

D.K.M. COLLEGE FOR WOMEN (AUTONOMOUS), VELLORE-1.

I SEMESTER

ORGANIC CHEMISTRY-I

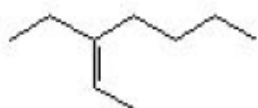
UNIT-I STEREOCHEMISTRY

Section-A (6 Marks)

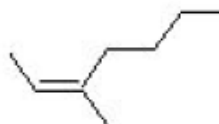
1. Discuss briefly about the chirality and stereocentres of the 1,2 dimethyl cyclobutane.
2. Draw the fischer projections of all the possible stereoisomers for 2,3-butanediol.
3. Explain R,S-notation of Allenes?
4. Write notes on asymmetry synthesis.
5. Draw Fischer projection formulas for all stereoisomers of 2,4-dibromohexane, giving stereochemical details for each structure.
6. Draw Fischer projection formulas for all stereoisomers of 2,4-dimethyl-3-hexanol, giving stereochemical details for each structure.
7. Represent erythro-3-bromo-2-butanol molecular geometry using Fischer, Newmann and Sawhorse formulae.
8. What is the advantage of using E,Z system of nomenclature over cis-trans system?
9. Illustrate homotopic and heterotopic hydrogens.

10.

Determine the double bond stereochemistry (*E* or *Z*) for the following molecules.



A

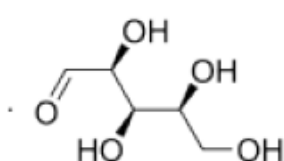


B

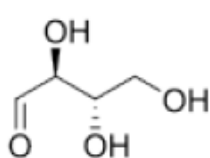
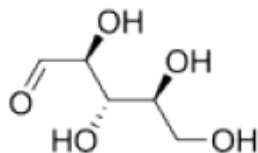
11. Write short note on distereomers properties with a suitable example.

12.

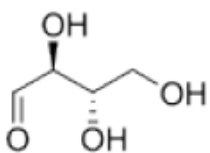
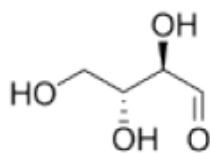
Identify the following compounds as enantiomers, diastereoisomers or different.



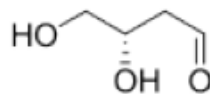
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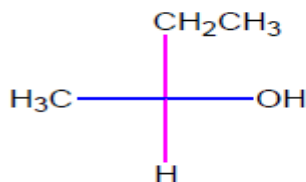
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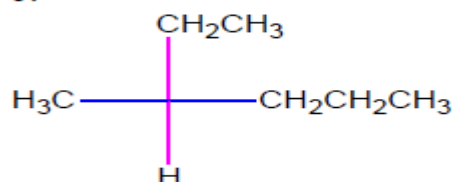
13.

Assign R/S configurations to the following Fischer Projections:

a.

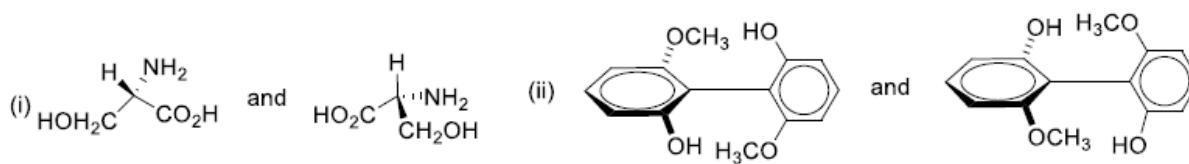


b.



14.

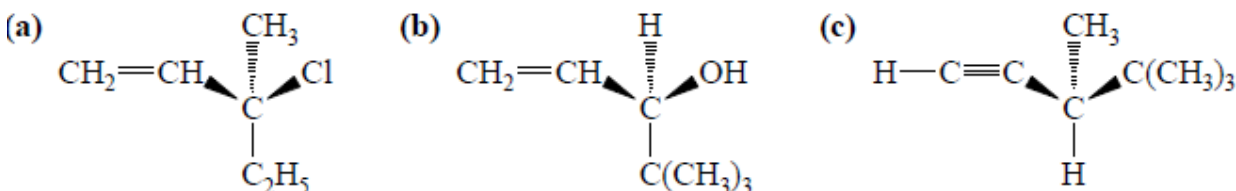
(a) What term best describes the relationship between the following pairs of compounds? (constitutional isomers, Enantiomers, configurational diastereomers, cis-trans diastereomers, atropisomers, identical structures). (2 Marks each)



15. Write the enantiomeric forms of bromochlorofluoromethane and assign each enantiomer its correct (R) or (S) designation

16.

