

ORGANIC CHEMISTRY-II

UNIT 4 NOTES

POLYNUCLEAR HYDROCARBONS

- NAPHTHALENE
- PHENANTHRENE
- ANTHRACENE
- DIPHENYLMETHANE
- TRIPHENYLMETHANE



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POLYNUCLEAR HYDROCARBONS

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

TYPES

Polynuclear Hydrocarbons are mainly divided into two types :

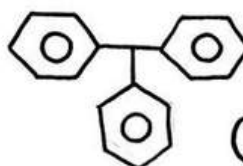
- ① Isolated Ring Compounds
- ② Fused Ring Compounds

① ISOLATED RING COMPOUNDS

In these compounds Aromatic rings are isolated.



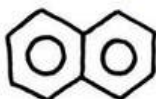
DIPHENYL METHANE



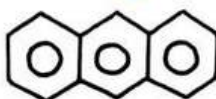
TRIPHENYL METHANE

② FUSED RING COMPOUNDS

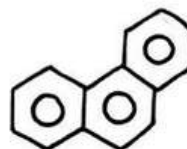
In these compounds Aromatic Rings are Fused.



NAPHTHALENE



ANTHRACENE

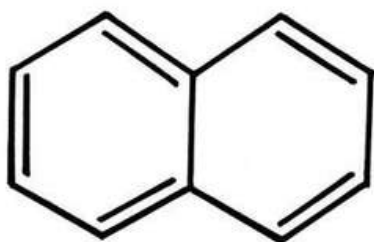


PHENANTHRENE



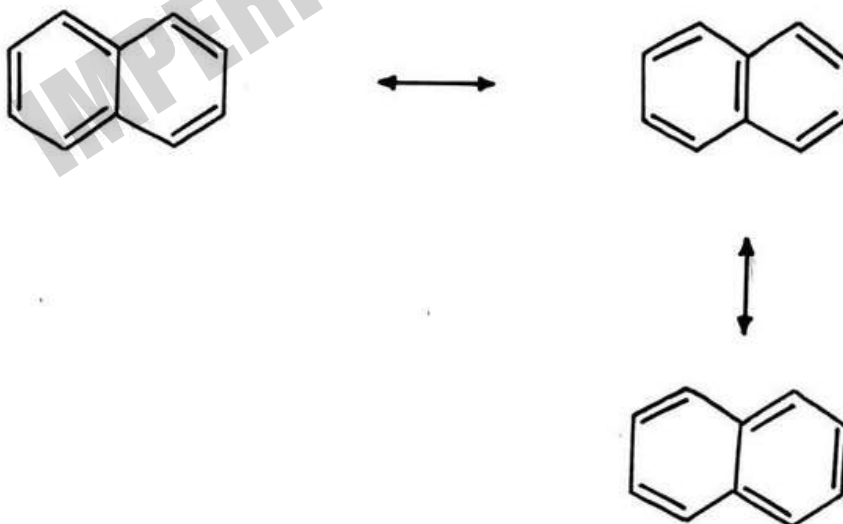
NAPHTHALENE

- A Naphthalene molecule is derived from fusion of pair of Benzene Ring.
- It is a member of fused ring hydrocarbons under the class of Polynuclear Hydrocarbons.
- Naphthalene is a crystalline, aromatic, white solid hydrocarbon.



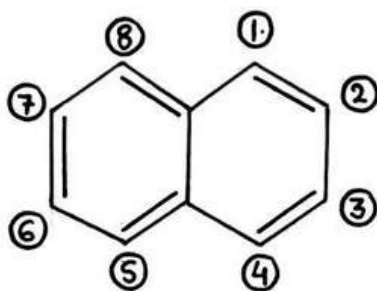
RESONANCE IN NAPHTHALENE

- Naphthalene forms 3 resonating structure.
- Delocalization of π bonds makes naphthalene stable.



CHEMICAL PROPERTIES

- Chemical Formula of Naphthalene is $C_{10}H_8$
- All carbons in naphthalene are sp^2 hybridized.
- Naphthalene are more reactive than benzene because resonance energy in naphthalene (61 kcal/mol) is less than twice to that of benzene (36 kcal/mol).



- In the above structure of Naphthalene Position 1, 4, 5, 8 $\rightarrow \alpha$
and Position 2, 3, 6, 7 $\rightarrow \beta$
- Also Unlike the Benzene, C-C bond length in naphthalene are not same.
- C1-C2 bond length in naphthalene is shorter ($1.36 \text{ \AA}$) than C2-C3 bond length ($1.40 \text{ \AA}$) due to more double bond character on C1-C2 bond.

PHYSICAL PROPERTIES

- Naphthalene is a white crystalline solid.
- Its Melting Point is 80°C .
- Its Boiling Point is 217°C .
- It is insoluble in water but soluble in organic solvents.

SYNTHESIS

Napthalene can be synthesized by following various methods :

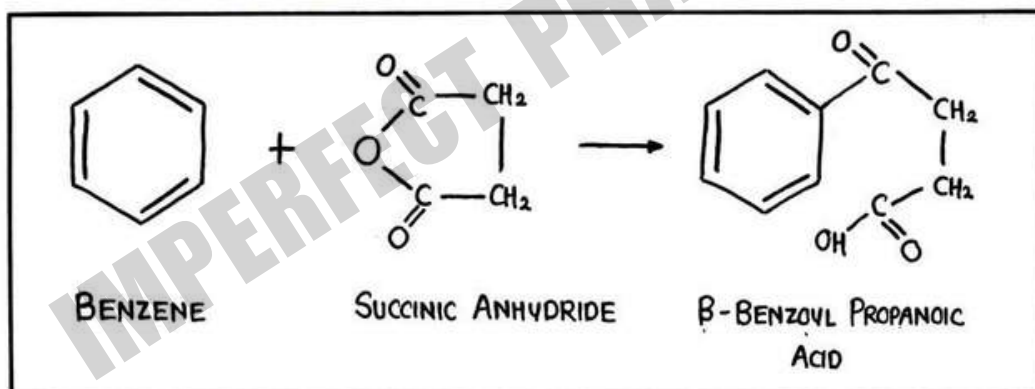
① HAWORTH SYNTHESIS

It is a Five step chemical reaction :

- Friede - Craft Acylation
- Clemmensen Reduction - I
- Ring Closure Reaction
- Clemmensen Reduction - II
- Aromatization

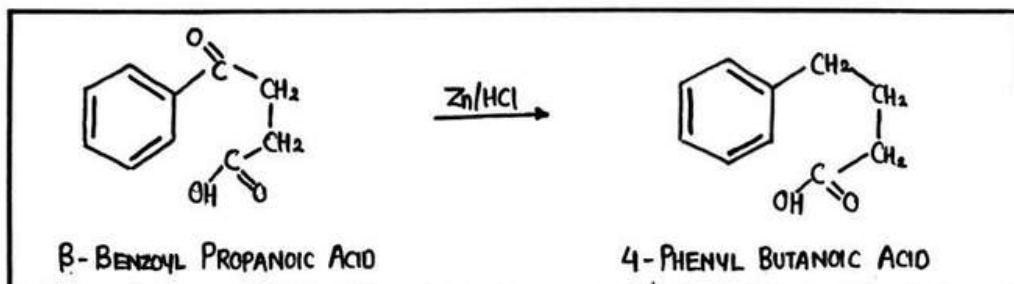
● STEP-I (Friedel Craft Acylation)

Benzene and succinic Anhydride are heated in the presence of $AlCl_3$ to form β - benzoyl Propanoic Acid.



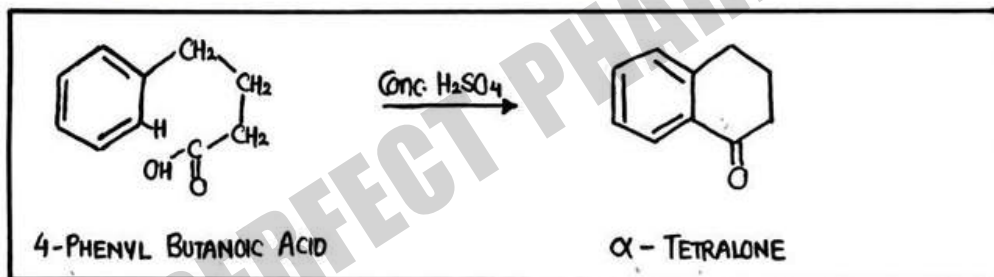
● **STEP - II (Clemmensen Reduction)**

β - Benzoyl Propanoic Acid is treated with Amalgamated zinc in the presence of HCl to give 4- Phenyl Butanoic Acid.



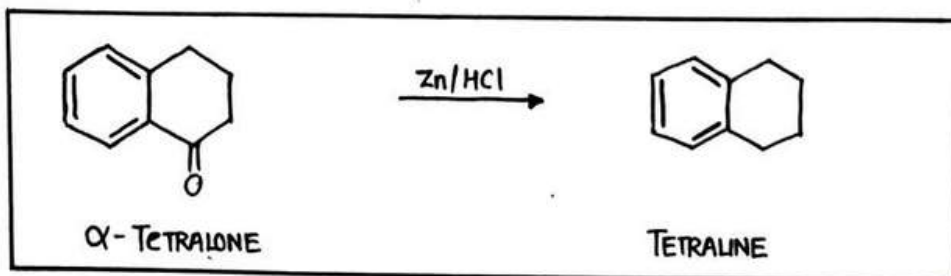
● **STEP - III (Ring Closure Reaction)**

4- Phenyl Butanoic Acid is heated with conc. H_2SO_4 to form α -tetralone.

