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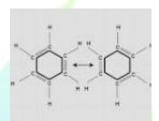


BPHARM 3RD SEMESTER MODEL QUESTIONS WITH ANSWERS

POC -II

Questions with Answers(Answer 1 out of 2) 1.Long (1x10)

1.Explain resonance & Kekule's structure of Benzene.



Benzene is best described by a resonance hybrid structure, not by Kekulé's single alternating double and single bond structure. Kekulé's structure is a simplified representation that doesn't fully explain benzene's unique properties like its stability and equal bond lengths. The resonance hybrid accounts for the delocalization of electrons within the ring, making all carbon-carbon bonds equivalent and more stable.

Kekulé's Structure:

- Kekulé initially proposed that benzene had a ring structure with alternating single and double bonds.
- This structure simplified benzene's representation and was a step forward in understanding organic compounds.
- However, it didn't account for benzene's actual bond lengths being equal, which lie between single and double bond lengths.

Resonance Hybrid:

The resonance hybrid describes benzene as a combination of multiple Kekulé-like structures, where the electrons are not localized in specific double bonds.



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- Instead, the pi electrons are delocalized throughout the entire ring, resulting in a continuous electron cloud.
- This delocalization contributes to benzene's stability and its tendency to undergo substitution reactions rather than addition reactions.
- The resonance hybrid is often represented with a circle within the hexagon to signify the delocalization of electrons.

2. Explain in detail about chemical properties of Phenol.

Phenol is highly reactive toward electrophilic aromatic substitution. The enhanced nucleophilicity is attributed to donation pi electron density from O into the ring. Many groups can be attached to the ring, via halogenation, acylation, sulfonation, and related processes.

Phenol is so strongly activated that bromination and chlorination lead readily to polysubstitution

Aqueous solutions of phenol are weakly acidic and turn blue litmus slightly to red. Phenol is neutralized by <u>sodium hydroxide</u> forming sodium phenate or phenolate, but being weaker than <u>carbonic acid</u>, it cannot be neutralized by <u>sodium bicarbonate</u> or <u>sodium</u> carbonate to liberate carbon dioxide.

$$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$$

When a mixture of phenol and <u>benzoyl chloride</u> are shaken in presence of dilute <u>sodium hydroxide</u> solution, <u>phenyl benzoate</u> is formed. This is an example of the Schotten–Baumann reaction:

$$C_6H_5COCI + HOC_6H_5 \rightarrow C_6H_5CO_2C_6H_5 + HCI$$

Phenol is reduced to <u>benzene</u> when it is distilled with <u>zinc</u> dust or when its vapour is passed over granules of zinc at 400 °C:

$$C_6H_5OH + Zn \rightarrow C_6H_6 + ZnO$$

When phenol is treated with <u>diazomethane</u> in the presence of <u>boron</u> <u>trifluoride</u> (BF₃), <u>anisole</u> is obtained as the main product and nitrogen gas as a byproduct.

$$C_6H_5OH + CH_2N_2 \rightarrow C_6H_5OCH_3 + N_2$$

Phenol and its derivatives react with iron(III) chloride to give intensely colored solutions containing phenoxide complexes.

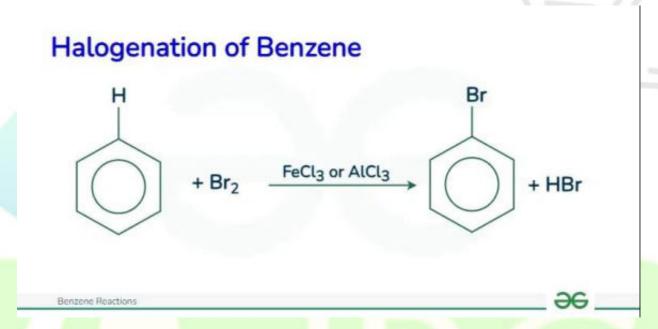
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II.Short Answer (Answer 2 out of 4)

2x5=10

1. Explain halogenation of Benzene.



Halogenation of benzene is an electrophilic aromatic substitution reaction where a hydrogen atom on the benzene ring is replaced by a halogen atom (e.g., chlorine, bromine). This reaction typically occurs in the presence of a catalyst, such as a Lewis acid (like aluminum chloride or iron).

2. Write notes on Friedel -Crafts Alkylation & Friedel Crafts Acylation of Benzene.

Friedel-Crafts Alkylation

Friedel-Crafts Alkylation refers to the replacement of an aromatic proton with an alkyl group. This is done through an electrophilic attack on the aromatic ring with the help of a carbocation. The Friedel-Crafts alkylation reaction is a method of generating alkylbenzenes by using alkyl halides as reactants.



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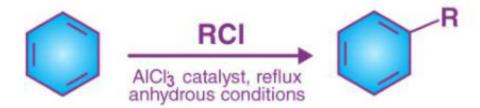


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The Friedel-Crafts alkylation reaction of benzene is illustrated below.





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A Lewis acid catalyst such as FeCl₃ or AlCl₃ is employed in this reaction in order to form a carbocation by facilitating the removal of the halide. The resulting carbocation undergoes a rearrangement before proceeding with the alkylation reaction.

Mechanism

The Friedel-Crafts alkylation reaction proceeds via a three-step mechanism.

Step 1

The <u>Lewis acid</u> catalyst (AlCl₃) undergoes reaction with the alkyl halide, resulting in the formation of an electrophilic carbocation.

Step 2

The carbocation proceeds to attack the aromatic ring, forming a cyclohexadienyl cation as an intermediate. The aromaticity of the arene is temporarily lost due to the breakage of the carbon-carbon double bond.

Step 3

The deprotonation of the intermediate leads to the reformation of the carbon-carbon double bond, restoring aromaticity to the compound. This proton goes on to form hydrochloric acid, regenerating the AlCl₃ catalyst.

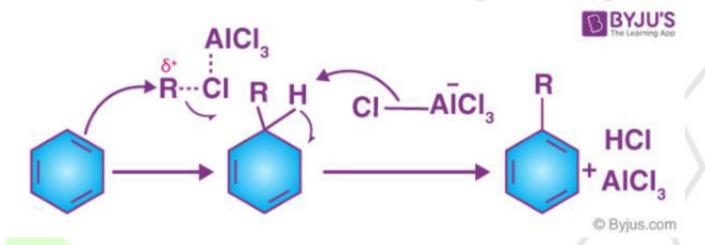


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An illustration describing the mechanism of the Friedel-Crafts alkylation reaction is provided above.