Assign (R) or (S) designations to each of the following compounds:



Section-B (15 Marks)

16).Discuss the importance of threo and Erythro nomenclature.

17). Write a short note on stereospecific and stereoselective reactions.

18). (i). identify the chiral centers in each of the following.

a) 2-Chlorobutane

b) 1,2-Dichloropropane.

c) 3-Bromo-1-pentene.

d) 1-Bromo-3-methylcyclohexane

e) 1-Bromo-4-methylcyclohexane

ii) Write notes on Cram's rule.

19. a. Write note of optical activity of compounds due to helicity.

b. What is the relationship, if any, between the sign of rotation of a chiral compound (+) or (-) and its designation as R or S?

c. What are stereospecific and stereoselective reactions? Give examples.

20.

Answer the following questions for each of the molecules shown below.

1) How many tetrahedral stereocenters does the molecule contain?

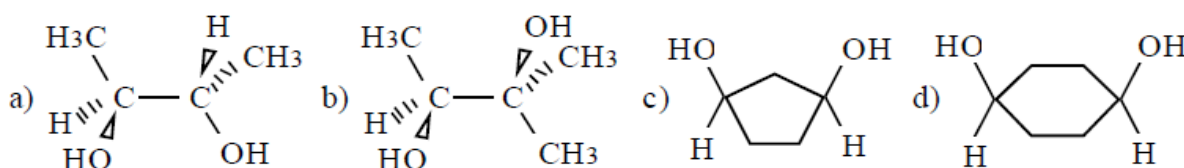
2) Does the molecule possess any internal planes of symmetry?

3) Is the molecule chiral?

4) Is the molecule superposable on its own mirror image?

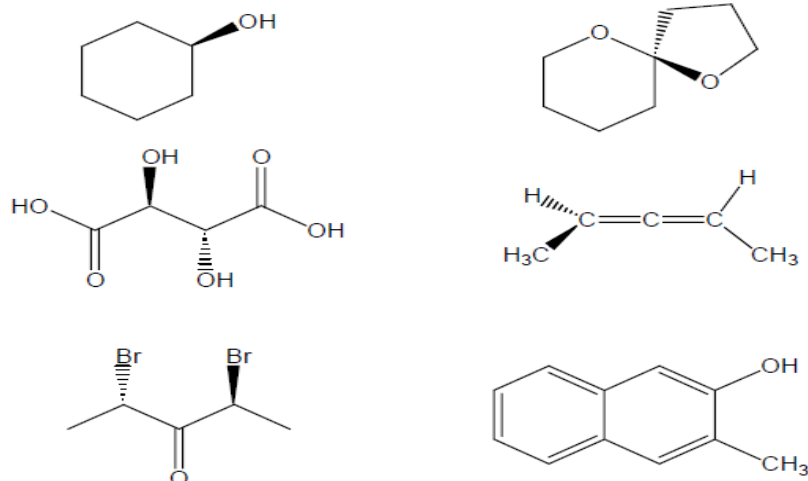
5) Is the molecule optically active?

6) Is this a meso compound?