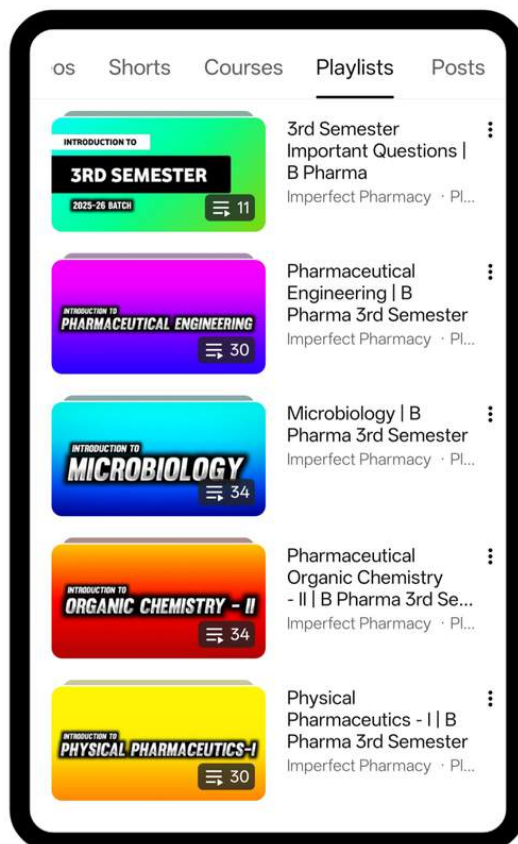
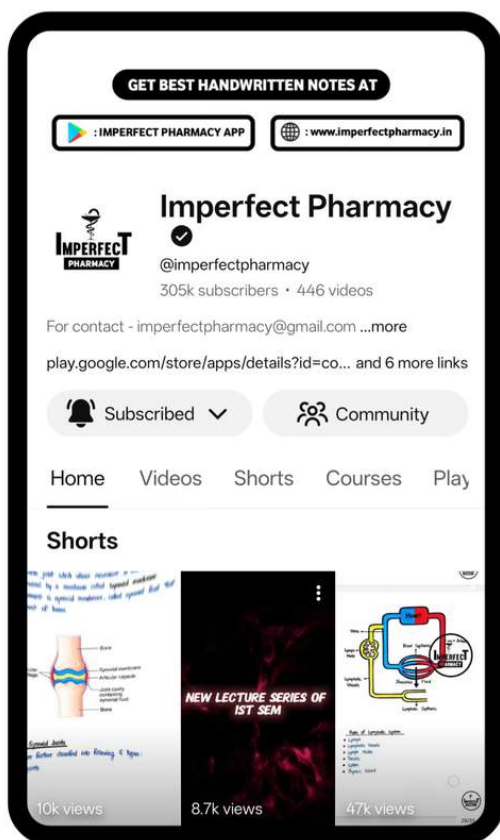


● **STEP - IV (Clemmensen Reduction)**

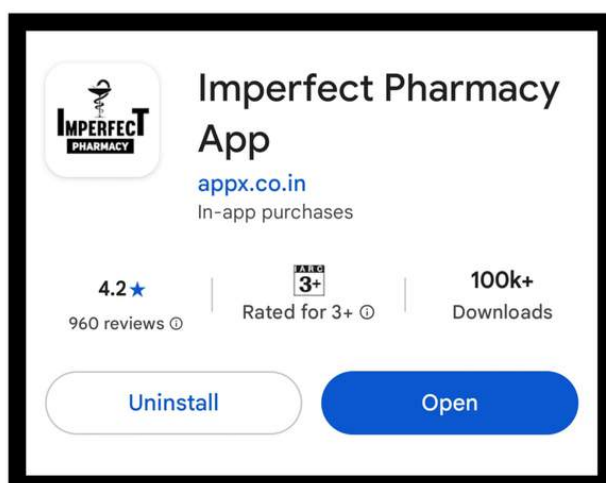
α Tetralone heated with zinc & HCl to give Tetraline



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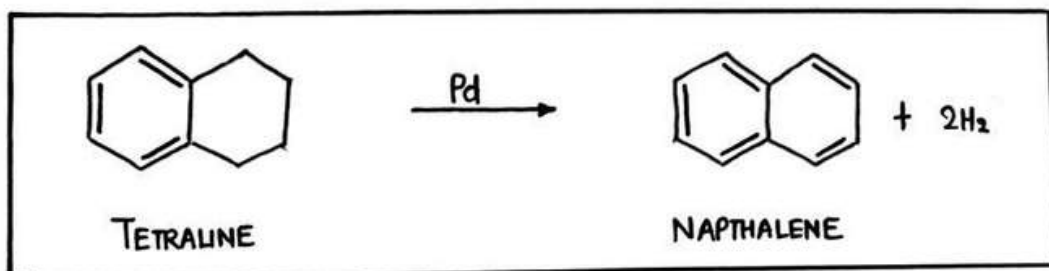


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STEP - V (Aromatization)

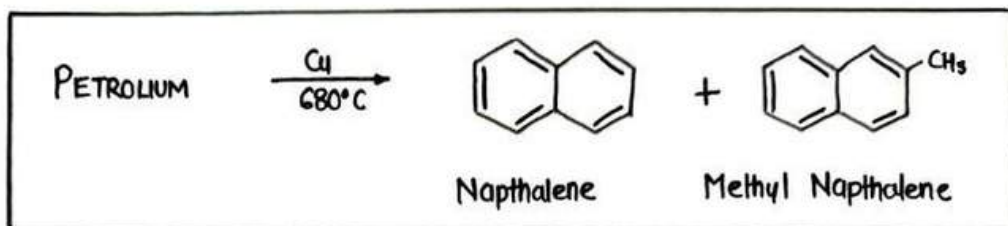
Tetralin is heated with Palladium to give Naphthalene.



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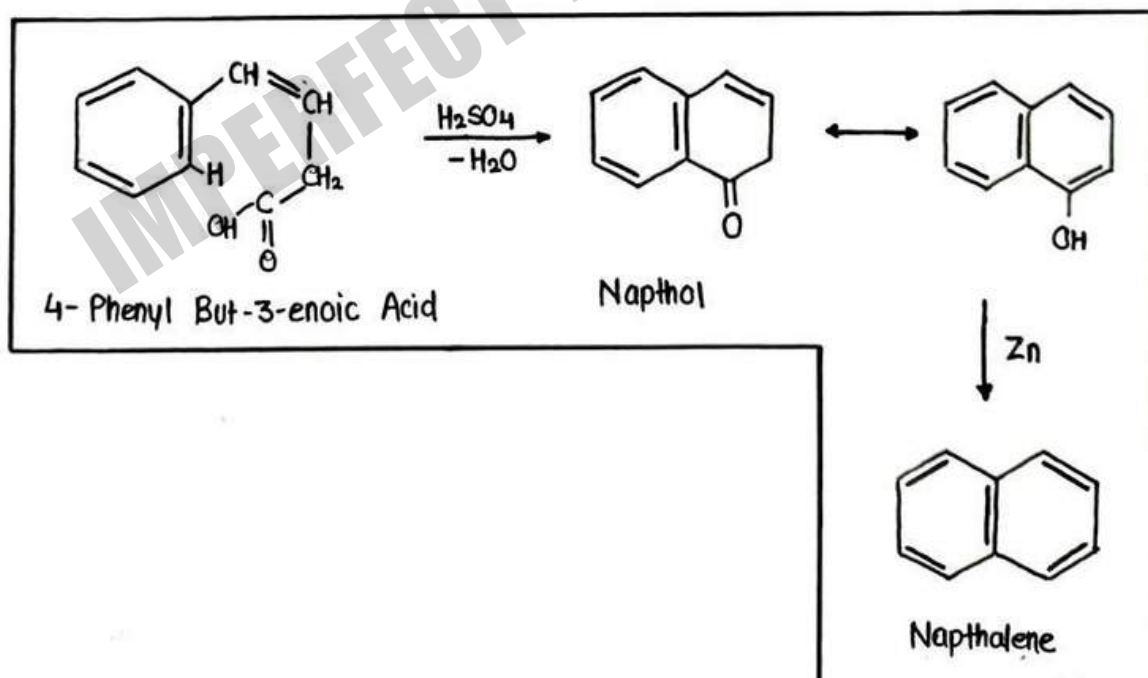
② FROM PETROLIUM

When Petroleum fraction passed over Copper (Cu) catalyst at 680°C , it leads to the formation of Naphthalene & Methyl naphthalene.



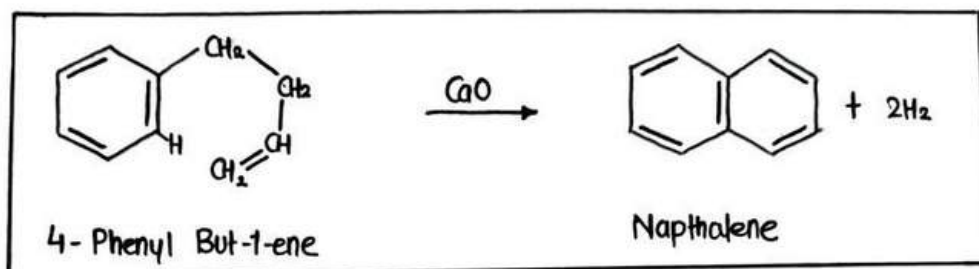
③ FROM 4-PHENYL BUT-3-ENOIC ACID

When 4-Phenyl But-3-enoic Acid is heated with concentrated H_2SO_4 it gives naphthol which on further distillation with zinc dust yields Naphthalene.



④ FROM 4-PHENYL BUT-1-ENE

When 4-Phenyl But-1-ene is passed over Red Hot Calcium Oxide, it yields the formation of Naphthalene.

