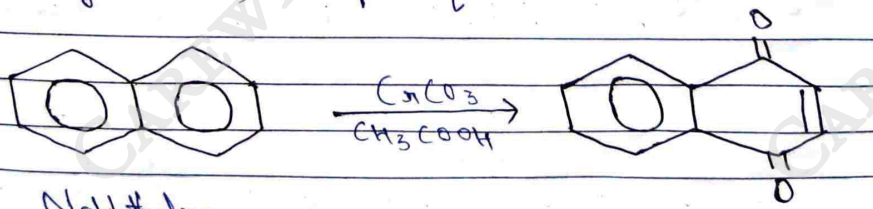
Naphthalene — 1-Nitronaphthalene

2) Reduction → Naphthalene undergoes reduction more readily than benzene, when it react with sodium & ethyl alcohol it gives 1,4-dihydronaphthalene.



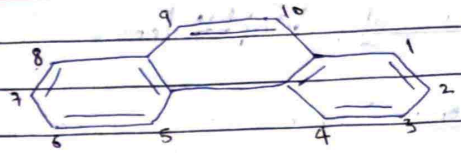
Naphthalene — 1,4-dihydronaphthalene

3) Oxidation → Naphthalene is much more easily oxidized than benzene, when it react with chromium trioxide in acetic acid at room temp, it gives 1,4-naphthaquinone.



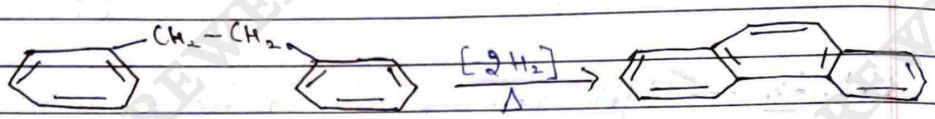
Naphthalene — 1,4-naphthaquinone

• Phenanthrene :



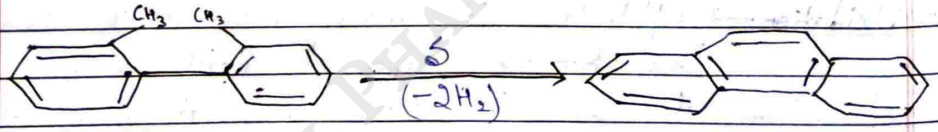
– Synthesis of Phenanthrene :

1) → From Dibenzyl → Phenanthrene can be obtained by passing dibenzyl through a red hot tube.



Dibenzyl — Phenanthrene

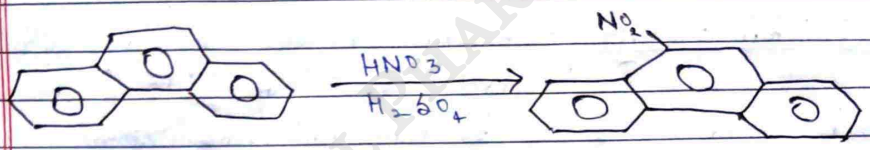
2) → From 2,2-dimethyl-diphenyl → Phenanthrene can also be obtained by cyclodehydrogenation of 2,2-dimethyl-diphenyl using sulphur.



Cyclodehydrogenation — 2,2-dimethyldiphenyl

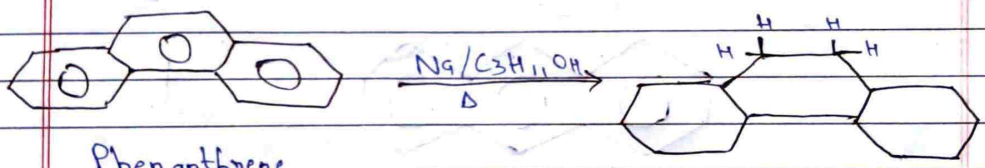
- Reactions of Phenanthrene :

1) Nitration → Phenanthrene undergoes nitration with concentrated nitric acid & sulfuric acid to yield 9-nitrophenanthrene.