Friedel-Crafts Alkylation

Friedel-Crafts Acylation

The Friedel-Crafts acylation reaction involves the addition of an acyl group to an aromatic ring. Typically, this is done by employing an acid chloride (R-(C=O)-CI) and a Lewis acid catalyst such as AlCI₃. In a Friedel-Crafts acylation reaction, the aromatic ring is transformed into a ketone. The reaction between benzene and an acyl chloride under these conditions is illustrated below.



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An acid anhydride can be used as an alternative to the acyl halide in Friedel-Crafts acylations. The halogen belonging to the acyl halide forms a complex with the Lewis acid, generating a highly electrophilic acylium ion, which has a general formula of RCO⁺ and is stabilized by <u>resonance</u>.

Mechanism

Friedel-Crafts acylations proceed through a four-step mechanism.

Step 1

A reaction occurs between the Lewis acid catalyst (AlCl₃) and the acyl halide. A complex is formed and the acyl halide loses a halide ion, forming an acylium ion which is stabilized by resonance.

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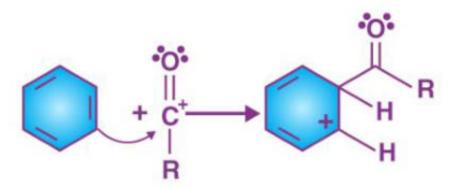




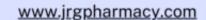
Step 2

The acylium ion (RCO+) goes on to execute an electrophilic attack on the aromatic ring. The aromaticity of the ring is temporarily lost as a complex is formed.





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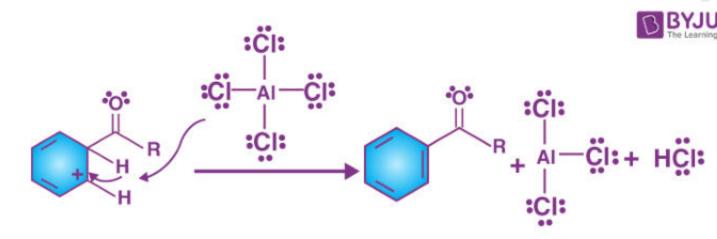






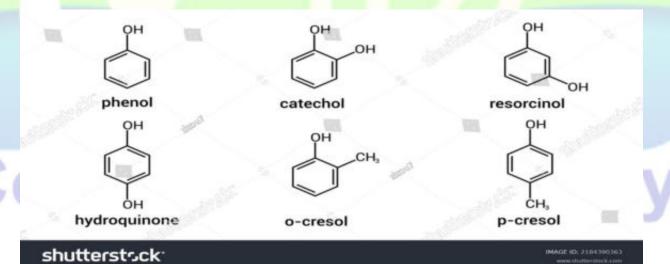


The intermediate complex is now deprotonated, restoring the aromaticity to the ring. This proton attaches itself to a chloride ion (from the complexed Lewis acid), forming HCl. The AlCl₃ catalyst is now regenerated.



Thus, the required acyl benzene product is obtained via the Friedel-Crafts acylation reaction.

3. Write structure & uses of Cresols & Resorcinol.



Cresol is a compound derived from phenol, with a methyl group added to the ring, while resorcinol is a benzene ring with two hydroxyl groups in the 1,3

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(meta) positions. Cresols are used as disinfectants, antiseptics, and in the production of other chemicals, while resorcinol is used for skin conditions like acne, seborrheic dermatitis, and in manufacturing resins.

Cresol:

Structure:

Cresol is a derivative of phenol, meaning it's a benzene ring with a hydroxyl group (OH) substituted with a methyl group (CH3). There are three isomers: o-cresol, m-cresol, and p-cresol, depending on the position of the methyl group on the benzene ring.

Uses:

- Disinfectant and Antiseptic: Cresols are effective against bacteria and other microorganisms, making them useful for disinfecting surfaces and in medical applications.
- **Industrial Applications:** They are used in the production of other chemicals, such as plastics, dyes, and pesticides.
- Other Uses: Cresol can also be found in paint removers, wood preservatives, and as intermediates in pharmaceutical and other chemical manufacturing.

Resorcinol:

Structure:

Resorcinol is a benzene ring with two hydroxyl groups (OH) attached in the 1,3 (meta) positions. Its chemical formula is C6H6O2.

Uses:

- Skin Conditions: Resorcinol is used in topical medications to treat skin conditions like acne, seborrheic dermatitis, eczema, and psoriasis. It works by removing hardened, scaly, or rough skin.
- Manufacturing: Resorcinol is used in the production of resins, particularly in the rubber industry and for high-quality wood adhesives.
- Other Uses: It can also be used as an analytical reagent and as a disinfectant in certain pharmaceutical products.

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4. Write in detail about Aromatic Amine.

Preparation of Aromatic amines

Aromatic amines can be prepared by reduction of Aromatic nitro compound.

Example- Nitrobenzene converted to aniline in presence of tin(Sn), concentrated HCl and NaOH.

C₆H₅NO₂ + Concentrated (HCI +NaOH)(In presence of Sn)----→C₆H₅NH₂

Chemical Properties

- Aromatic amines are basic in nature due to the presence of two nonbonded electrons on the nitrogen atom.
- · Aromatic amines and acid form salt.
- Aromatic amines denote electron pairs.

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Reactions of Aromatic Amine

- · Primary aromatic amine, aniline forms stable Diazonium salts at 0 degree temperature in presence of HCl and NaNO₂.
- Secondary Aromatic amines with nitrous acid in presence of HCl and NaNO2 form nitrosamine.

(CH₃)₂NH + HCl + NaNO₂ (HONO/H₂O)----→ (CH₃)₂N-N=O Dimethylamine N-Ntrosodimethylamine

- Aromatic amines with Hydrochloric acid to form Salt as amines are basic in nature. NaNO₂+Ar-NH₂+2HCl →Ar-N₂Cl +NaCl+2H₂O
- The reaction of benzenesulphonyl chloride yields N- ethylbenzenesulphonyl amide when reacted with primary amine. $C_6H_6SO_2CI + NH_2-C_2H_6 \rightarrow C_6H_6SO_2-NH_2C_2H_6$
- Secondary amine and benzene sulphonyl chloride form N,N- Diethyl Benzene Sulphonamide. $C_8H_6SO_2CI + C_2H_6-NH-C_2H_6 \rightarrow C_8H_6SO_2-NH(C_2H_6)_2$
- Aniline in reaction with bromine water forms 2,4,6 tribromoaniline.