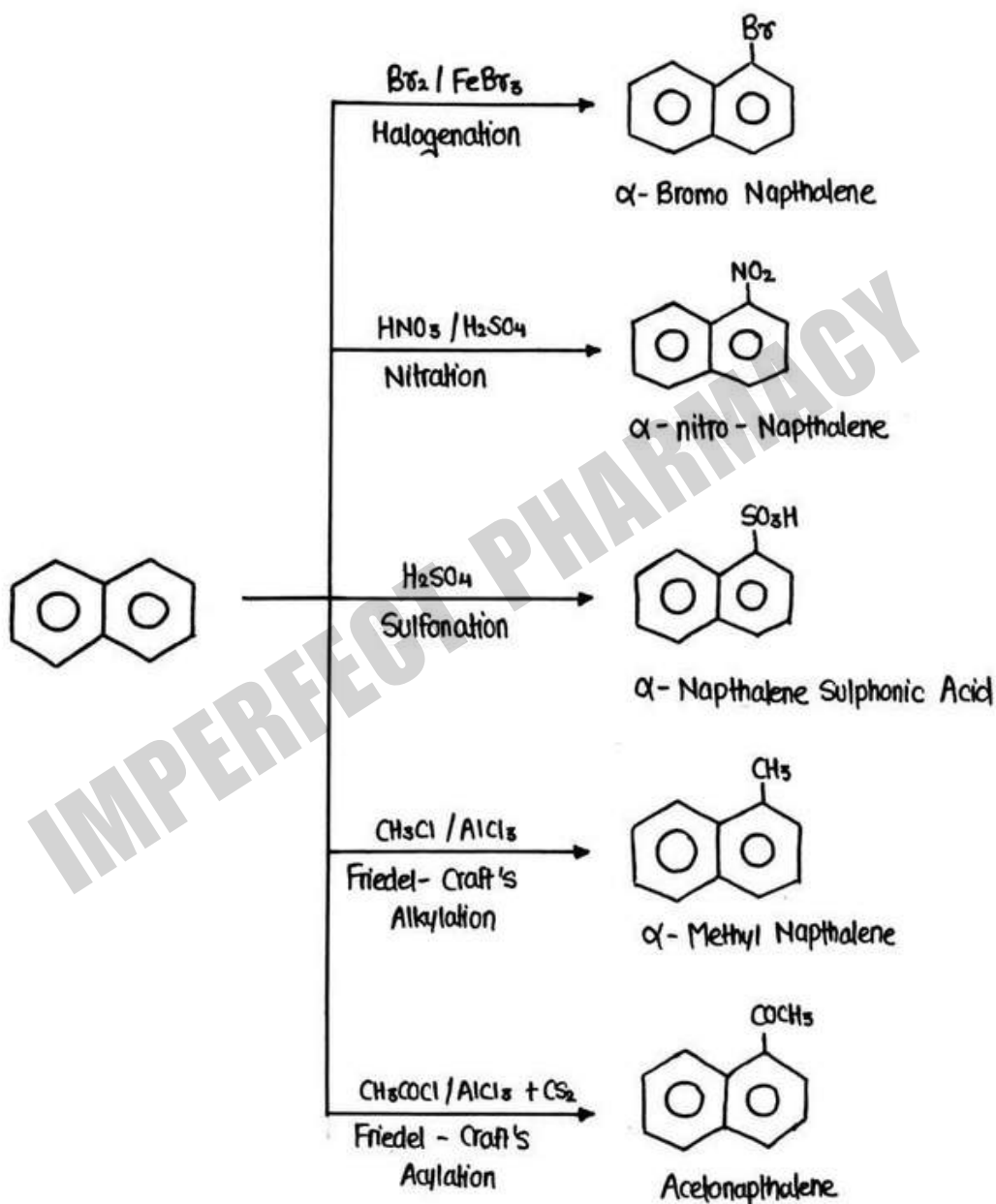


IMPERFECT PHARMACY

CHEMICAL REACTIONS

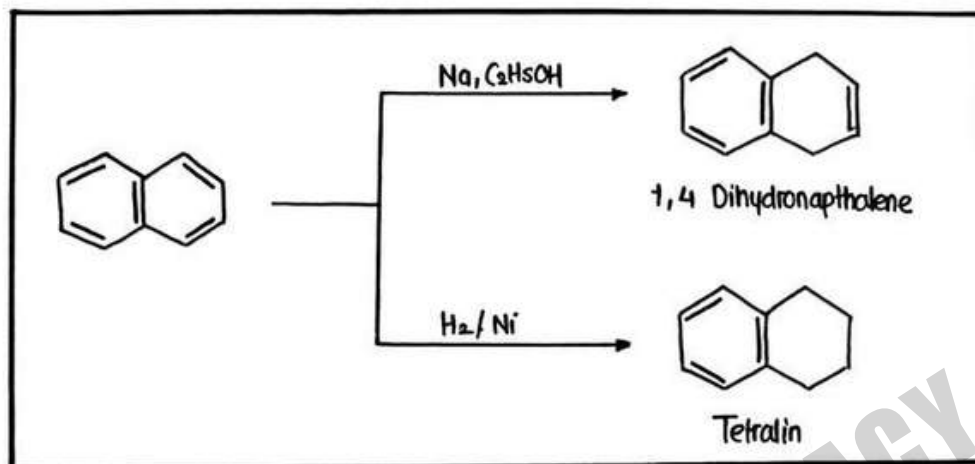
Napthalene undergoes the following chemical reactions :

① ELECTROPHILIC SUBSTITUTION REACTION



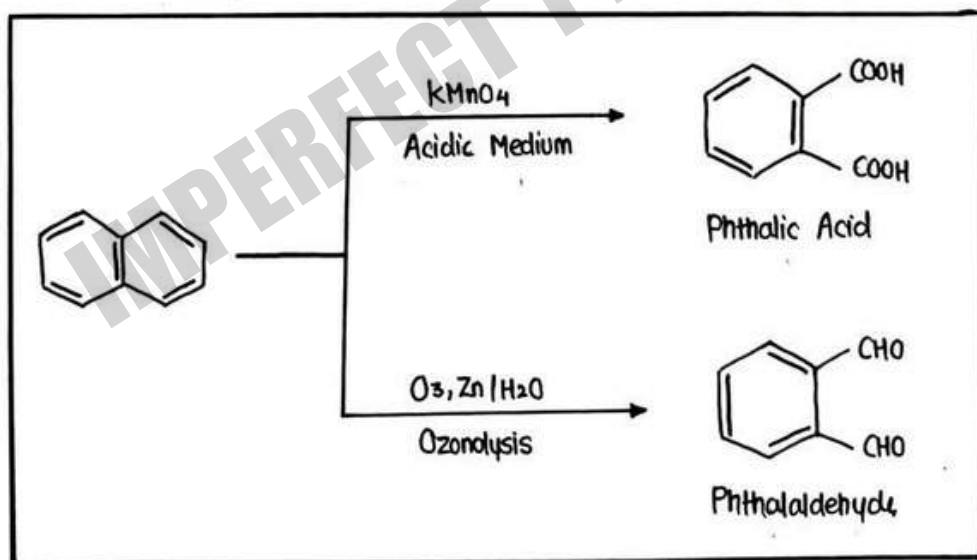
② REDUCTION

The reduction reaction in benzenes depends upon different reducing agent.



③ OXIDATION

Oxidation in naphthalene depends upon different oxidizing agent.



MEDICINAL USES

- It is used as Antiseptic Agent.
- It is used as Preservative.
- It is effectively used in Eye troubles.
- It is effective in treating the symptoms of cold, Fever, Gonorrhoea etc.
- It is used in synthesis of various dyes.
- It is also used in synthesis of various drugs like Nadoxolol.

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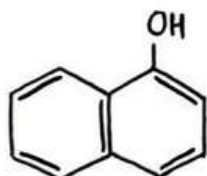
NAPHTHALENE DERIVATIVES

There are various Naphthalene derivatives given below :

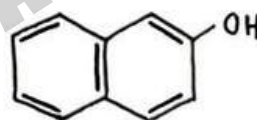
- Naphthols
- Naphthylamines
- Naphtholic Acid
- Naphthoquinones

NAPTHOLS

- It is the hydroxyl derivative of Naphthalene.
- It is the precursor for various drug synthesis.
- α -Naphthol is the main ingredient of Molisch Reagent.
- β -Naphthols are used as antiseptic for skin diseases.



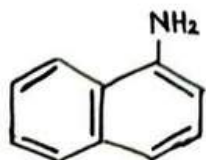
α -Naphthol



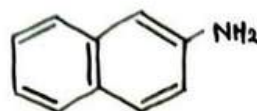
β -Naphthol

NAPHTHYLAMINES

- Naphthylamine is a white or yellow crystalline substance.
- It is used in dye manufacturing, rubber, pesticides & various pharmaceuticals.



α -Naphthylamine

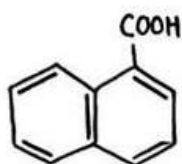


β -Naphthylamine

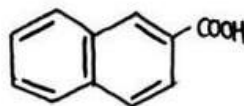


③ NAPTHOIC ACID

- They are aromatic carboxylic acids used in various organic synthesis.
- It is used as intermediates in production of dyes & pharmaceuticals.



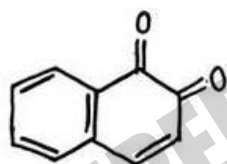
α -Naphthoic Acid



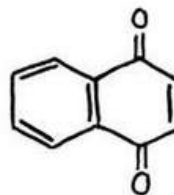
β -Naphthoic Acid.

④ NAPTHOQUINONES

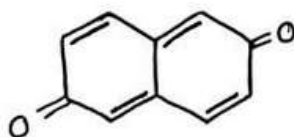
- These are compounds that contain a naphthalene ring with two ketone groups.
- They have Antimicrobial & Antifungal Properties.
- They are used in various dyes & drug development.



1,2 Naphthoquinone



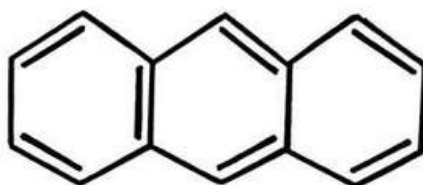
1,4 Naphthoquinone



2,6 Naphthoquinone

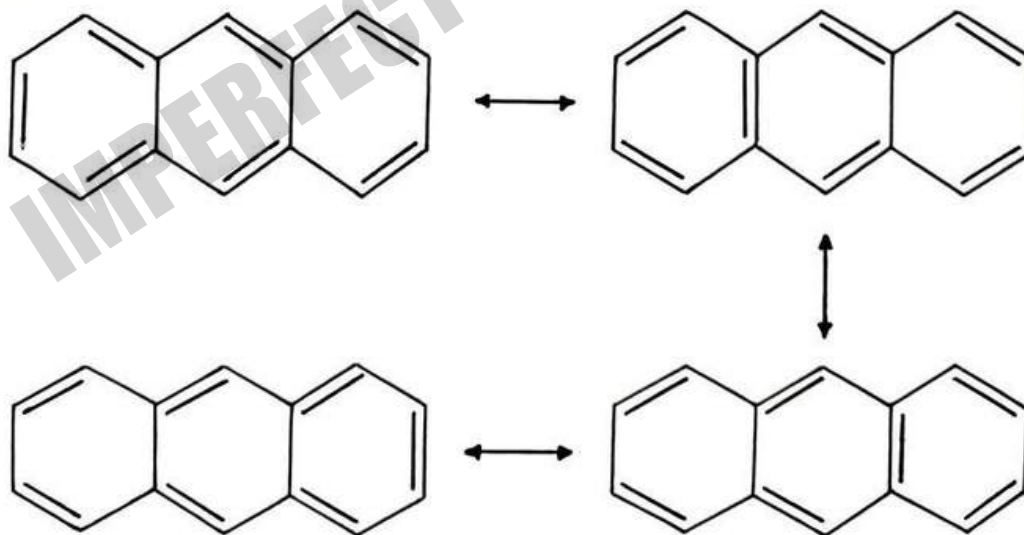
ANTHRACENE

- Anthracene is a solid polycyclic Aromatic hydrocarbon consist of 3 linear fused benzene ring.
- It is a member of Fused ring hydrocarbons under the class of Polynuclear Hydrocarbons.



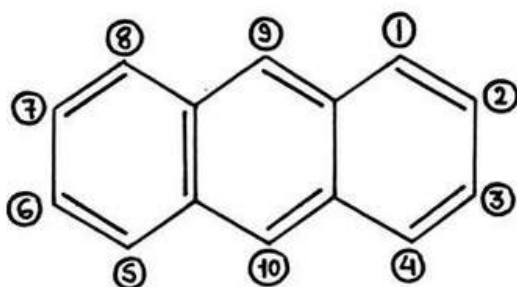
RESONANCE IN ANTHRACENE

- Anthracene undergoes delocalization to give 4 resonance structure :
- The presence of resonance makes Anthracene stable .



CHEMICAL PROPERTIES OF ANTHRACENE

- The chemical formula for Anthracene is $C_{14}H_{10}$ & molecular weight is 178 g/mol.
- All the carbons in Anthracene are sp^2 hybridized.
- Anthracene is more reactive than benzene because resonance energy of Anthracene is 84 kcal/mol which is less than three of benzene (36 kcal/mol).



- Position no 1, 4, 5, 8 are similar known as : α Position
- Position no 2, 3, 6, 7 are similar known as : β Position
- Position no 9, 10 are similar and known as : γ Position
- C₁-C₂ bond have more double bond character & hence shorter bond length (1.37 Å).
- C₂-C₃ bond have more single bond character & hence longer bond length (1.42 Å).