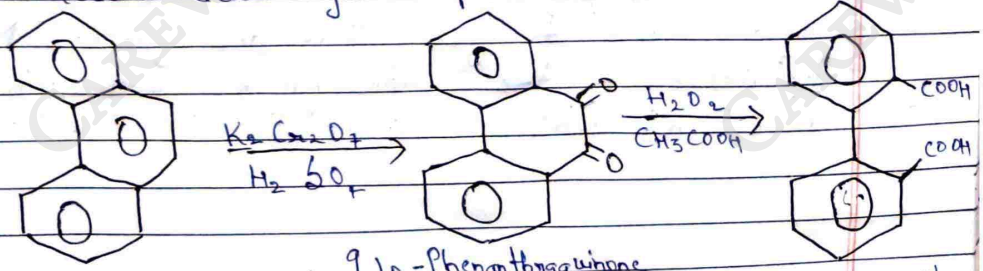
Phenanthrene — 9-Nitrophenanthrene

2) Reduction → Phenanthrene undergoes reduction with sodium & isopentanol to form 9,10-dihydrophenanthrene.



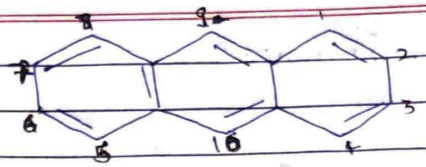
Phenanthrene — 9,10-Dihydrophenanthrene

3) Oxidation → Phenanthrene undergoes oxidation with potassium dichromate & sulfuric acid in acetic acid to give 9,10-phenanthraquinone. Further oxidation of this with hydrogen peroxide in acetic acid give diphenic acid.



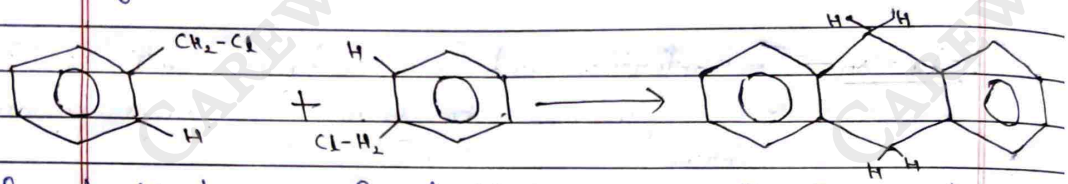
Phenanthrene — 9,10-Phenanthraquinone — Diphenic acid

• Anthracene

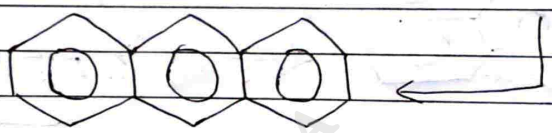


– Synthesis of Anthracene:

1) By Friedal - Craft → Benzene chloride reacts with itself to form 9,10-dihydroanthracene which readily loses two hydrogen atoms to yield anthracene.