 $C_8H_5NH_2 + Br_2/H_2O \rightarrow C_8H_4Br_3N$

III. Very short type of questions. (5x2=10)

1. What is Aromaticity?

Aromaticity is a chemical property describing a specific type of enhanced stability found in certain cyclic, planar compounds containing conjugated pi bonds. This stability arises from the delocalization of pi electrons across the ring system, resulting in a uniform distribution of electrons and increased resistance to chemical reactions.

Importance of Aromaticity:

Stability:

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Aromatic compounds are generally more stable than their non-aromatic counterparts due to the delocalization of pi electrons.

Chemical Reactions:

Aromatic compounds tend to undergo substitution reactions rather than addition reactions because the delocalized pi electron system is less reactive.

Biological Importance:

Many biologically important molecules, such as amino acids, nucleotides, and vitamins, contain aromatic rings.

2.Explain Huckel's rule.

Hückel's rule is a principle in organic chemistry used to predict whether a cyclic, planar molecule with a continuous ring of π -electrons will be aromatic or not. It states that a molecule is aromatic if it contains $4n + 2\pi$ electrons, where n is an integer (0, 1, 2, 3...).

3.Out of ortho & para nitrophenols, which one has higher boiling point & why?

Para nitro phenol has higher boiling point due to the formation of inter - molecular hydrogen bonding.

4.On reaction with Sodium Hydroxide phenol forms salts where as alcohol does not, why?

Because phenols are sufficiently acidic in nature & react with NaOH to form their sodium salt. Where as alcohols are practically neutral in character.

5. Why N-Alkylamines are stronger base than aniline?

This is due to the presence of electron releasing alkyl groups on nitrogen atom. So the electron pair is more available for sharing than the electron pair in aniline . Moreover the substituted anilinium ion formed on protonation of these amines gets stabilized due to the dispersal of the positive charge by alkyl group.



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Model Questions & Answers B. Pharmacy, 3rd Semester

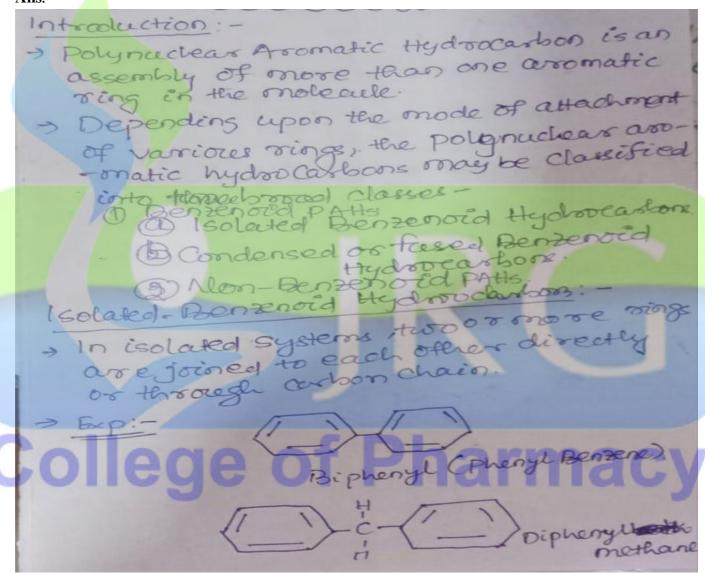
Sub: Ph. Organic Chemistry-II, Sub. Code: BP301T **Unit-IV** (Polynuclear Hydrocarbons)

Long Answer Type Questions

(10 marks)

Q1. Define and classify Polynuclear hydrocarbons. Enumerate the synthesis, reactions and medicinal uses of Naphthalene.

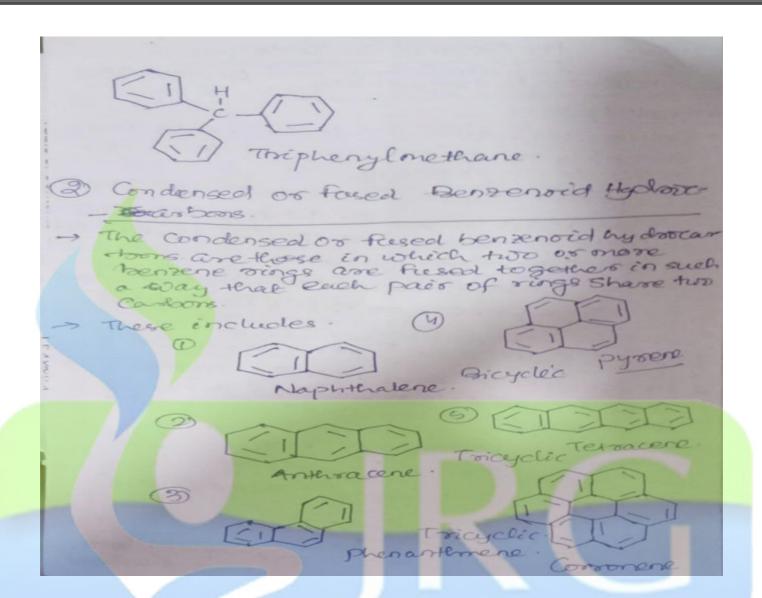
Ans.





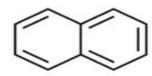
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Naphthalene:

- Naphthalene is the simplest example of polynuclear hydrocarbon containing benzene ring fused at other position.
- It is obtained from crude oil or coil tar it can be produced when the things burn naphthalene is found in smoke of forest fire, car exhaust etc.
- Poly nuclear hydrocarbon and their derivative such as naphthalene numbering should be start from carbon of fused carbon in the ring.