PHYSICAL PROPERTIES

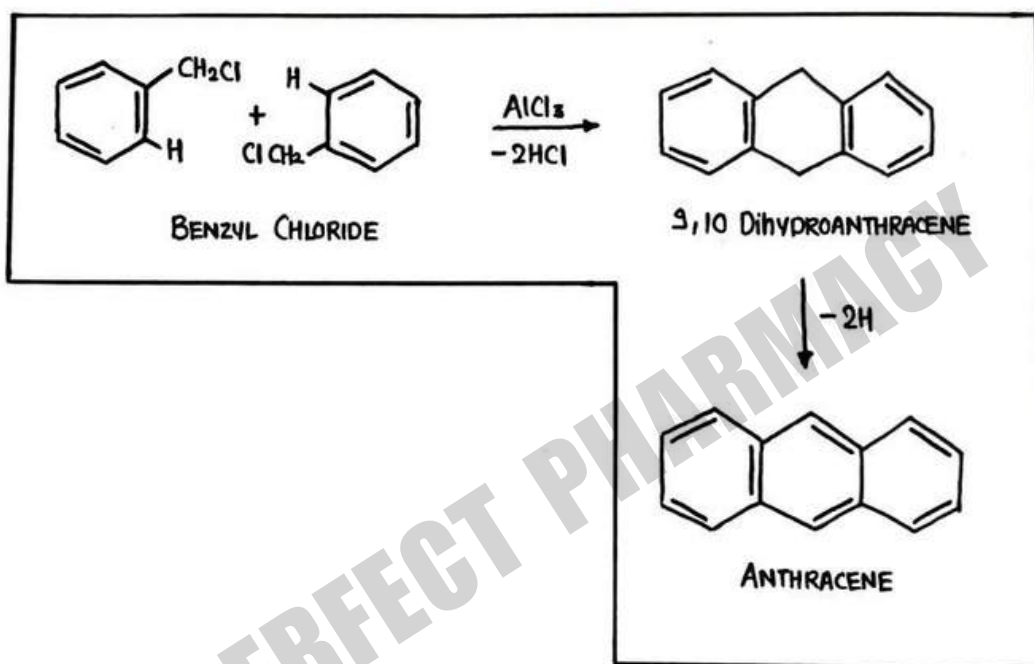
- It is a colourless solid.
- Its Melting Point is 218°C
- Its boiling point is 340°C
- It is insoluble in water but soluble in organic solvent.

SYNTHESIS

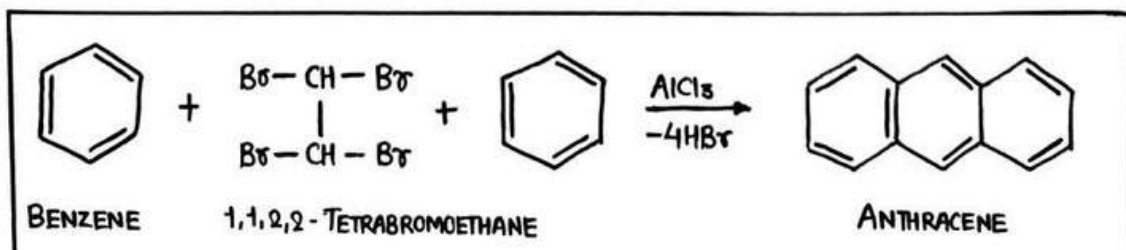
Anthracene can be synthesized / prepared by following methods :

① FRIEDEL CRAFTS REACTION

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



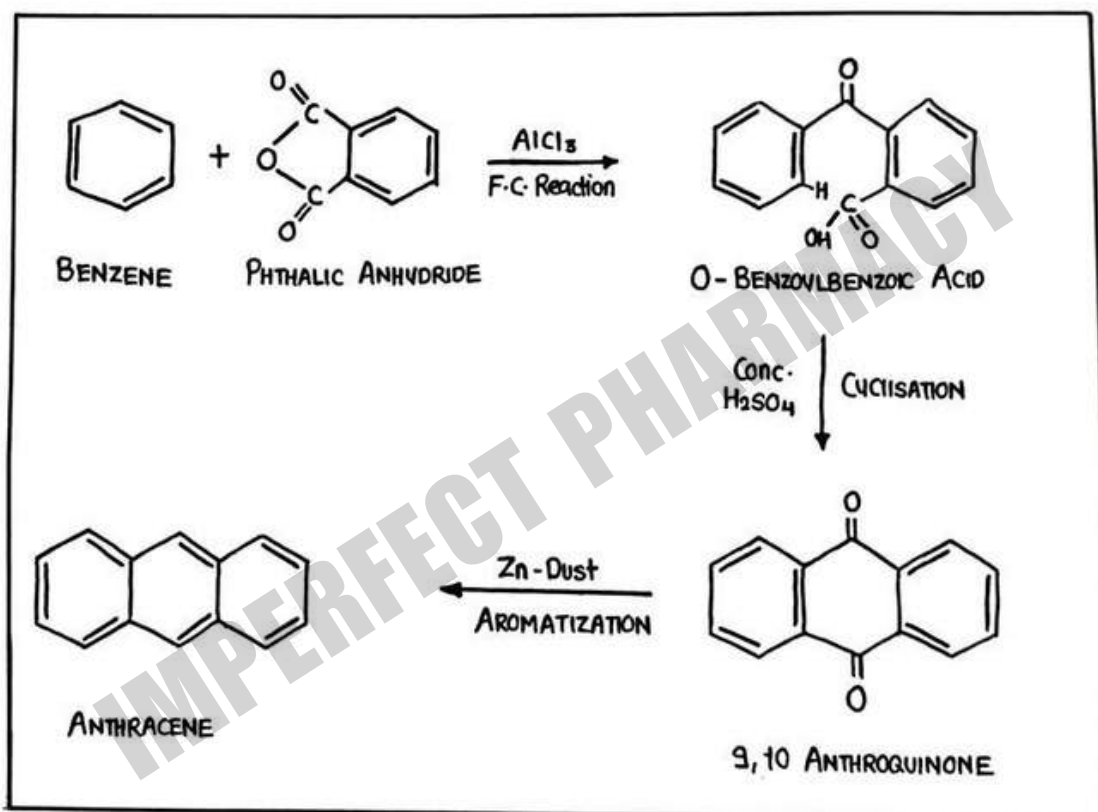
- Anthracene can also be prepared by reaction of 2 benzene molecules with 1,1,2,2 - Tetrabromo Ethane.



② By HAWORTH SYNTHESIS

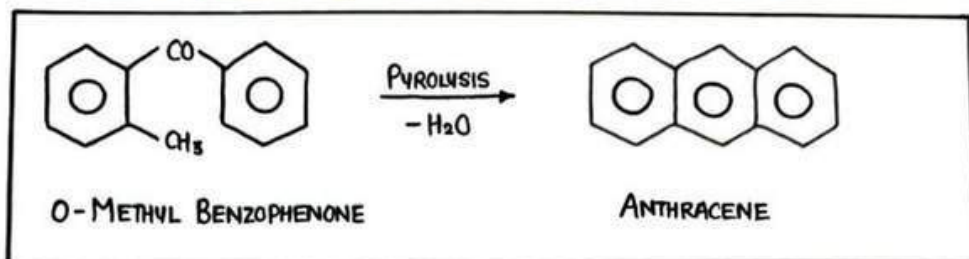
In Haworth synthesis, Benzene reacts with Phthalic Anhydride in the presence of Aluminium Chloride to form O-Benzoyl Benzoic Acid, then O-Benzoyl Benzoic Acid heated with concentrated Sulphuric Acid (H_2SO_4) to give 9,10-anthraquinone.

Now this 9,10-anthraquinone on further distillation with zinc dust yields anthracene.



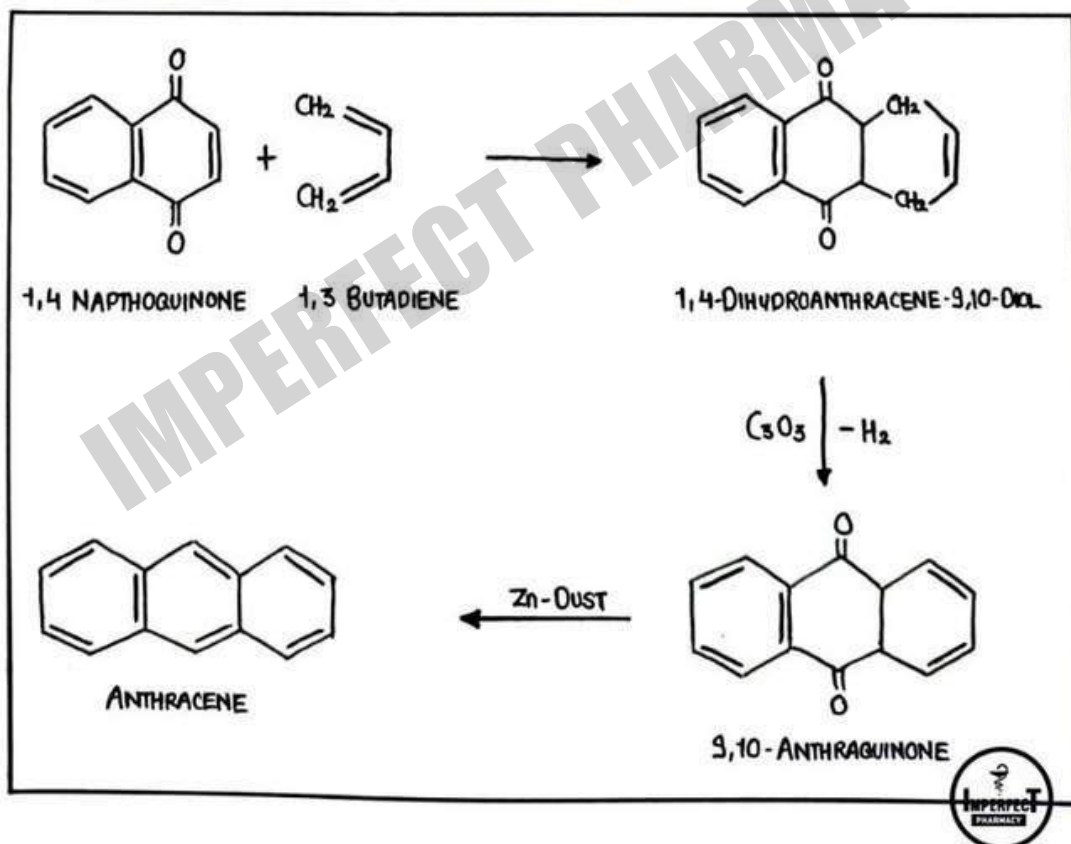
③ ELBS REACTION

Anthracene is prepared by pyrolysis of O-Methyl benzophenone.