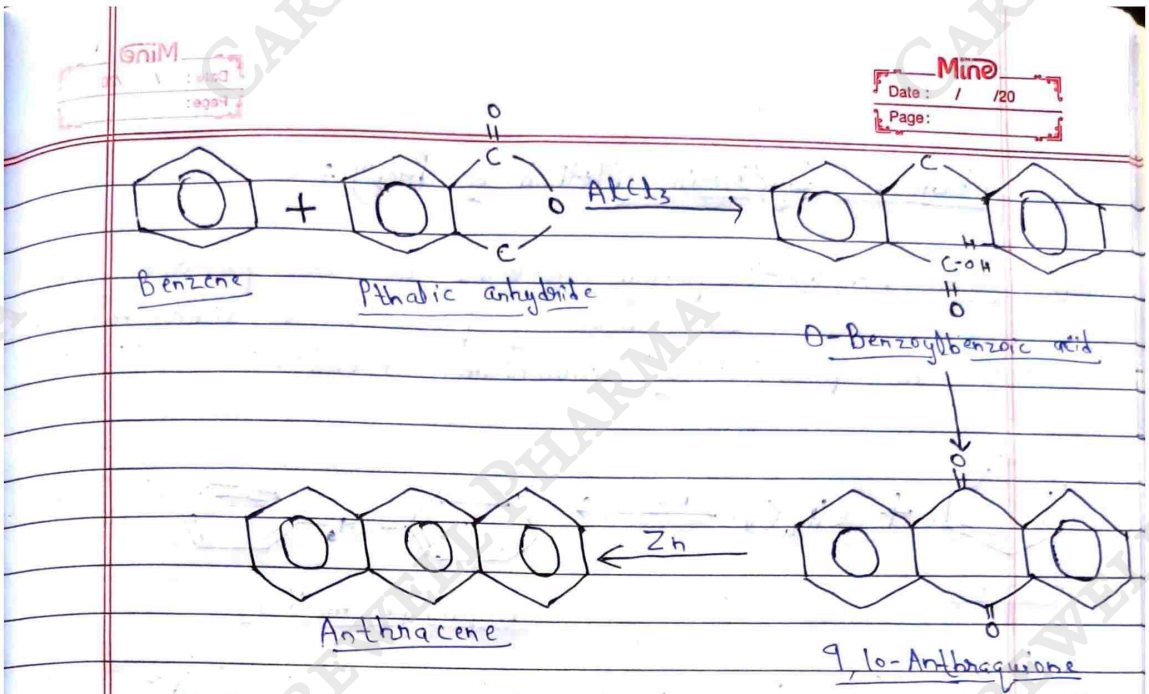


Benzyl chloride Benzyl chloride 9,10-Dihydroanthracene

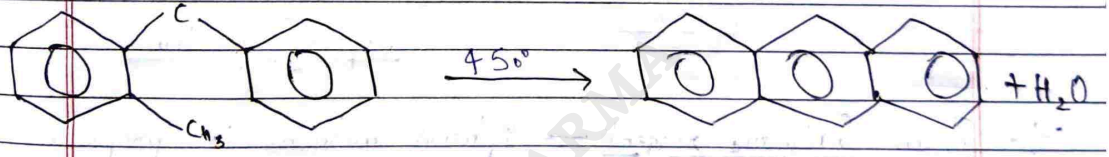


Anthracene

2) By Haworth synthesis → This involves the treated of benzene with pthalic anhydride in the presence of aluminium chloride to form O-benzoylbenzoic acid.
Then O-benzoylbenzoic acid heated with concentrated sulfuric acid to give 9,10-anthraquinone. Now, distillation of the anthraquinone with zinc dust yield anthracene.



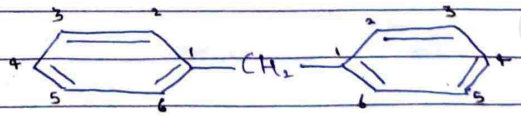
3) → By Elbs reaction → The conversion of a diaryl Ketones containing a methyl or methylene group to the carbonyl function is known as the Elbs reaction.



Q-2 → Structure, chemical synthesis & medicinal use of Diphenylmethane, Triphenylmethane.

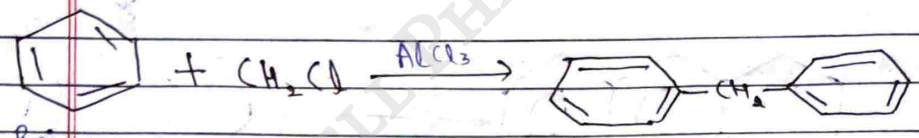
Ans → • Diphenylmethane :

– Structure :



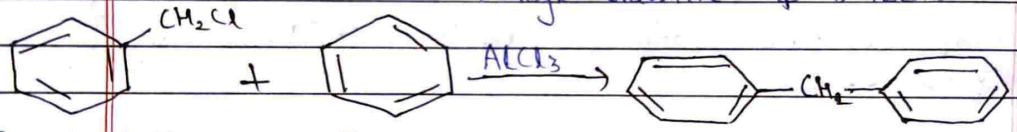
– Chemical Synthesis (Method of Preph) :-

1)→ From Benzene → Diphenyl methane is also prepared from two moles of benzene & dichloromethane in the presence of aluminium chloride.