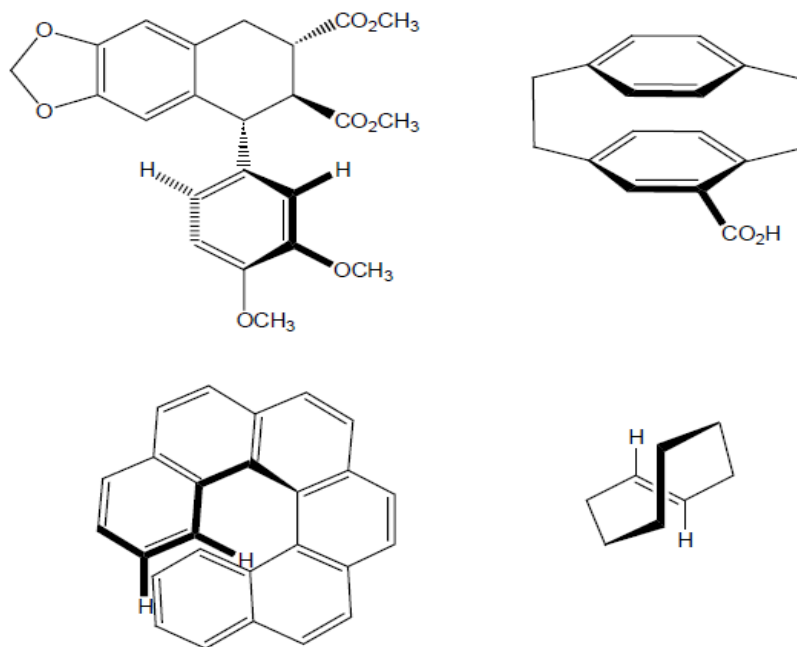


21.

- 1) For each of the following structures, determine whether it is chiral or not. Can you identify all the stereogenic centres(s) and name their absolute configurations? Recall that a molecule may possess stereogenic centres but not be chiral, or vice versa.



- 2) Some molecules have stereochemistry despite the fact that they have no stereogenic centres. Usually, this arises because of structural hindrance to internal motion. Can you draw the *enantiomer* of each of the following chiral molecules?



UNIT-II CONFORMATIONAL ANALYSIS

Section-A (6 Marks)

1. Write a short note on oxidation of cyclohexanone.
2. Give an account on conformation of ethane and 2-bromo 1-chloro ethane.
3. Explain the conformation of cyclohexanone and its esterification process.
4. Briefly explain the difference between the conformation and configuration.
5. Write a note on 9-methyl decalin with comparison on decalin.
6. Explain the reduction of cyclohexane carboxylic acid.

Section-B (15 Marks)

7. Describe in detail about conformation of cyclohexane and di substituted cyclohexane.
8. i. Explain the conformation of decalin and 9-methyl decalin.(7)
ii. Explain the esterification process of carboxylic acid and which stable form Cis or Trans conformation.(8)

UNIT-III

ALIPHATIC NUCLEOPHILIC AND ELECTROPHILIC SUBSTITUTION REACTIONS

Section-A (6 Marks)

1. Explain the HVZ reaction with suitable examples.
2. Discuss the S_E1 , S_E2 and S_{Ei} mechanism.
3. Write a note on the double bond shift and Migration of double bond.
4. Briefly explain the Von-Braun reaction and Stark-Enamine reaction.
5. Write a short note on substitution at allylic and vinylic carbons –
6. Give an account on substitution by ambident nucleophiles.
7. Explain the hydrolysis of esters process
8. Explain the Claisen and Dieckmann condensation.

9. Explain the ion pair mechanism of uni-molecular mechanism of substitution.
10. Which is stable bornyl or nor-bornyl carbo cation.

Section-B (15 Marks)

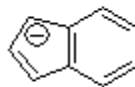
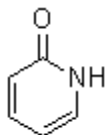
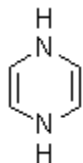
11. Discuss in detail about the S_N1 and S_N2 reaction.
12. i. Describe in detail about the Hydrolysis of esters process. (7)
ii. Give an account on HVZ reaction with suitable examples. (8)
13. i. Explain in detail about the Neighbouring group participation and its effects. (10)
ii. What is classical carbo cation explain it. (5)
14. write a short on
i. Claisen condensation. (5)
ii. Stark enamine reactions. (5)
iii. Halogenation of ketones and aldehyde. (5)

UNIT-IV

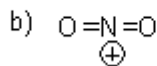
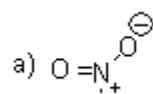
AROMATICITY AND AROMATIC ELECTROPHILIC SUBSTITUTION REACTIONS

Section-A (6 Marks)

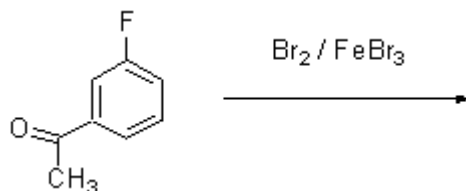
1. Draw the highest occupied molecular orbital (HOMO) for 1,3,5-hexatriene. How many bonding and anti-bonding interactions in this MO?
2. Label the following molecules as aromatic, anti-aromatic, or nonaromatic. Assume planarity.