④ BY DIELS-ALDER REACTION

When 1,4-naphthoquinone reacts with 1,3-butadiene it forms 1,4-Dihydroanthracene-9,10-diol which on oxidation with Chromium Trioxide gives 9,10-anthraquinone which on further distillation with zinc dust gives anthracene.

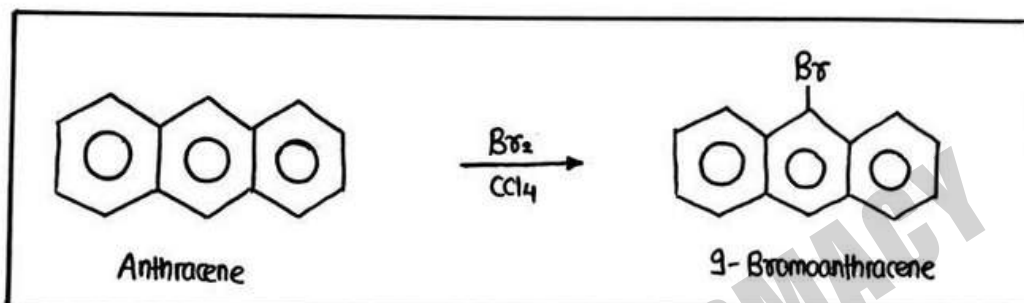


CHEMICAL REACTIONS

Anthracene undergoes following chemical reactions :

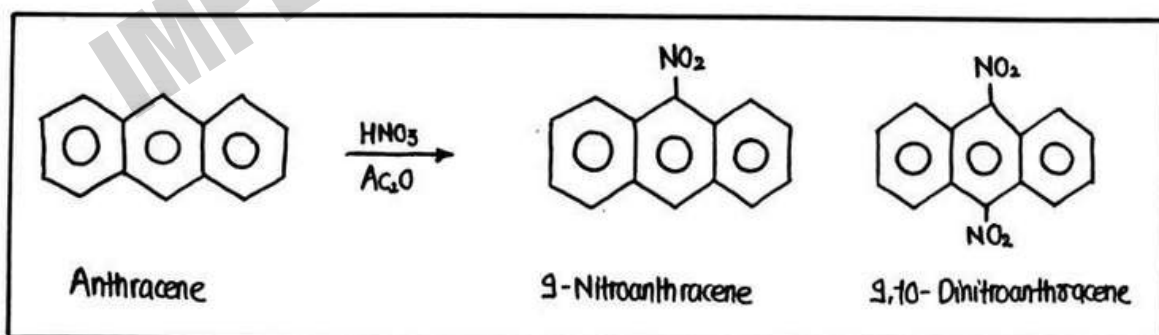
① HALOGENATION

Anthracene reacts with Halogens (Cl/Br) in the presence of CCl_4 to form 9-Bromoanthracene.



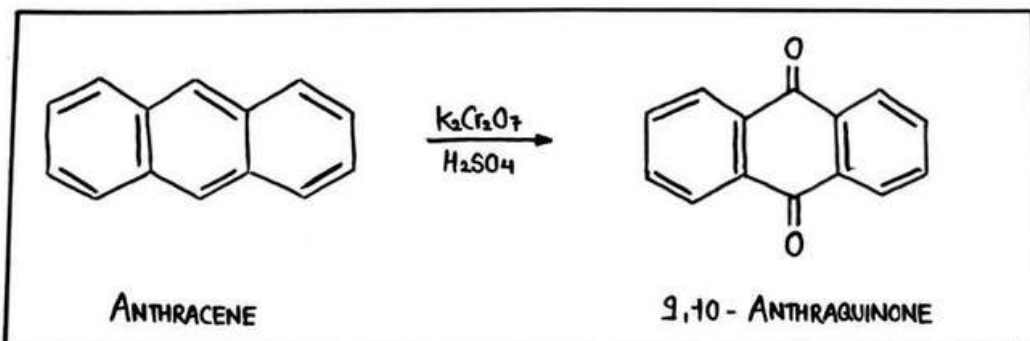
② NITRATION

Anthracene reacts with concentrated HNO_3 in the presence of Acetic Anhydride to form mixture of 9-Nitroanthracene & 9,10-Dinitroanthracene.



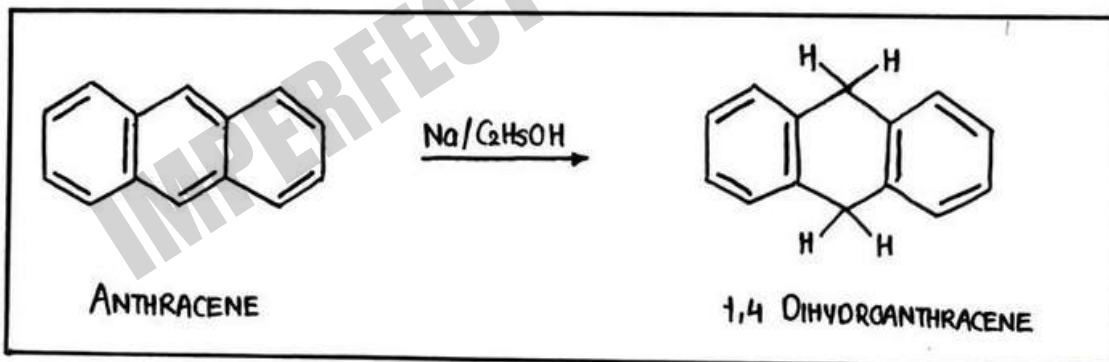
③ OXIDATION

Anthracene undergoes oxidation in the presence of strong oxidizing Agent like Potassium Dichromate ($K_2Cr_2O_7$) to give 9,10 Anthraquinone.



④ REDUCTION

Anthracene undergoes reduction in the presence of sodium & ethanol to form 9,10-Dihydroanthracene.



MEDICINAL USES

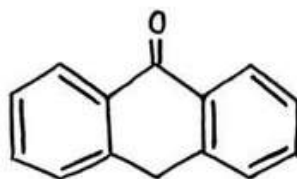
- It is used as Wood Preservatives.
- It is used as insecticides.
- It is also used Antifungal & Antiviral Agent.
- Used as constituents of drugs like Senna, Cascara etc.
- It is also used in manufacturing of various dyes.

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ANTHRACENE DERIVATIVES

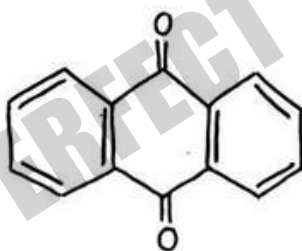
There are various Anthracene derivatives as follows :-

① ANTHRONE



- It is used for determination of Carbohydrates.
- It is used to detect & quantify sugars in different samples.
- It is also used as Laxative

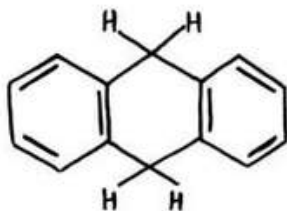
② ANTHRAQUINONE



USES

- It is used for manufacturing various dyes.
- It is used as herbicides & pesticides.
- It serves as building block for the synthesis of various organic compounds.

③ DIHYDRO- ANTHRACENE



USES

- It is used in Photographic techniques.
- It serves as building blocks in synthesis of various organic compounds.

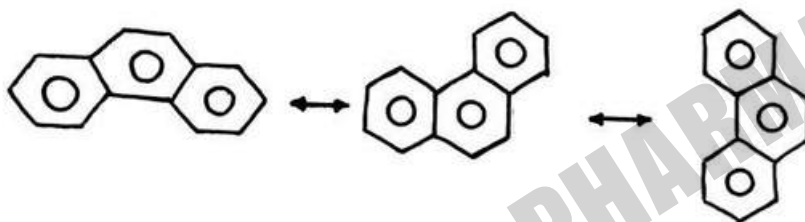
IMPERFECT PHARMACY

PHENANTHERENE

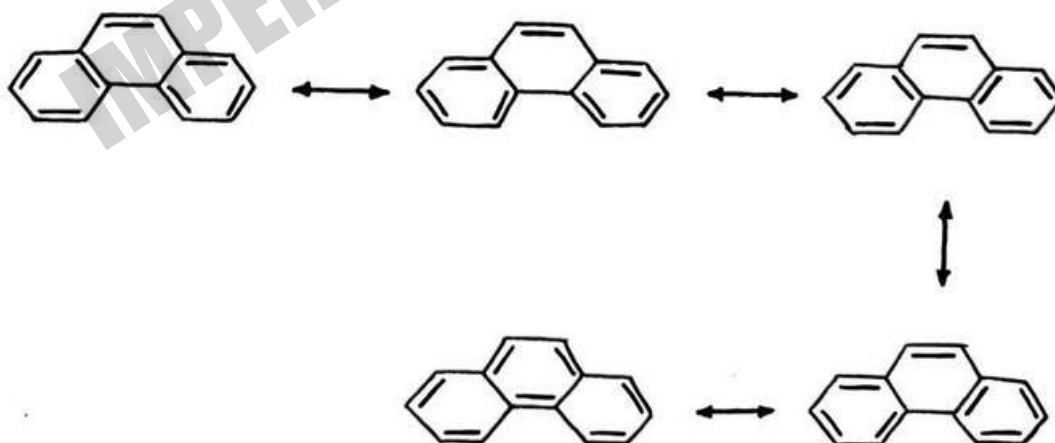
- Phenanthrene is a polycyclic aromatic hydrocarbon composed of three fused benzene rings.
- It is a structural isomer of Anthracene.
- It is a member of Fused Ring Hydrocarbons under the class of Polynuclear Hydrocarbons.

REPRESENTATION

Phenanthrene can be represent in following 3 ways :

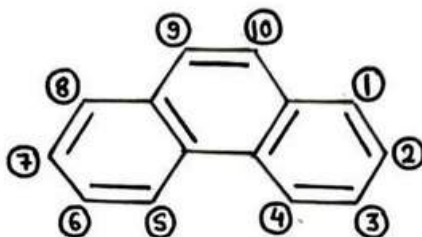


RESONANCE IN PHENANTHERENE



CHEMICAL PROPERTIES

- Its chemical formula is $C_{14}H_{10}$.
- It is an isomer of Anthracene.
- Its molecular weight is 178 g/mol.
- All the carbons of Phenanthrene are sp^2 hybridized.
- It follows Hückle Rule.



PHYSICAL PROPERTIES

- Phenanthrene is a colourless crystalline solid.
- Its Melting Point is 101°C .
- Its boiling point is 340°C .
- Its Insoluble in water but soluble in organic solvents.