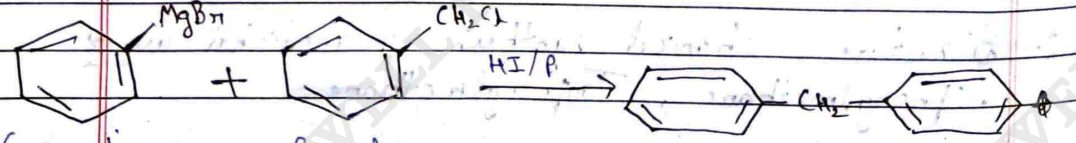
Benzene — Diphenyl methane

2)→ Friedal Crafts → Diphenyl methane is prepared by friedal crafts condensation b/w benzyl chloride & benzene.



Benzyl chloride + Benzene → Diphenyl methane

3)→ From Grignard reagent → Diphenyl methane is prepared by Grignard reagent.

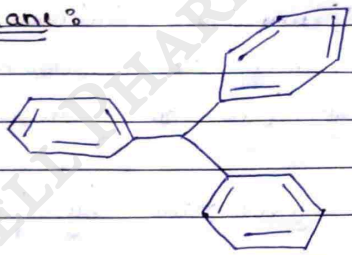


Grignard reagent + Benzyl chloride → Diphenyl methane + $MgBrCl$

- **Medicinal use** → It is used in the synthesis of methylene diphenyl diisocyanate, which is used in the manufacture of polymethane & as an industrial strength adhesive.

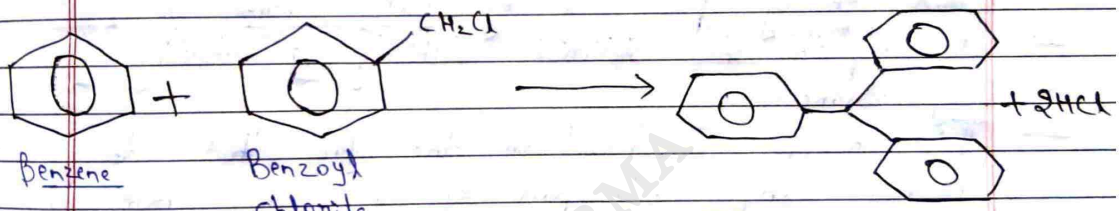
- **Triphenyl Methane:**

- **Structure** →



- **Chemical Synthesis [Method of preparation]:**

1) **Friedal Craft's** → It is prepared by the condensation b/w benzyl chloride & benzene.



Benzene — Benzoyl chloride — Triphenyl methane

- **~~Method~~ Medicinal Uses:**

→ It is a triarylmethane compound used as a backbone of synthetic dyes.

→ It has also been shown to inhibit 3-methylcholanthrene - induced neoplastic transformation of Hela cells.

Unit - 5

Q-1→ Define Cycloalkanes, Write down difference theory of stability of cycloalkanes in details → (10).

Ans: Cycloalkanes → They are saturated hydrocarbons in which the carbon atoms joined by simple covalent bond to form a ring.

e.g., Cyclopropane, Cyclobutane, Cyclopentane, Cyclohexane etc.

This are involves in three theory :

1) → Baeyer's Stain Theory :

→ This theory proposed by Adolf Baeyer in 1885.
→ He explain the relative stability of starting few cycloalkanes.
→ This theory is based on the fact that, the normal angle b/w pair of a carbon atom is 109°28'.
→ Now, he assumed that all cycloalkanes are planer.
→ Stability of cycloalkanes depends upon the angle strain.

Bird Angle strain = Stability bised

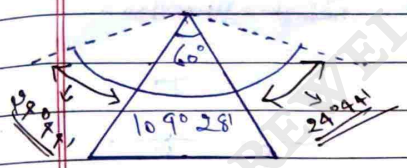
→ In cycloalkanes → Are more angle strain, then more unstable.