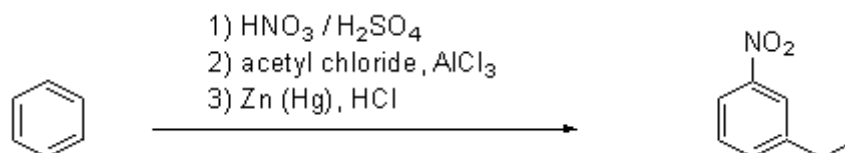
3. Which of the following is the reactive electrophile in the nitration of aromatic rings?



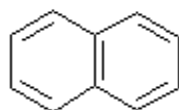
4. Provide the product of the following reaction:



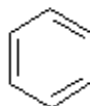
5. Explain why the following synthesis was unsuccessful



6. Rate the resonance energies (in comparison to one another) of each of the following:



(i)

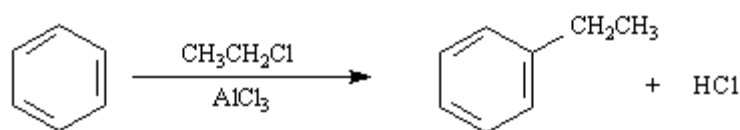


(ii)



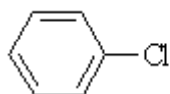
(iii)

7. Consider the Friedel-Crafts alkylation reaction below to answer the following question(s):

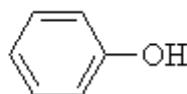


What is the role of the AlCl_3 in the reaction ?

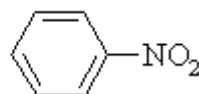
8. Arrange the following in according to their relative rate of reaction with bromine / Fe. Justify the order.



(i)

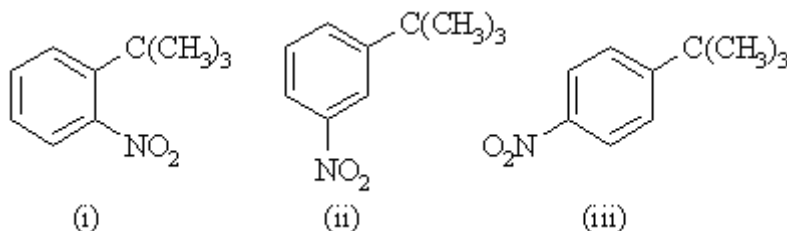


(ii)

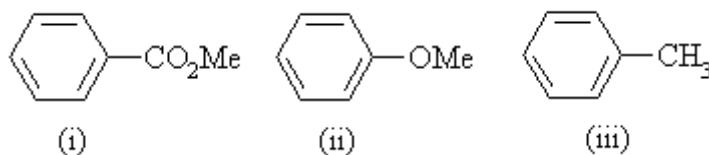


(iii)

9. Arrange the following products according to the % yield obtained from the nitration of t-butylbenzene. Justify the order.



10. Arrange the following according to their relative rate of reaction with ethanoyl chloride / AlCl_3 . Justify the order.

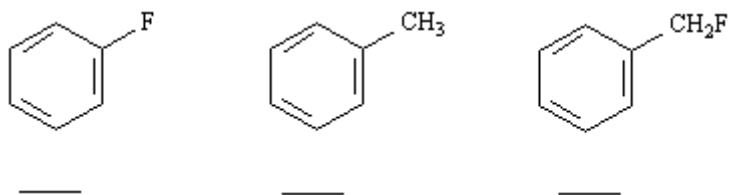


11. What are the major products from the reactions of phenyl ethanoate and ethyl benzoate with HNO_3 / H_2SO_4 / heat ?

12. Based on the resonance energies of polycyclic aromatics like naphthalene and phenanthrene, suggest why they are more reactive than benzene.