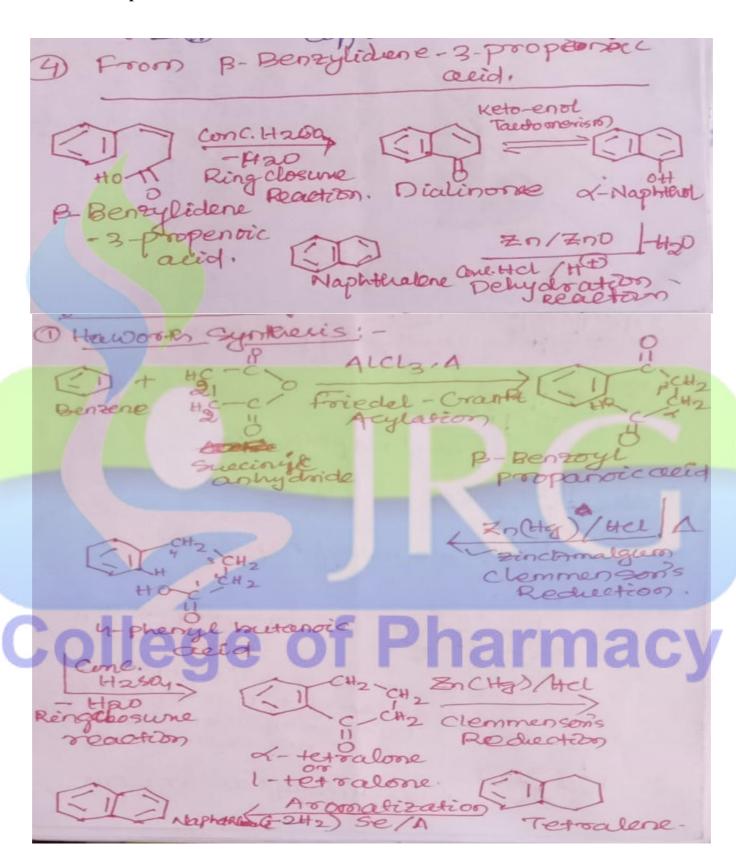
(Naphthalene)



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Method of Preparations:



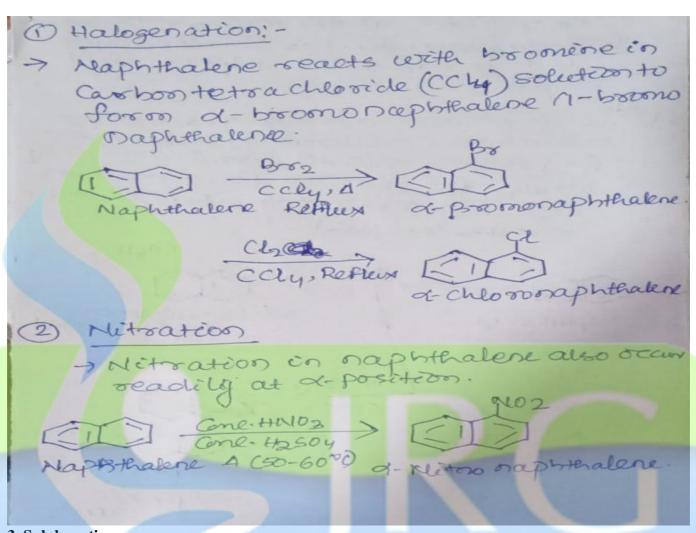


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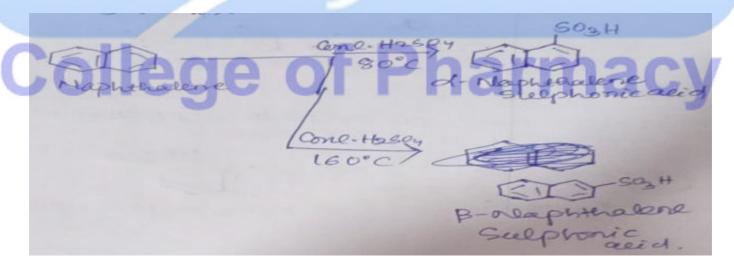


Reactions of Naphthalene: -

Electrophilic Aromatic Substitution Reactions: -



3. Sulphonation: -

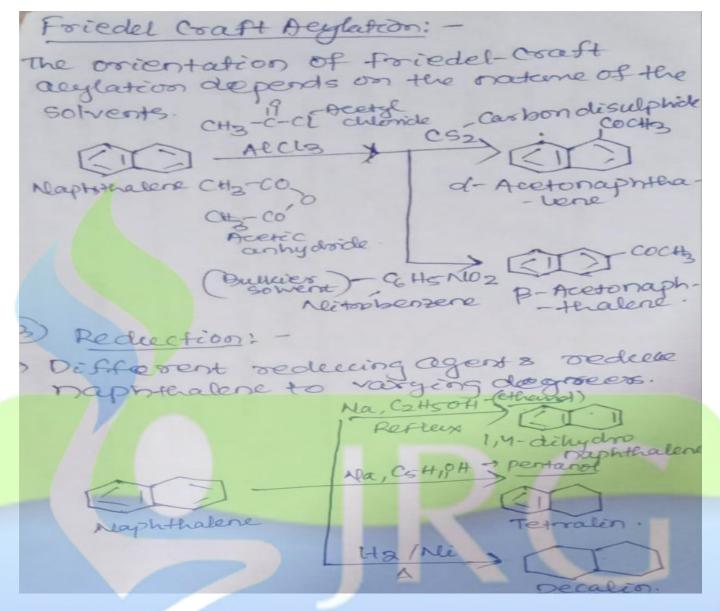


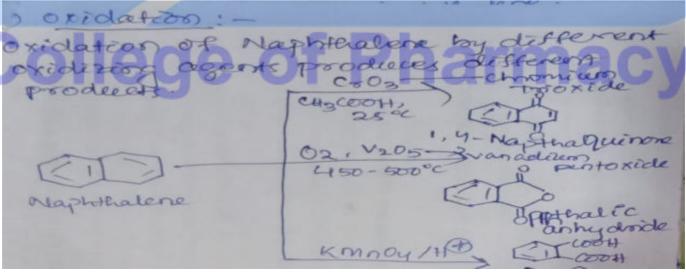
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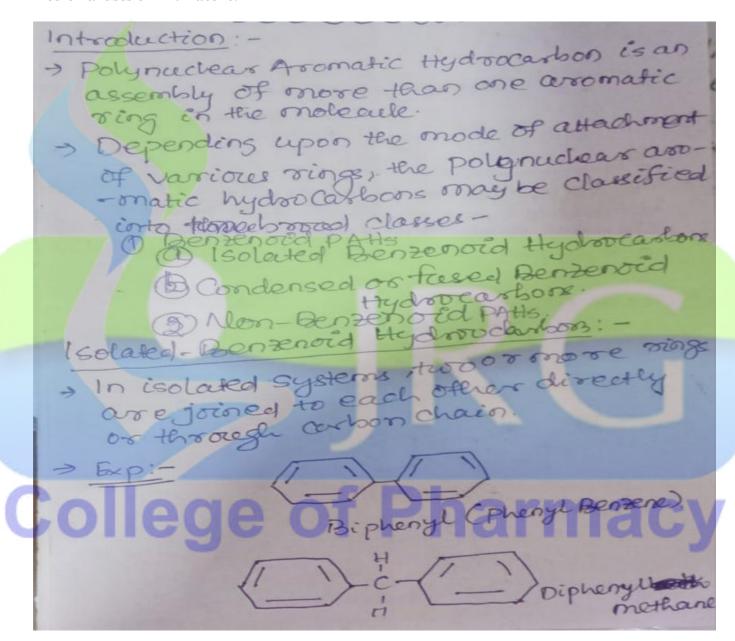
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Medicinal Uses:

- Primarily used for synthesis of phthalic anhydride.
- Used in synthesis of plastics, insecticides and fungicides etc.
- Naphthalene derivatives are used in synthesis of an antimicrobial agent like Naftifine, Terbinafine and antiprotozoal agent such as Atovaquone and Buparvaquone.