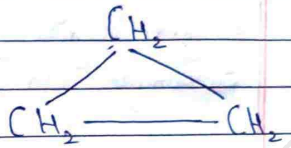
- **Angle Strain** → It is angle difference b/w desired angle [109°28'] & actual angle.

Angle strain → $\frac{1}{2}$ [Desired angle − Actual angle]

→ $\frac{1}{2}$ [109°28' − Actual angle]

e.g., **Cyclopropane:**





- Desired angle → 109°28'
- Actual angle → 60

Angle strain → $\frac{1}{2}$ [109°28']

= $\frac{1}{2}$ [49°28']

= $\frac{49°28'}{2}$ = **24°44'**

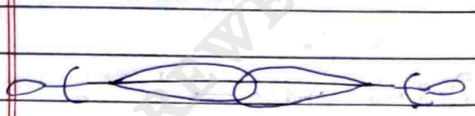
1° = 60'

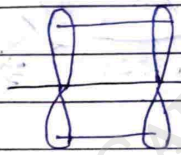
Compound	Desired angle	Actual angle	Angle strain	Structure
Cyclopropane	109°28'	60°	24°44'	60°
Cyclobutane	109°28'	90°	9°44'	90°
Cyclopentane	109°28'	108°	0°-44'	108°
Cyclohexane	109°28'	120°	-5°16'/5°16	120°

2) :- Coulson & Moffit's Modification Theory :-

→ It is also known as Bent Bond / Banana bond theory.
→ This concept of maximum overlap of carbon orbitals.
→ It is also called as banana bond theory, because bond is look like as banana shape.
→ This theory also explain the stability of cycloalkanes [by cyclopropane most unstable].
→ Stronger is the bond ↑ied = Stability ↑ied.

e.g.,

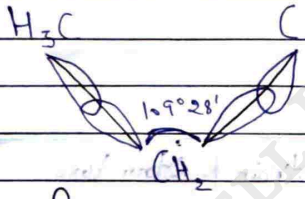




Sigma - bond
[Stronger & better overlaping]

Pi - bond
[Weaker & bad overlaping]

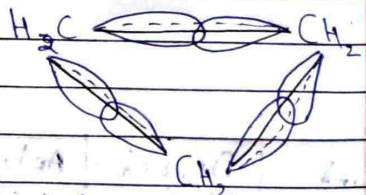
→ But in cyclopropane bent bond is formed, which is intermediate b/w Sigma & pi-bond.



Propane

sp^3 hybridization

S → 25%
P → 75%



Cyclopropane

S → 16%
P → 84%

- Cyclopropane :

Bent bond
Bad overlaping
↓
Weaken → Stability fixed.

→ So, due to weaken bond cyclopropane is unstable & it can give ring opening reaction early.

→ In cyclopropane, C-C-C bond angle is fixed slightly from 109°28' to 104°.

→ This decreased in overlap result in weakening of the bond & therefore partially explain the instability of cyclopropane.

→ Bent bond is formed in cyclopropane, due to their less angle [60°] than 109°28'.

→ Cyclobutane is more stable than cyclopropane but less than cyclopentane.

3) Sachse-Mohr Theory :

→ It is also known as Theory of Strainless Rings.

→ This theory proposed by Sachse & Mohr in 1918. to explain about the stability of cyclohexane & higher cycloalkanes.

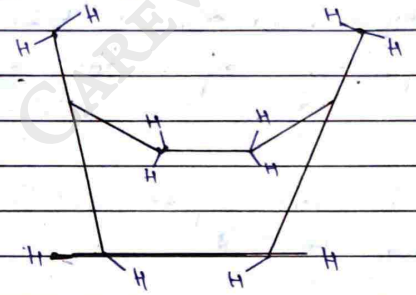
→ According to Baeyer's members higher than cyclopentane should be increasingle unstable [limitation].