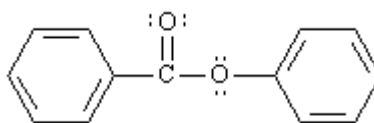
13. Rank the compounds in each group below according to their reactivity toward electrophilic aromatic substitution (most reactive = 1; least reactive = 3).

Place the number corresponding to the compounds' relative reactivity in the blank below the compound



14. At what position, and on what ring, is bromination of phenyl benzoate expected to occur?

Explain your answer.



phenylbenzoate

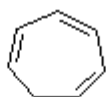
15. Propose a synthesis for isobutylbenzene which avoids the problems of direct Friedel-Crafts alkylation.
16. Would you expect (nitromethyl)benzene to be more reactive or less reactive than toluene toward electrophilic substitution? Explain.

Section-B(15 Marks)

17. Use the following list of compounds to answer the questions below:



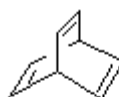
A



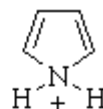
B



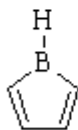
C



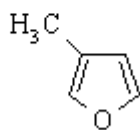
D



E



AB



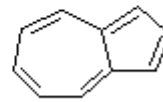
AC



AD



AE



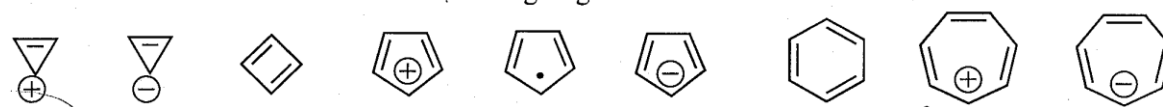
BC

Select the compound that is best described as:

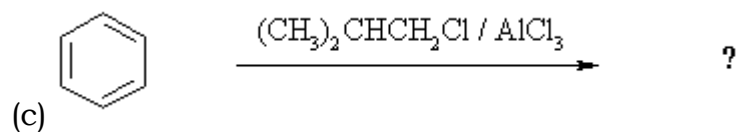
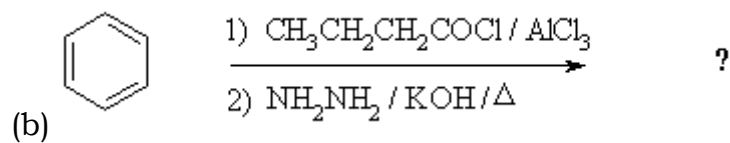
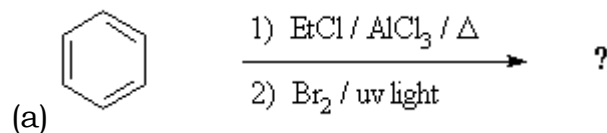
- (a) A neutral, 4 p-electron, anti-aromatic system.
- (b) A 6 p-electron, aromatic system.
- (c) An aromatic system because $n=2$ in the Huckel $4n+2$ rule.
- (d) A non-aromatic, conjugated 6 p-electron system
- (e) A non conjugated hydrocarbon.
- (f) Non-aromatic as drawn, but if H^- were removed would give an aromatic cation.
- (g) Non-aromatic as drawn, but has an important resonance structure that is aromatic.
- (h) Non-aromatic as drawn but has an aromatic conjugate base.