SYNTHESIS

Phenanthrene can be synthesized by following reactions :

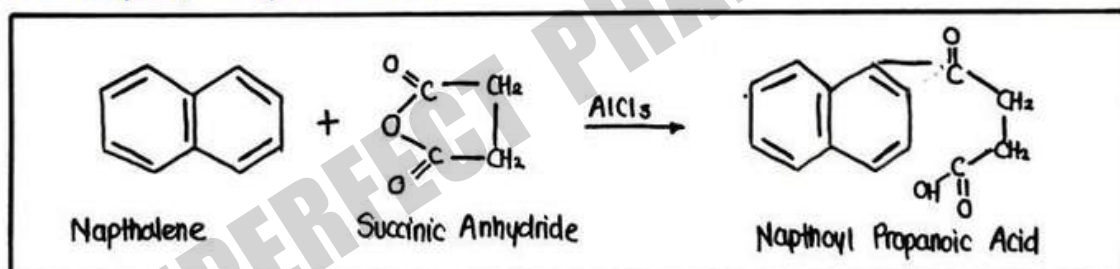
① HAWORTH SYNTHESIS

It involves 5- step chemical reaction :

- Friedel Craft Acylation
- Clemmensen Reduction
- Ring Closure Reaction
- Clemmensen Reduction
- Aromatization

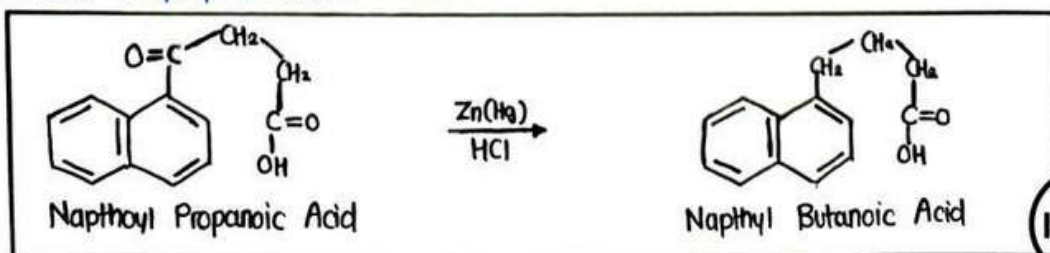
● Friedel Craft Acylation

Napthalene reacts with succinic anhydride in the presence of $AlCl_3$ to form Napthoyl Propanoic Acid.



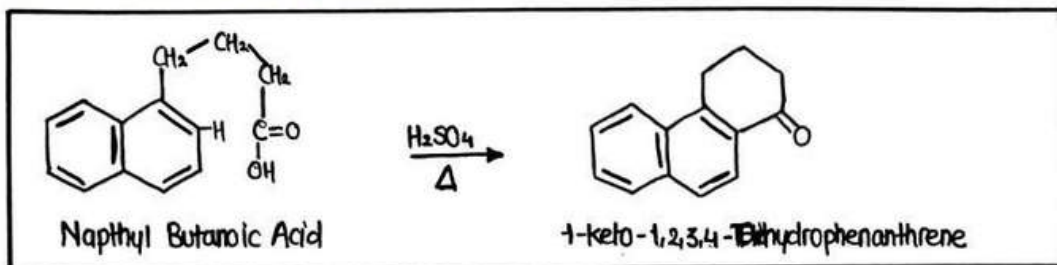
● Clemmensen Reduction

Napthyl Propanoic Acid reacts with amalgated zinc in the presence of HCl to form Napthyl Butanoic Acid.



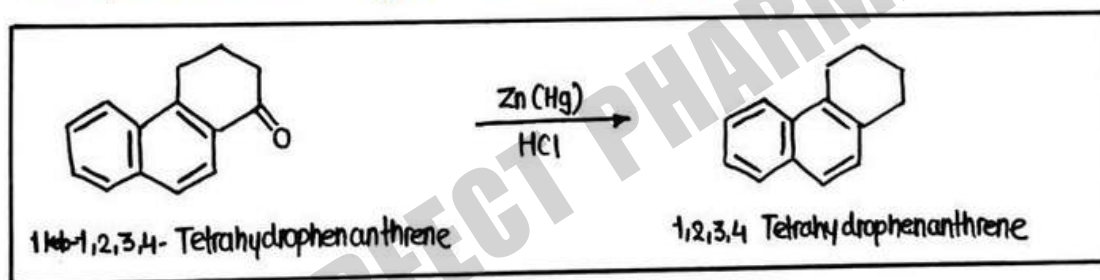
● CYCLOSATION

Naphthyl Butanoic Acid heated in the presence of H_2SO_4 to give 1-keto-1,2,3,4-Tetrahydrophenanthrene.



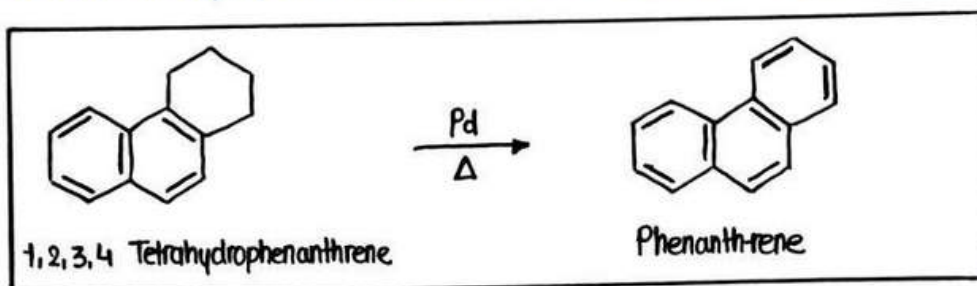
● CLEMMENSEN REDUCTION

1-keto-1,2,3,4 Tetrahydrophenanthrene reacts with Amalgamated zinc in the presence of HCl to give 1,2,3,4 Tetrahydrophenanthrene.



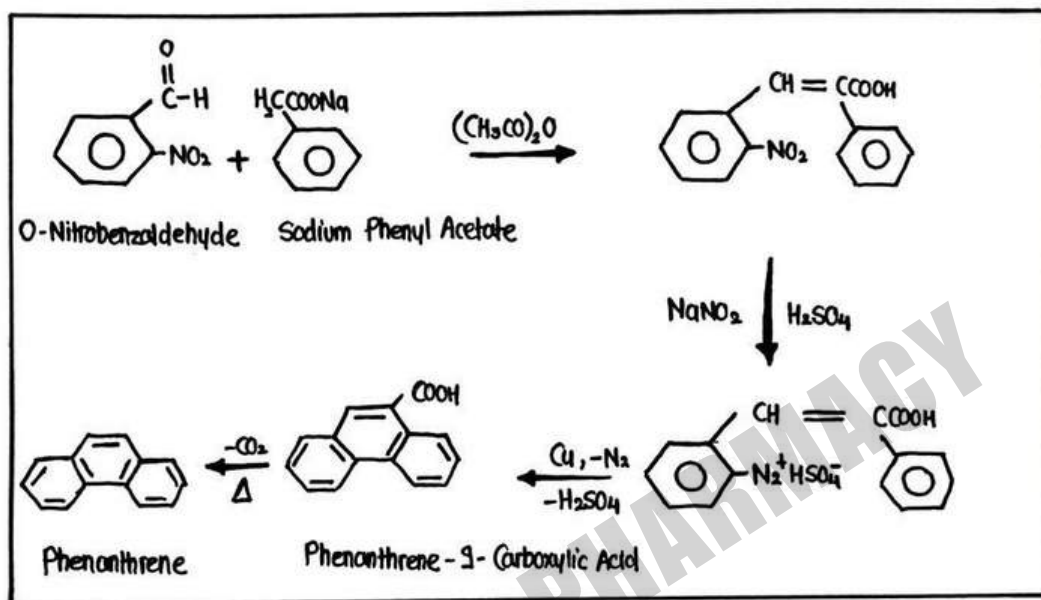
● AROMATISATION

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



② PSCHORR SYNTHESIS

O-Nitrobenzaldehyde is heated with Sodium phenyl acetate in the presence of acetic anhydride to give Phenyl-O-nitro cinnamic acid which undergoes diazotization which on further reaction gives Phenanthrene-9-carboxylic acid which on heating give Phenanthrene.

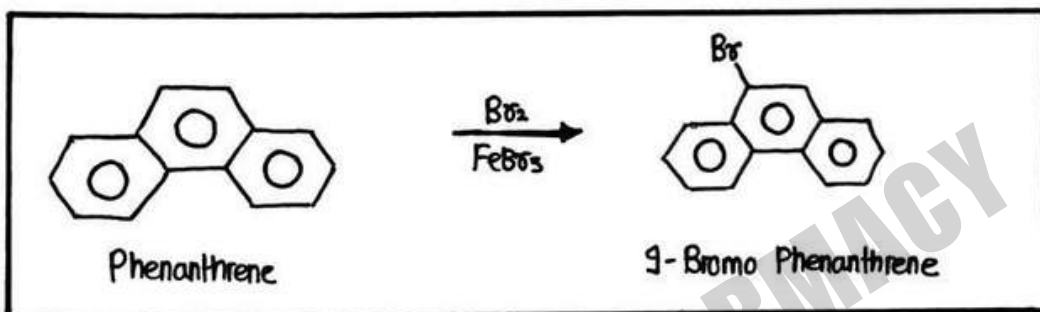


CHEMICAL REACTIONS

Phenanthrene undergoes following chemical reactions :

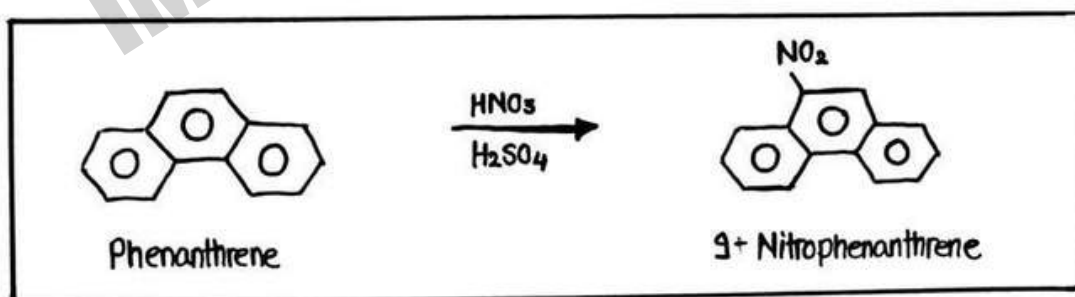
① HALOGENATION

Phenanthrene reacts with Bromine in the presence of FeBr_3 to give 9-bromophenanthrene.



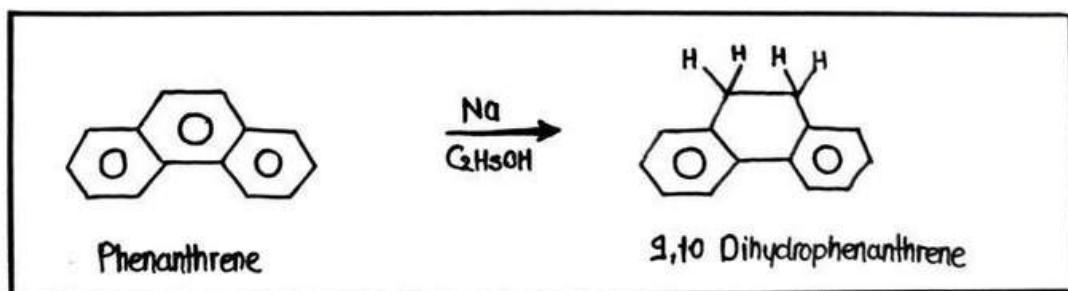
② NITRATION

Phenanthrene undergoes Nitration with concentrated Nitric Acid & Sulphuric Acid to give 9-Nitrophenanthrene.