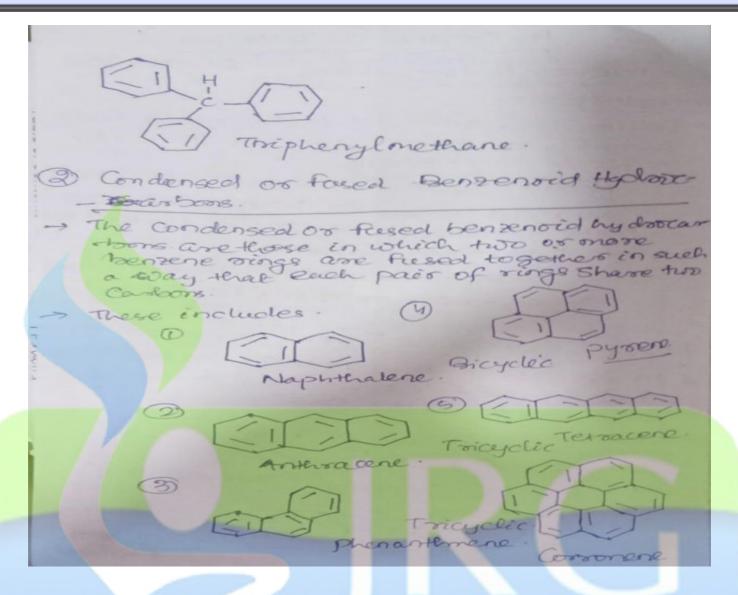
Q2. Define and classify Polynuclear hydrocarbons. Enumerate the synthesis, reactions and medicinal uses of Anthracene.





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Molecular formula C14H10

Anthracene is an example of condensed polynuclear hydrocarbons containing three benzene rings fused with each other in a linear manner.

a- position equivalent to 1,4,5,8

B- position equivalent to 2,3,6,7

y- position equivalent to 9,10

If monosubstitution is carried out in anthracene, three monosubtituted product are obtained, a or 1- substituted. β or 2 substituted and γ or 9 substituted.

Methods of Preparation

Haworth synthesis

It involve mainly four type of reactions-

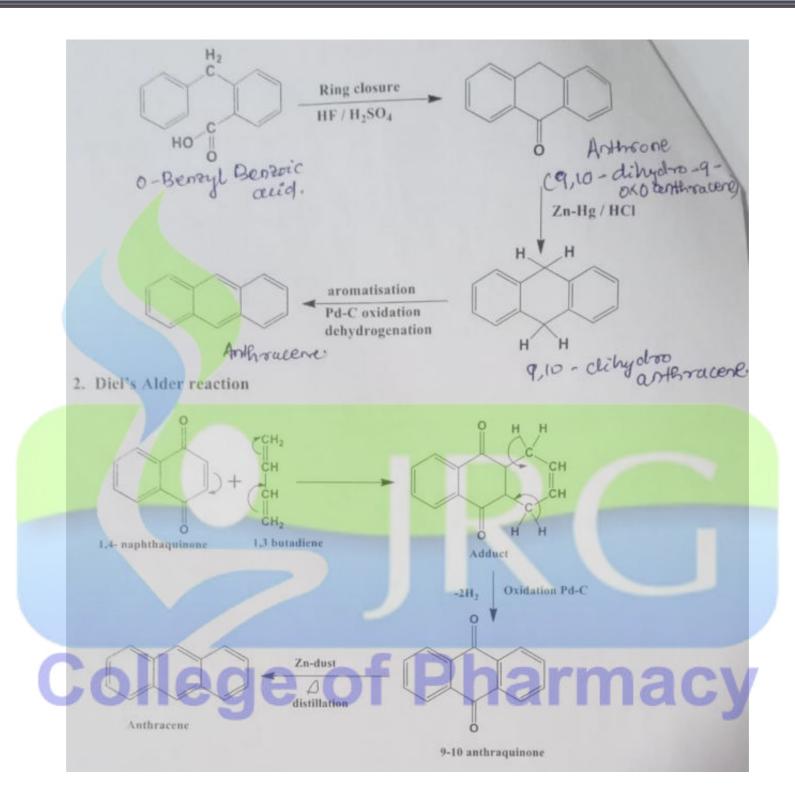
- Friedel craft acylation
- Clemmensen reduction
- Ring closure
- Aromatization

benzyl benzose acid



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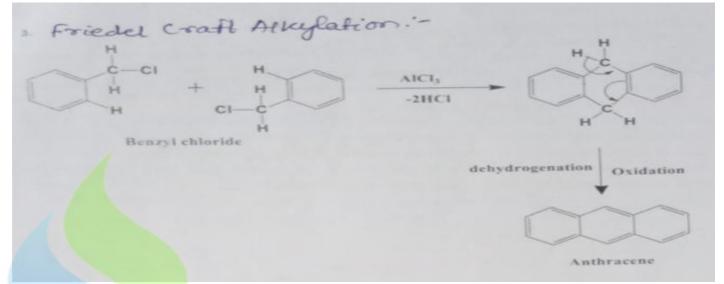