18. Explain the following:

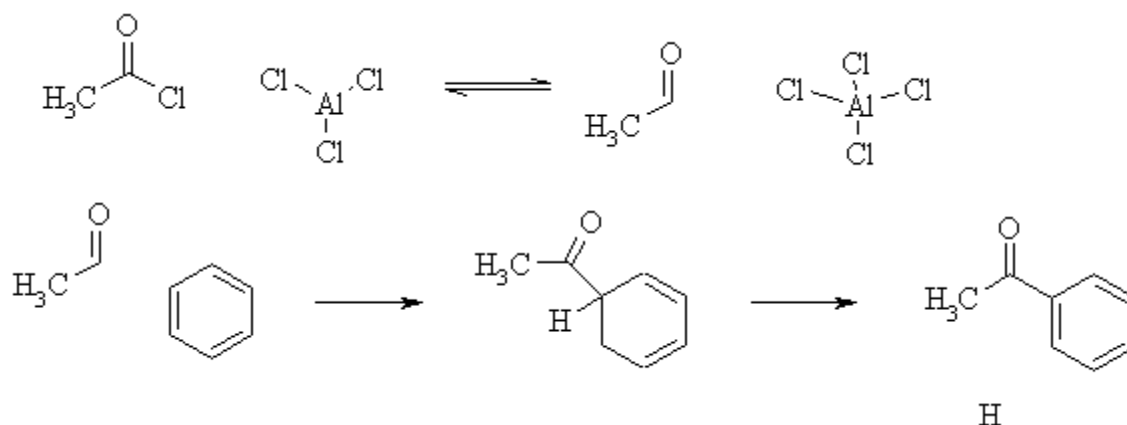
1. Draw the MO's for 3-, 4-, 5-, and 6-membered cyclic π systems.
2. Fill in the orbitals and circle the following as good=stable=aromatic or not.

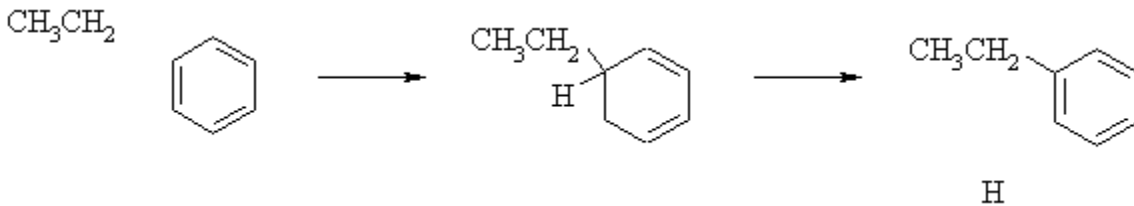


19. What are the major products of the following reactions ?

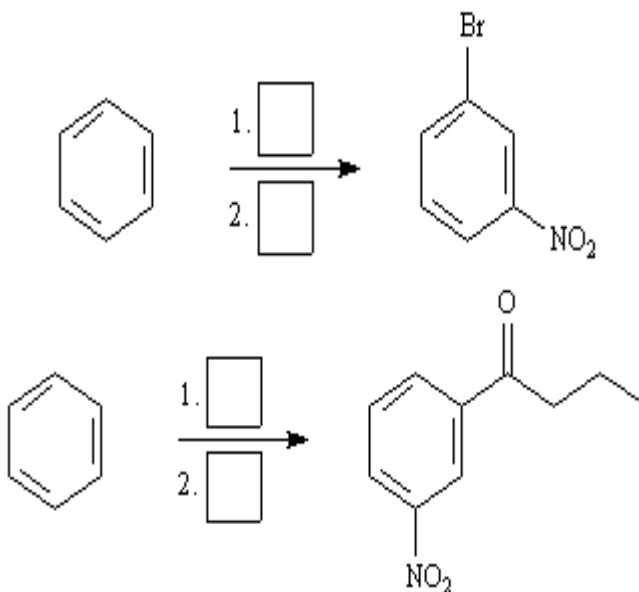


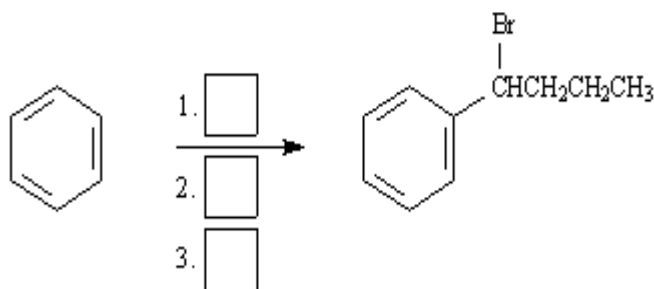
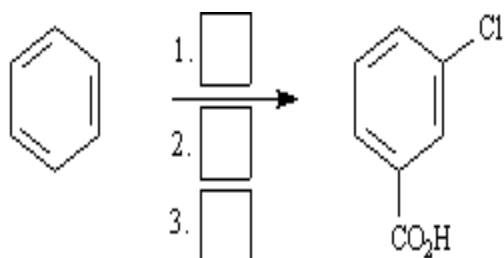
20. Draw in all of the curly arrows and any required charges to complete the step-by-step mechanisms for each of the following reaction schemes. All the required bonds have been shown.