→ But, According to this theory, cycloalkanes are not in a plane [co-planer].

→ Sachse Mohr's theory proposed that higher members ring can free from strain if all the ring carbon are not forced into one plane.

→ They exhibit in two non-planer 'folded' or 'puckered' conformation both of which are completely free from strain.

→ These are stainless as the carbon atom lie in different planes & the normal angle [109°28'] is retained.



Boat form of Cycloalkanes

Q-2:- Give Baeyer's strain theory with its limitation?

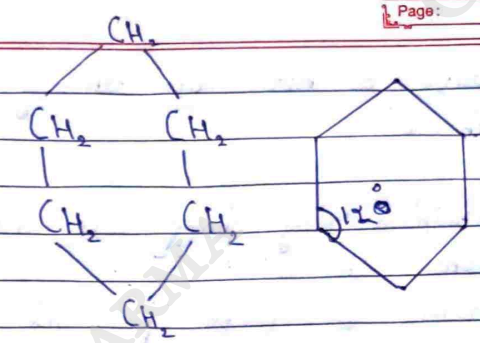
Ans:- This theory proposed by Adolf Baeyer in 1885.

→ It theory is based on the fact that, the normal angle b/w pair of a carbon atom is 109°28'.

→ Stability of cycloalkanes depends upon angle strain.

Angle strain ↑ = Stability ↓

e.g. Cyclohexane:



Angle strain = $\frac{1}{2}$ [109°28'] − [120°]

120°28'
↓
119°60
− 109°28
10°32'

= $\frac{10°32'}{2}$ 5°16

= 5°16

- Limitation of Baeyer theory:

→ This theory only applies on the lower cycloalkanes, Baeyer was not able to explain the effect of angle strain in larger ring systems.

→ Acc. to Baeyer cycloalkane should be much stable than ~~cycloalkane~~, to cyclohexane, but practically it is reversed. [cyclohexane is more stable than cyclopentane.]

→ They don't give ring opening reaction easily like cyclopropane.

Q-3. Write a note on theory of Strainless ring theory?

Ans:- Strainless ring theory is also known as Sachse - Mohr theory.

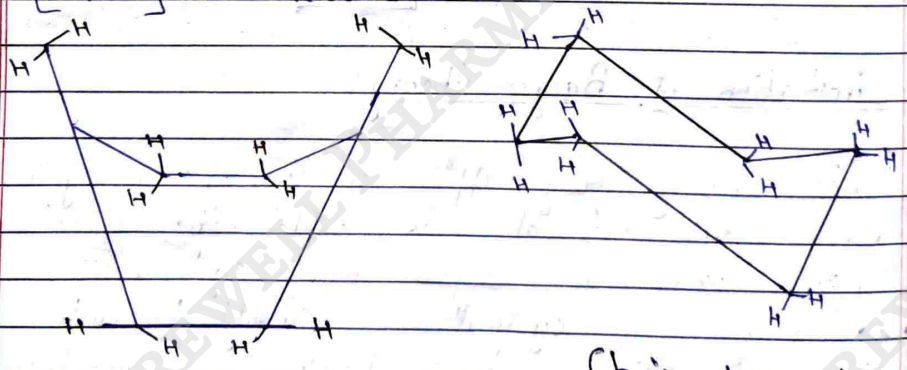
→ Sachse & Mohr proposed this theory in 1918 to explain about the stability of cyclohexane & higher ~~cyclohe~~ cycloalkanes.

→ Acc. to this theory, cycloalkanes are not in a plane it is co-planer.

→ Sachse Mohr's theory proposed that higher member ring can free ~~form~~ from strain if all the ring carbon are not forced into one plane.

→ They exhibit in two non-planer 'folded' or 'puckered' conformation both of which are completely free from strain.

→ These are strainless as the carbon atom lie in different planes & the normal angle [109°28'] is retained.



Boat form of Cyclohexane

Chair form of Cyclohexane

→ Chair form is more stable than boat form.