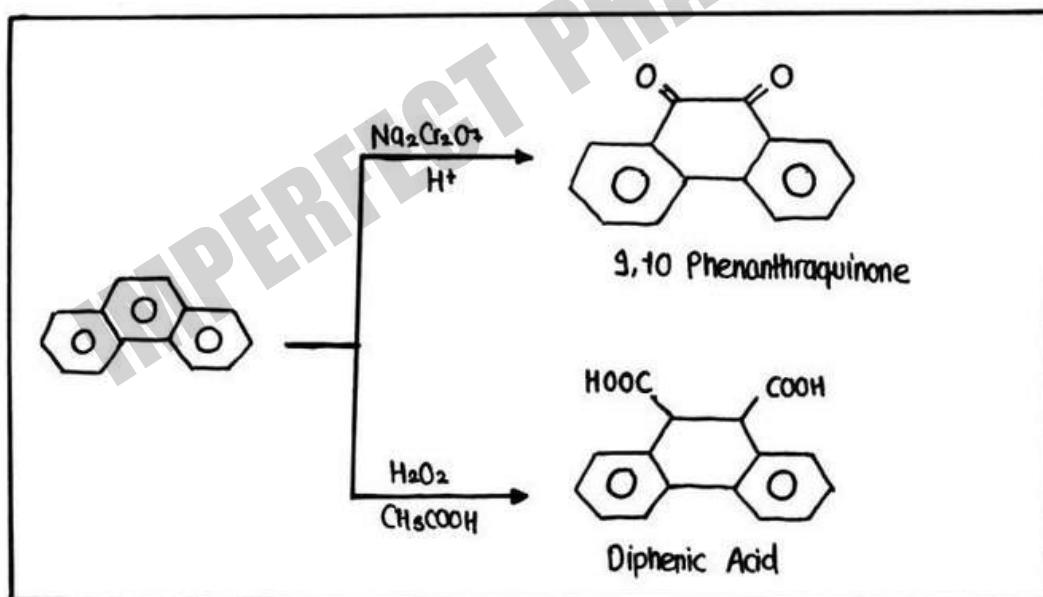
③ REDUCTION

Phenanthrene undergoes reduction in the presence of sodium & ethanol to form 9,10 Dihydrophenanthrene.



④ OXIDATION

Oxidation product of Phenanthrene depends on oxidizing agent.



USES OF PHENANTHRENE

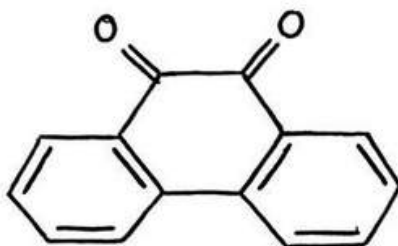
- It is used in the manufacturing of Pesticides & dyes..
- It is used in the production of Jet Fuel.
- It can be used in the synthesis of Morphine, Caffeine etc.
- It is used as Anticancer Agent.
- It is used as Antimalarial drugs.
- It is also used as Antioxidant & Antimicrobial

IMPERFECT PHARMACY

DERIVATIVES

The most important derivative of Phenanthrene is Phenanthraquinone.

PHENANTHRAQUINONE

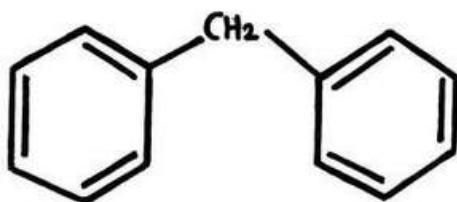


USES

- It is used in the synthesis of various dyes.
- It is used as precursor for synthesis of various organic compounds.
- It is also used as Antimicrobial & Anticancer Agent.
- It can also be used as redox indicator in Analytical Chemistry.

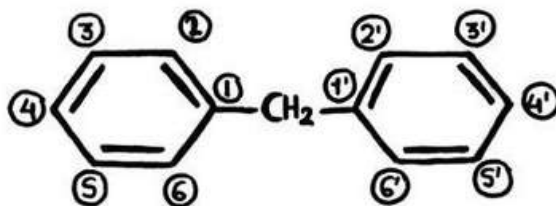
DIPHENYL METHANE

- Diphenyl Methane is an organic compound consist of Methane where two hydrogen atoms are replaced by two hydrogen atoms Phenyl Groups.
- It is a member of isolated ring hydrocarbons under the class of Polynuclear Hydrocarbons.
- It is also known as Benzhydryl.



PHYSICAL & CHEMICAL PROPERTIES

- Its Chemical formula is C₁₃H₁₂.
- It is crystalline solid.
- Its Melting Point is 22-24°C.
- Its boiling point is 264°C.
- It is insoluble in water & soluble in organic solvents.

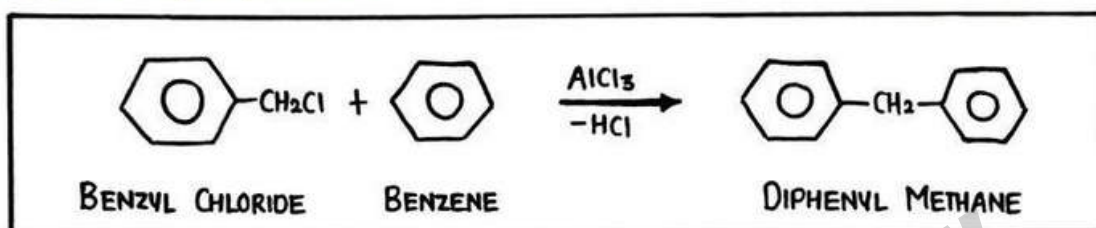


SYNTHESIS

Diphenyl Methane is synthesized by following methods :

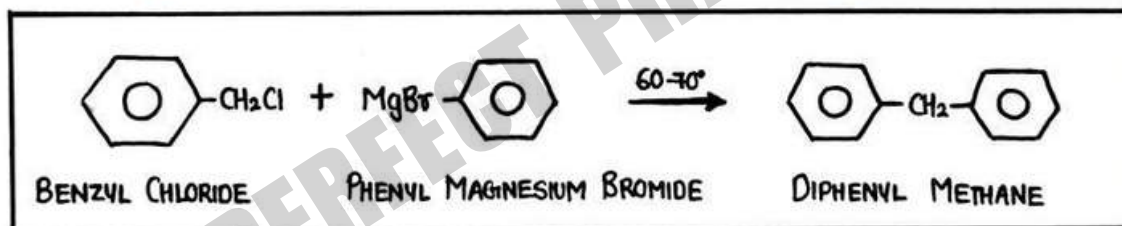
① FRIEDEL CRAFT'S CONDENSATION

When Benzyl Chloride reacts with benzene in the presence of AlCl_3 , it yields Diphenylmethane.



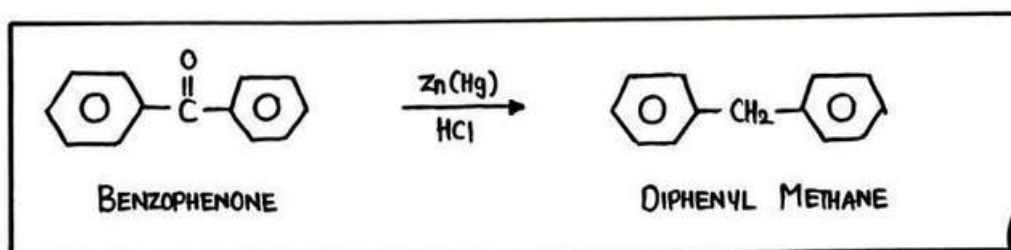
② FROM GRIGNARD REAGENT

Phenyl Magnesium Bromide reacts with Benzyl Chloride to give Diphenyl Methane.



③ WOLF - KISHNER REACTION

Benzophenone reduced to Diphenyl methane through Clemmensen Reduction.

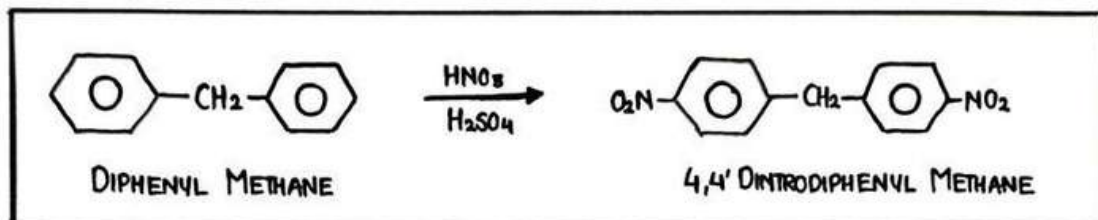


CHEMICAL REACTIONS

Diphenyl Methane undergoes following chemical reactions :

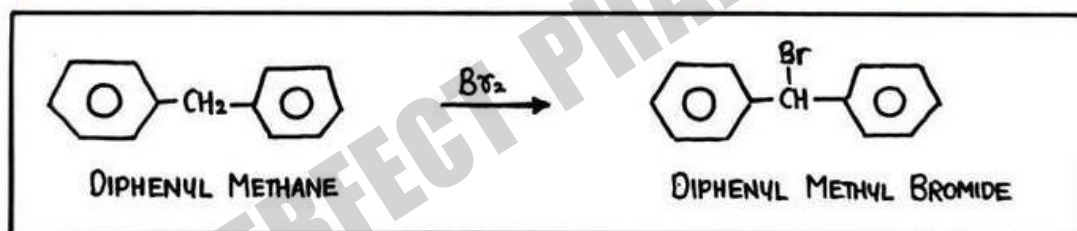
① NITRATION

Diphenyl Methane reacts with conc. HNO_3 to form 4,4' Dinitro-Diphenyl Methane.



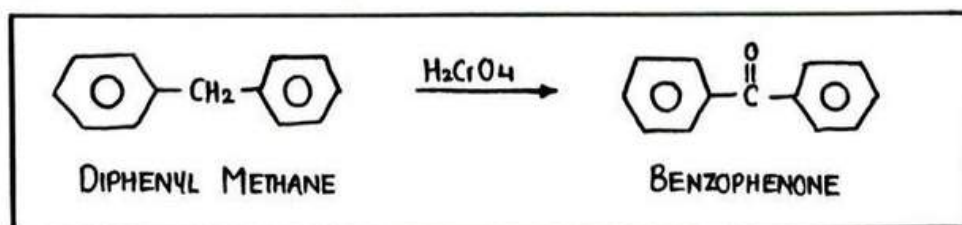
② BROMINATION

Diphenyl Methane reacts with Bromine to form Diphenyl Methyl Bromide.