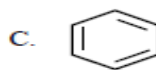
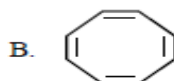
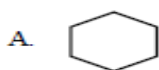
- a. KMnO_4 , H_3O^+
b. Br_2 , FeBr_3
c. Cl_2 , FeCl_3
d. CH_3Cl , AlCl_3
e. HNO_3 , H_2SO_4
f. $\text{ClCO}(\text{CH}_2)_2\text{CH}_3$, AlCl_3
g. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$, AlCl_3
h. H_2/Pd
i. NBS, peroxides
j. $(\text{CH}_3)_3\text{CCH}_2\text{Cl}$





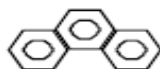
22. Explain the following reactions

- 3.3 Which of the following compounds contains the longest carbon- carbon bonds? Which one contains the shortest carbon-carbon bonds?



- 3.4 Draw a resonance structure having localized bonds for each of the following compounds. (Note: All 3 were found in the "Mars Rock" ALH84001, and are possibly evidence of past life on Mars.)

a) phenanthrene



b) pyrene



c) perylene



- 4.1 Cyclopentadiene is a much stronger acid than cycloheptatriene. Explain the reason for this, using equations and complete sentences.

23. Predict the mechanism for the symmetrical tribromo benzene, 2-amino 5-methylphenol, 3 - nitro 4-bromobenzoic acid, 3, 4-dibromonitrobenzene, 1,2,3 - trimethylbenzene, starting from benzene or any monosubstituted benzene.

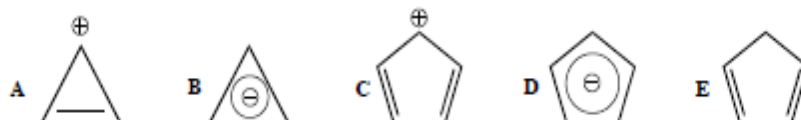
24. Explain the mechanism of the following reactions

a. Reimer – Tieman reaction,

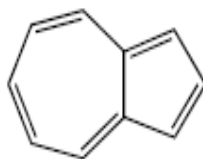
b. Vilsmeier – Hack,

- c. Gattermann, Gattermann – Koch,
 - d. Kolbe reaction
25. Predict the mechanism of the following Typical reactions –
- a. nitration,
 - b. halogenation,
 - c. alkylation,
 - d. acylation
26. Explain the conditions and examples for the following
- a. Aromaticity of benzenoid,
 - b. heterocyclic,
 - c. non-benzenoid compounds
 - d. Huckel's rule –Annulenes.
27. Explain the following reactions

Question 1. Provide molecular orbital diagrams for each of the following compounds. In addition, label each compound as aromatic, antiaromatic or nonaromatic (nonaromatic compounds are neither aromatic or antiaromatic).

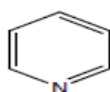


Question 4. Why does the following compound have a large molecular dipole?

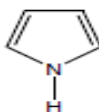


azulene

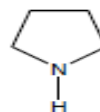
Question 5. Rank the following compounds from most to least basic. Clearly explain your reasoning.



pyridine

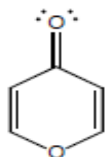


pyrrole

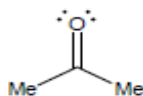


pyrrolidine

Question 3. Which of the following compounds is more basic (*i.e.*, which lone pair of electrons shown below is more likely to become protonated)? Clearly explain your choice.



4-pyrone



acetone

UNIT -V

AROMATIC NUCLEOPHILIC SUBSTITUTIONS AND DETERMINATION OF REACTION MECHANISM

Section-A (6 Marks)

1. Explain in detail about the methods for the generation of benzyne intermediate.
2. Explain in detail about the kinetic and non-kinetic methods of determining organic reaction mechanism
3. Give an account for Hammett and Taft equation.

Section-B (15 Marks)

4 (a). Explain in detail about the nucleophilic substitution involving diazonium ions

(b). Give a brief account on the Chichibabin reaction and Zeigler alkylation.