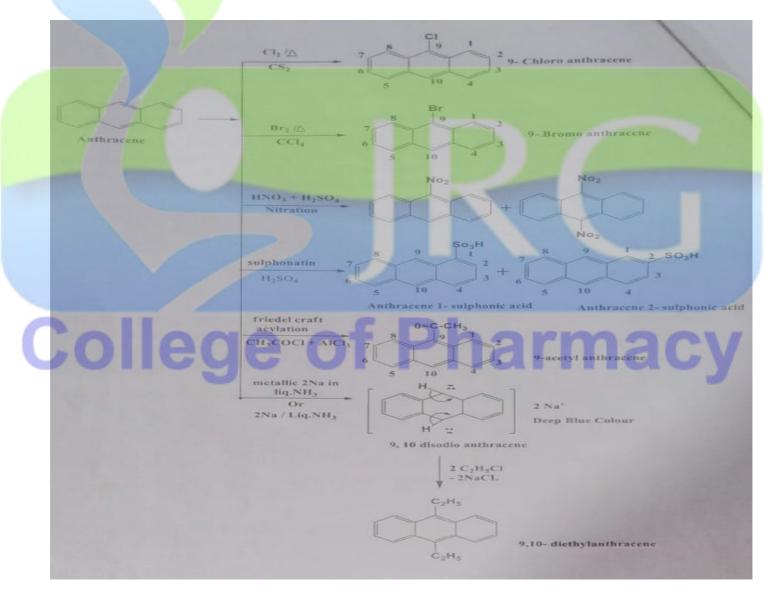


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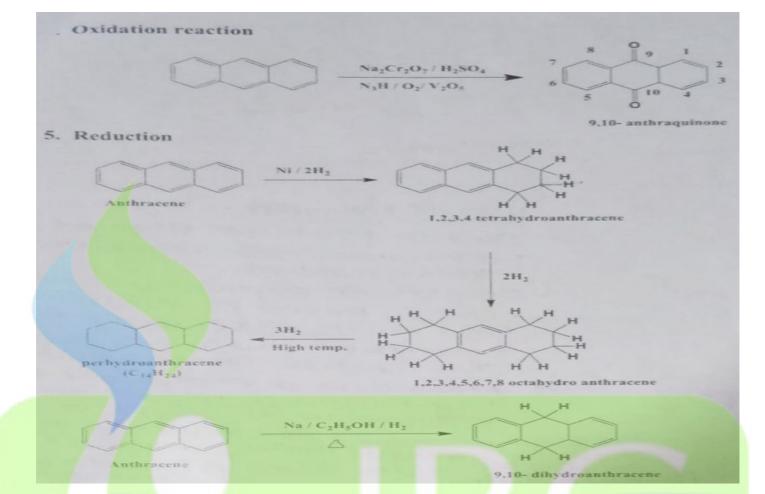
Reactions of Anthracene: -





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Medicinal uses:

- Used in production of wood preservatives, insecticides and coating materials.
- Used in synthesis of antineoplastic agent like Bisantrene and sedative-anxiolytic agent like Benzoctamine.

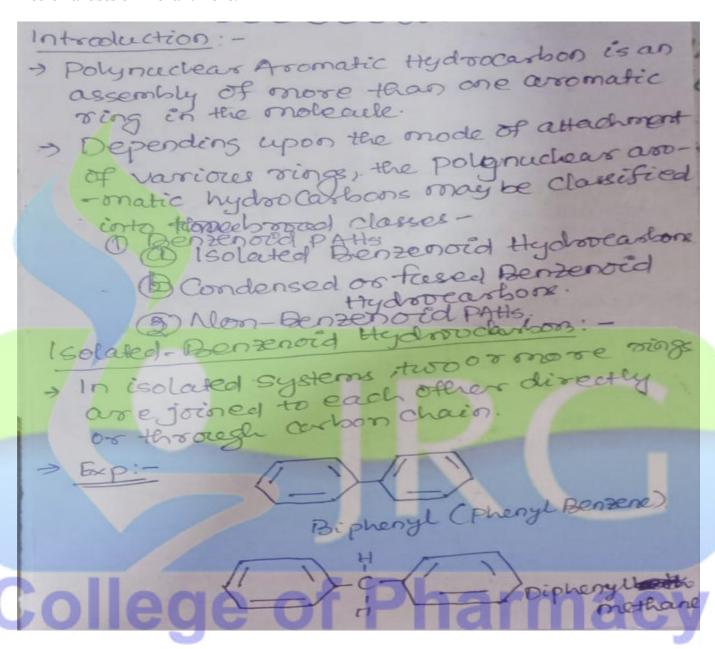
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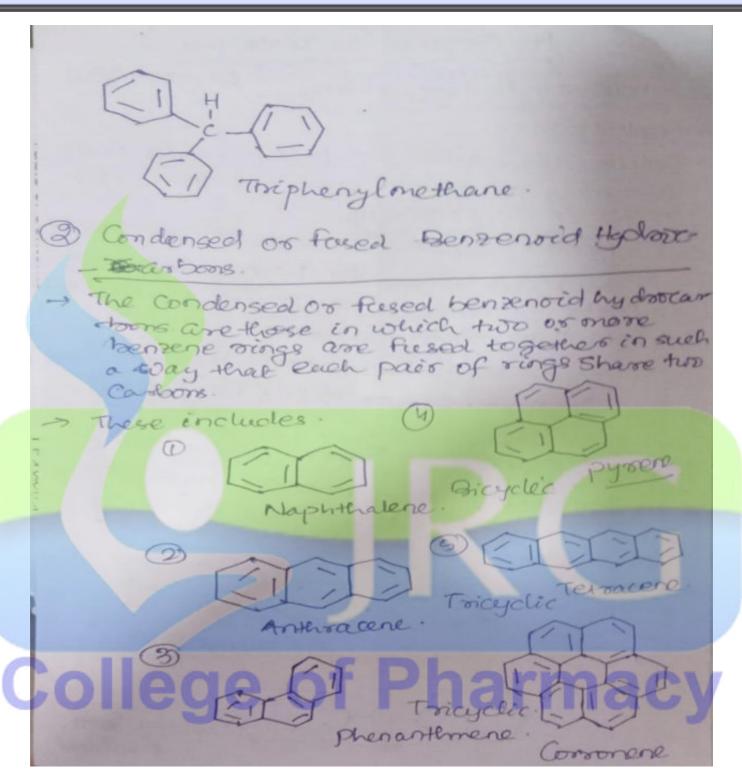
Q3. Define and classify Polynuclear hydrocarbons. Enumerate the synthesis, reactions and medicinal uses of Phenanthrene.