③ OXIDATION

Diphenyl Methane undergoes oxidation to form Benzophenone



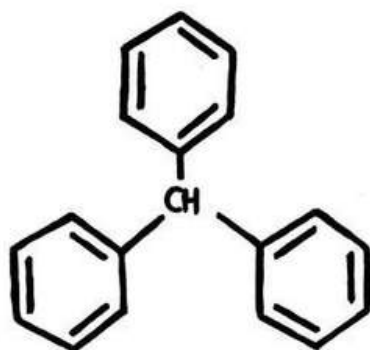
USES OF DIPHENYL METHANE

- It is used for manufacturing of soaps, Pesticides & Insecticides.
- It is also used as Jet Fuels.
- It is used for synthesis of various dyes.
- It is used as Antiulcer Agent.
- It is used as Antihistamine Agent.
- It is also used as Anti-Anxiety Drugs.

IMPERFECT PHARMACY

TRIPHENYL METHANE

- Triphenyl Methane is an organic compound in which 3 hydrogen atoms of Methane are replaced by Phenyl Groups.
- It is a part of isolated ring hydrocarbons under the class of Polynuclear Hydrocarbons.



PHYSICAL & CHEMICAL PROPERTIES

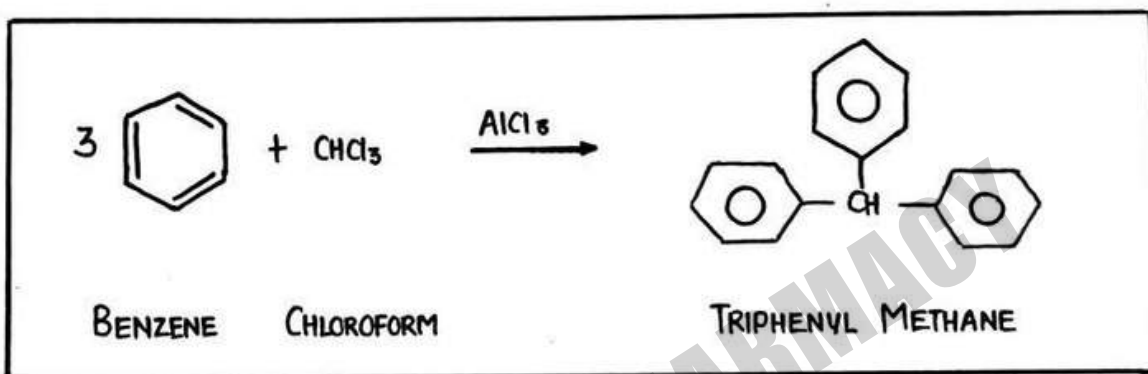
- Its chemical formula is $C_{19}H_{16}$.
- It is a colourless solid.
- Its Melting Point is $92-94^{\circ}\text{C}$.
- Its boiling point is 359°C .
- It is insoluble in water but soluble in organic solvents.

SYNTHESIS

Triphenyl Methane is synthesized by following reactions :

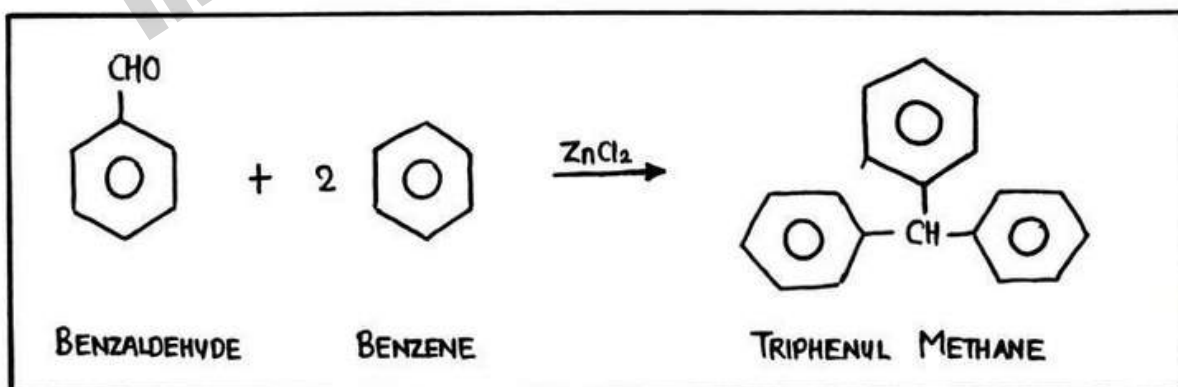
① FRIEDEL CRAFT'S REACTION

3 Molecules of Benzene reacts with Chloroform to form Triphenyl Methane.



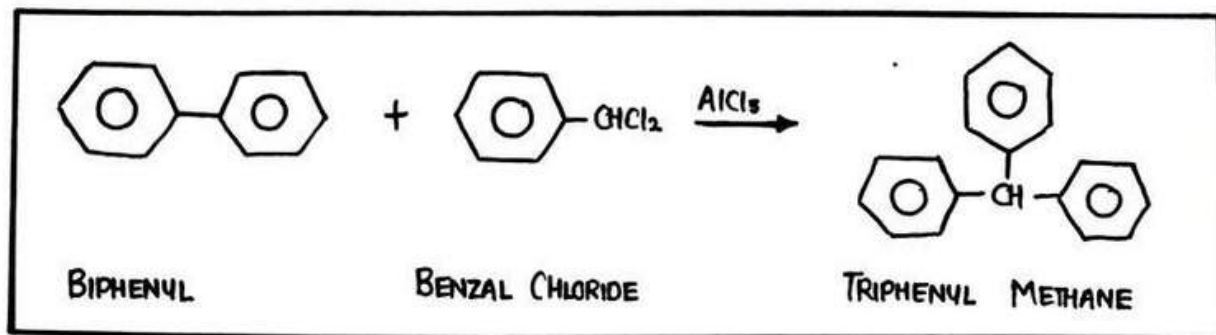
② FROM BENZALDEHYDE

Benzaldehyde reacts with 2 molecules of benzene in the presence of $ZnCl_2$ to yield Triphenyl Methane



③ FROM BIPHENYL

Biphenyl reacts with Benzal chloride to form Triphenyl Methane.



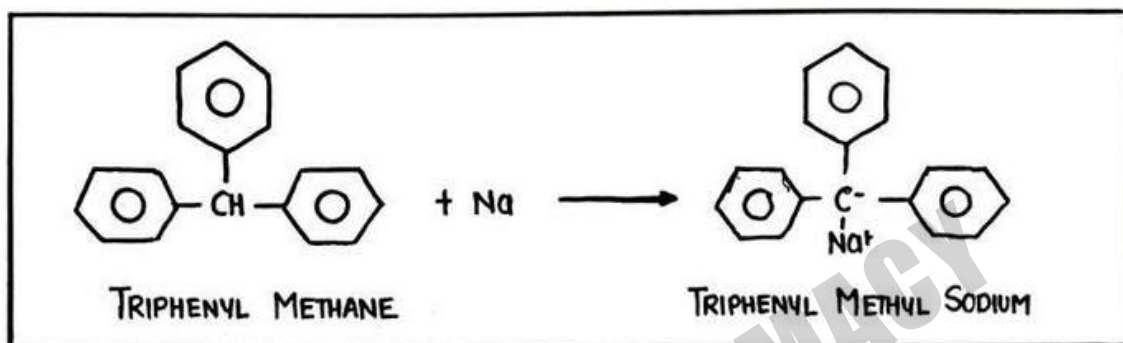
IMPERFECT PHARMACY

CHEMICAL REACTIONS

Triphenyl Methane undergoes following chemical reactions :

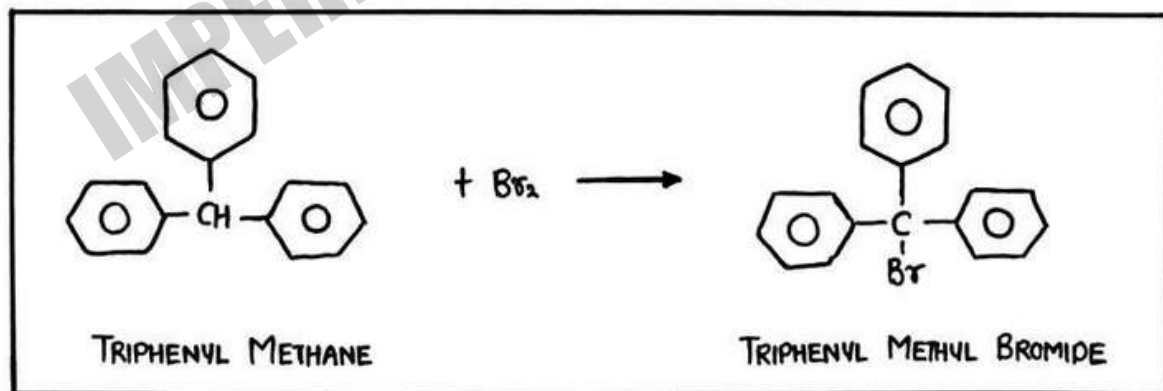
① REACTION WITH SODIUM

Triphenyl Methane reacts with sodium to give Triphenyl Methyl Sodium.



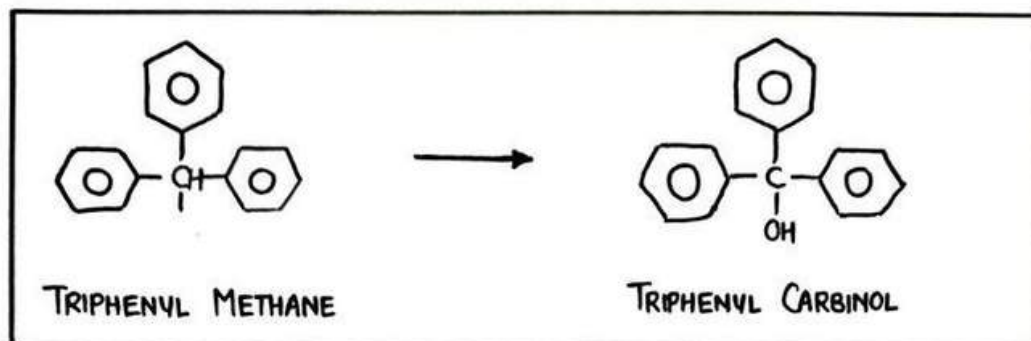
② BROMINATION

Triphenyl Methane reacts with Bromine to yield Triphenyl Methyl Bromide.



③ OXIDATION

Triphenyl Methane undergoes oxidation to form Triphenylcarbinol.



USES OF TRIPHENYL METHANE

- It is used for synthesis of various dyes.
- They also possess Antibacterial & Antifungal properties.
- They are also used as Disinfectants.
- It is also used as Antimicrobial Agent.

THANK YOU

FOR CHOOSING IMPERFECT PHARMACY AS YOUR STUDY PARTNER



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