



Registration Number:

Date & session:

ST. JOSEPH'S UNIVERSITY, BENGALURU -27
M.Sc CHEMISTRY- I SEMESTER
SEMESTER EXAMINATION: OCTOBER 2023
(Examination conducted in November /December 2023)

CH 7222- ORGANIC CHEMISTRY I
(For current batch students only)

Time: 2 Hours

Max Marks: 50

This paper contains three printed pages and three parts

PART-A

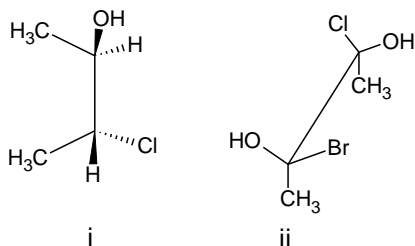
Answer any eight questions.

[8 X 2 = 16]

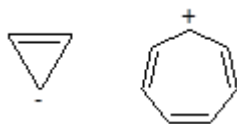
1. Draw the free energy diagram for the following reaction in which $A \rightarrow B$ is kinetically controlled and $A \rightarrow C$ is thermodynamically controlled.



2. Write the hyperconjugative structures of $\text{CH}_3\text{CH}=\text{CH}_2$.
3. RCOX is more reactive than RCH_2X in nucleophilic substitution reactions. Give reason.
4. What are ambident substrates? Give an example.
5. Give two factors favouring E_2C mechanism.
6. Convert the following structures to Fischer projections.



7. What are the products formed on nitrating the following compounds?
i) *p*-methoxybenzaldehyde ii) *p*-nitrotoluene.
8. Identify the following compounds as aromatic, antiaromatic or nonaromatic and give reason.



9. Write the structures of i) bicyclo[2.2.2]octane ii) [4.4.0]decalin.
10. Give an example of axially chiral spirane and write its configuration.

PART-B

Answer any two questions.

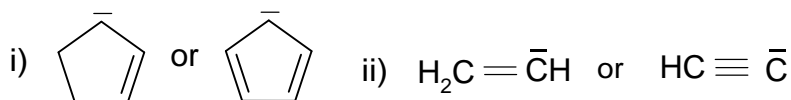
[2 X 12 = 24]

11. a) i) The pK_a of *m*-chlorobenzoic acid is 3.9 whereas that of benzoic acid is 4.19. Calculate the Hammett substituent constant, σ , for *m*-Cl substituent. ii) Write Taft equation and explain the terms.

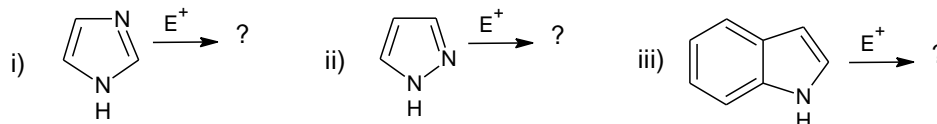
b) What is meant by secondary kinetic isotope effect? Explain the different types with an example each.

c) Identify the more stable species in each of the following sets. Justify your choice in each case.

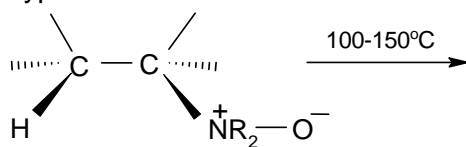
(4+4+4)



12. a) Write the major electrophilic substitution product in the following:

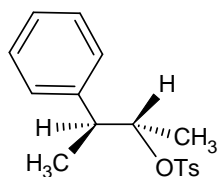


b) Complete the following reaction and write its mechanism. Give an advantage of reactions of this type.



c) The substrate given below undergoes solvolysis faster than CH_3CH_2OTs to give a product with retention of configuration. Explain this observation based on the mechanism of the reaction. Which solvent, CH_3COOH or CF_3COOH will favour mechanisms of this type? Give reason.

(3+3+6)



13. a) Give the Fischer projection formulae of all the stereoisomers of 2,3,4- trihydroxyglutaric acid ($COOH-CH(OH)-CH(OH)-CH(OH)-COOH$) and assign configuration notation to the pseudoasymmetric centers.

b) Explain Smiles rearrangement with an example.

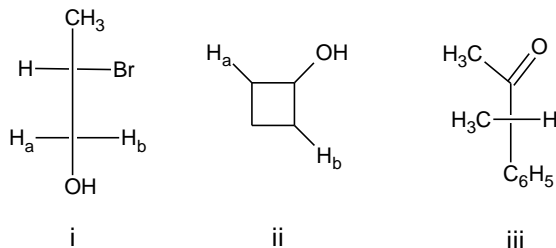
c) Draw the graph to show variation of the potential energy with dihedral angle for the limiting conformers of *n*-butane and explain the relative stabilities of the conformers. (3+3+6)

PART-C

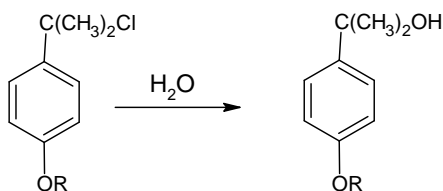
Answer any two questions.

[2 X 5 = 10]

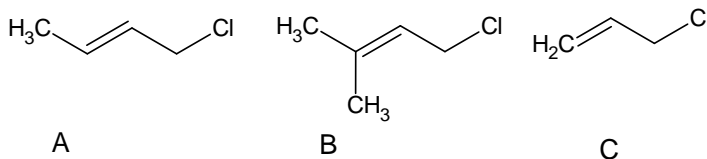
14. Identify the topicity relationship of H_a and H_b atoms in (i) and (ii) and between the faces of the carbonyl group in (iii).



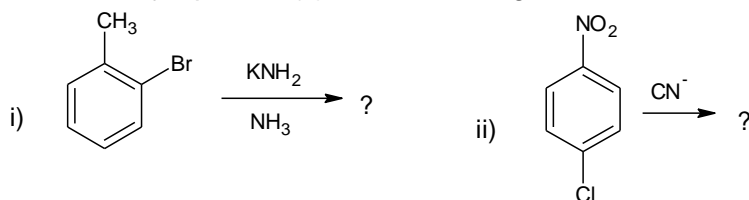
15. a) Which of the following Hammett substituent constants, σ^- , σ^+ , or σ , is the most appropriate to account for substituent effects in the following reaction? Justify your choice.



b) Among the following, identify the most reactive and the least reactive alkyl halide towards S_N1 reactions. Give reason. (2+3)



16. a) Write the major product(s) in the following reactions. (2+3)



b) Predict which mechanism will be favoured in each of the following cases. Justify your answer.

- Alkyl group at the α -position (E1/E2/E1cB).
 - Ionizing solvent and absence of base (S_N1/S_N2/E1/E2).
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