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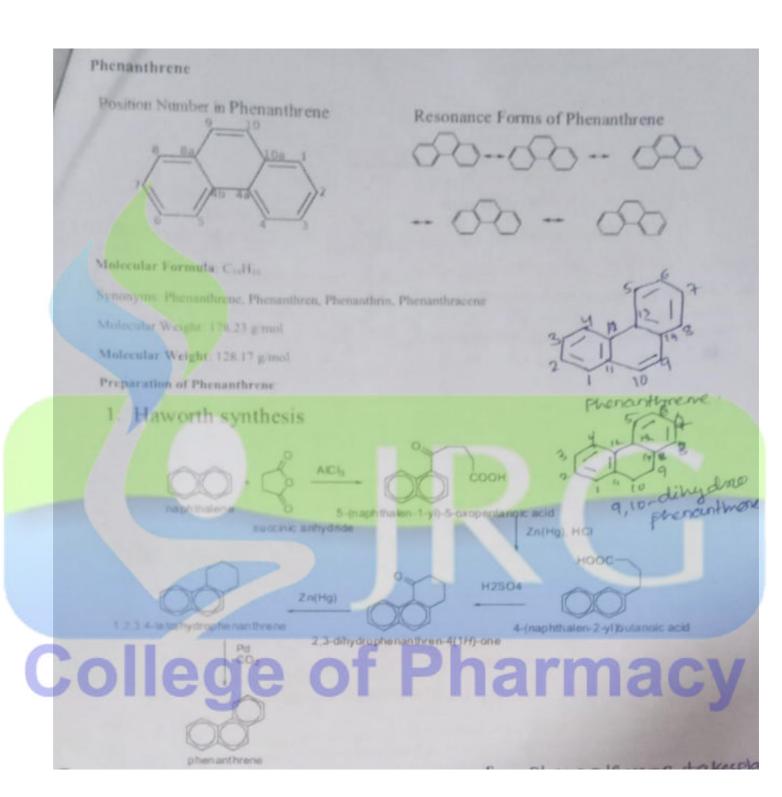






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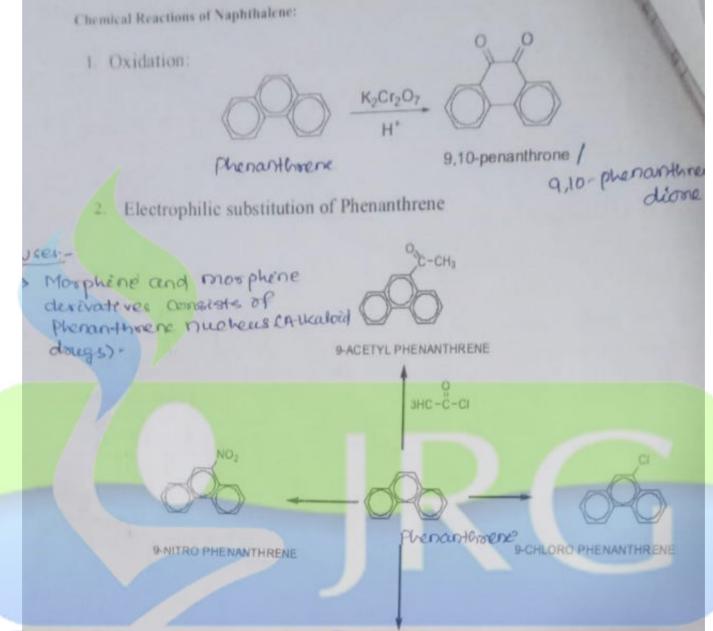






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2-PHENANTHRENE SULPHONIC ACID

Medicinal Uses: Phenanthrene appears as colorless monoclinic crystals with a faint aromatic odor. Solutions exhibit a blue fluorescence. Phenanthrene is a polycyclic aromatic hydrocarbon composed of three fused benzene rings which takes its name from the two terms 'phenyl' and 'anthracene,' It has a role as an environmental contaminant and a mouse metabolite. It is an ortho-fused polycyclic arene, an ortho-fused tricyclic hydrocarbon and a member of phenanthrenes. Used for Synthesis of anthrquinone. Anthraquinone is used in the manufacture of alizarin and several other dyes. Present in Purgative drugs-Senna, Rhubarb, Cascara, Dithrol-Antifungal,

MODEL QUESTION ANSWER SET OF POC II FOR 2ND SESSIONAL EXAM

10×1=10

1.(a)Write about synthetic application of aryl diazonium salt.

Aryl diazonium salts are prepared by reacting an aromatic primary amine with nitrous acid at a temperature between 0-5 °C.

Diazonium salts are very useful intermediates in the synthesis of a number of aromatic compounds. Some of them are as follows.

1. Replacement of Hydrogen:

Synthesis of 1,3,5,-tribromobenzene

2. Replacement by halogen atom:

Synthesis of chlorobenzene

3. Replacement by Cyano group:

Synthesis of p-toluinitrile

4. Replacement by hydroxy group:

Synthesis of o-cresol

(b)Write about chemical properties of aromatic acid.

- Formation of salts through acid-base reactions
- Synthesis of esters by reacting with alcohols
- Conversion into acyl halides via halogenation
- Reduction processes yielding benzyl alcohol
- Removal of the carboxyl group by decarboxylation

1.

1.Salt formation

2.

2.Ester formation

3.

3.Acyl halide formation

4.

4. Reduction to benzyl alcohol

5. Decarboxylation

5.

5×2=10

2. Answer any 2 out of 3

(a) Write about Hydrogenolysis & Saponification reaction of fats & oils.

HYDROGENOLYSIS – In this reaction fats or oil get splits up into glycerol and heigher aliphatic alcohol.

SAPONIFICATION-

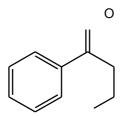
Saponification is a process by which triglycerides are reacted with sodium or potassium hydroxide (lye) to produce glycerol and a fatty acid salt called "soap.

(b)Write about Synthesis of Napthalene.

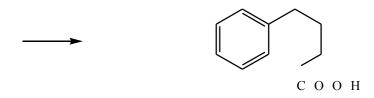
Preparation of Napthalene:

i) From 3-Benzoyl propanoic acid:

When 3-benzoyl propanoicacid is heated with sulphuric acid, α napthol is formed, which on distillation with zinc dust forms naphthalene.



Zn(Hg) Hcl



3-Benzoyl propanoic acid

4-Phenyl butanoic Acid

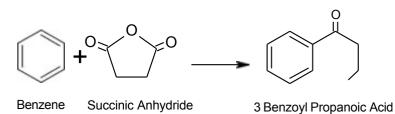
ii) From 4-phenyl-1-butene:

When 4-phenyl 1 butene is passed over red hot calcium oxide naphthalene is formed.

iii) Haworth synthesis:

It involves five steps.

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





3 Benzoyl Propanoic Acid

4 Phenyl Butanoic Acid

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

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

Step V: Tetraline is heated with palladium to yield naphthalene.



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©Write about evidence in favour of Bayer's stain theory.

Postulates of Baeyer's strain theory

Baeyer's strain theory is based on the different assumptions. They are as follows:

- 1. All cycloalkanes are planar or flat, that is, they all lie in the same plane. As a result, the bond angle between the two adjacent carbon atoms of the ring no longer remains 109°28′. The values of this angle differ between different rings. For instance, the cyclopropane ring is an equilateral triangle with a C-C-C angle of 60°.
- 2. Any variation, positive or negative, from the ideal tetrahedral bond angle of 109°28' during ring formation causes a strain in the molecule, making it unsuitable. This bond angle deviation is called Baeyer angle strain or simply angle strain.
- 3. The bigger the deviation from the normal angle, the greater the strain and hence the lower the stability. However, the sign of deviation does not make any difference.
- 4. The more stable a ring system is, the easier it is to synthesize.
- 5. The amount of angle strain can be expressed in term of the valence angle deviation 'd' which can be mathmatically calculated as,

angle strain (or angle of deviation) d = 1/2 ($109^{\circ}28' - \alpha$) where α is the bond angle of various cycloalkanes. The factor '1/2' indicates that the deviation of the angle strain has been assumed to be equally shared between two bonds.

Relative stabilities of cycloalkanes

Cyclopropane

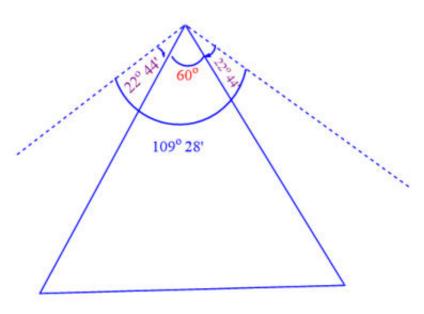
Three carbon atoms make up the corners of an equilateral triangle in cyclopropane. Hence, the C-C-C bond angle of cyclopropane is 60°. This means that a normal tetrahedral angle of 109°28′ between any two bonds is compressed to 60° and each bond is pulled in by angle strain.

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Angle of deviation or angle strain = 1/2 ($109^{\circ}28' - 60^{\circ}$)

$$= \frac{1}{2} \times 49^{\circ}28' = 24^{\circ}28'$$

The value of 24°28' then represent the angle strain through which each bond bends from normal tetrahedral direction.

Cyclobutane

Four carbon atoms make up the corners of the square in cyclobutane. Hence, the C-C-C bond angle of cyclopropane is 90°. This means that a normal tetrahedral angle of 109°28' between any two bonds is compressed to 90° and each bond is pulled in by angle strain.

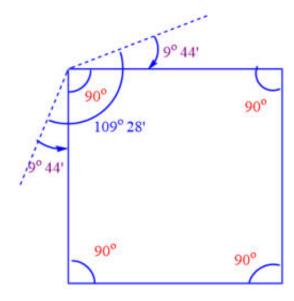
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Angle of deviation or angle strain = 1/2 ($109^{\circ}28' - 90^{\circ}$)

$$= \frac{1}{2} \times 19^{\circ}28' = 9^{\circ}44'$$

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The value of 9°44′ then represents the angle strain through which each bond bends from the normal tetrahedral direction.

2×5=10

- 3.Answer all.
- (a) Write physical properties of aromatic acid.
- 1. Aromatic acids are colourless solid.
- 2.All aromatic acid are insoluble in water
- 3. The boiling point of aromatic acid is high.
- 4. The melting point of aromatic acid is high.

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(b)Write difference between fats & oils.

Aspect		Fats	Oils
State at Room Temp		Solid	Liquid
Source Usually from animals (e.g. lard)		ls (e.g., butter,	Usually from plants (e.g., olive oil, sunflower oil)
		stly saturated fats	Mostly unsaturated fats
Melting Po	oint	Higher melting p	oint Lower melting point
Storage to	Less prone More prone to oxidation (rancidity) (especially polyunsaturated oils)		
Examples		er, ghee, lard	Olive oil, coconut oil, canola oil
Health Impact	,		Often considered healthier (especially unsaturated oils)

©Write example of polynuclear hydrocarbon with structure.

POLYNUCLEARHYDROCARBONS:-

A polynuclear aromatic hydrocarbon is a <u>hydrocarbon</u> made up of fused <u>aromatic</u> ring molecules. These rings share one or more sides and contain delocalized electrons. Another way to consider PAHs is molecules made by fusing two or more benzene rings. Polynuclear aromatic hydrocarbon molecules contain only <u>carbon</u> and <u>hydrogen atoms</u>.

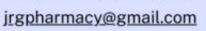


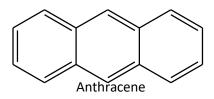
Napthalene



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(d)Write about nomenclature of cycloalkane with structure.









Cyclopropane

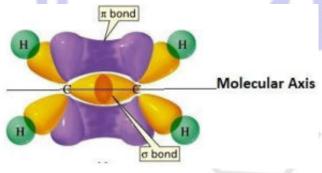
Cyclobutane

Cyclopentane

Cyclohexane

(e)Write about Coulson -Moffit's modification.

Coulson and Moffitt's modification (Bent bond/Banana bond) Coulson-Moffitt modify Baeyer strain theory to show the actual position of carbon-carbon bonds in cyclopropane, which somewhat relieves the strain on C-C bonds. So, to satisfy regular tetrahedral geometry (1090 28') and equilateral triangle angle (600) they introduce a new type of bond called banana bond/bent bond which is intermediate between sigma bond and pi-bond in case of overlapping. What is this Bent bond: Sigma bonds have head-on or end-to-end overlapping. The hybrid orbitals including the intersection bonding region are present equally on both side of the molecular axis. But in case of pi-bonds the lateral or sidewise overlapping of p-orbitals occur and here the bonding intersection area is totally out of the molecular axis.



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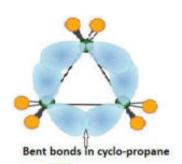


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In Bent-bond (usually they are sigma bonds) the hybrid orbitals and intersection bonding area are not present equally on the both side of molecular axis. The bonds are bent towards the direction of angle strain. So they are somewhat more unstable than sigma bonds and less unstable than pi bonds.

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