



Date:

Registration number:

ST. JOSEPH'S COLLEGE (AUTONOMOUS), BENGALURU-27
M.Sc. CHEMISTRY– I SEMESTER
SEMESTER EXAMINATION: OCTOBER 2021
(Examination conducted in February-March 2022)
CH 7221/ CH 7118/OCH 7118: ORGANIC CHEMISTRY

Time- 2½ hrs

Max Marks-70

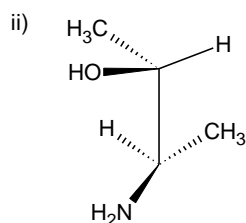
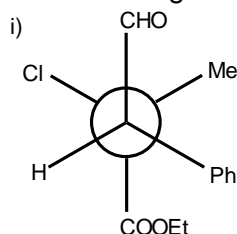
This paper contains **FOUR** printed pages and **THREE** parts

PART A

Answer any **SIX** questions. Each question carries **2** marks.

6x2=12

1. What is the geometry of a i) carbanion ii) singlet carbene?
2. Give the principle of microscopic reversibility.
3. Which of the following is a stronger acid, $\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$ or $\text{CH}_3\text{CH}=\text{CHOH}$?
Give reason.
4. Write the structure of i) 8-chlorobicyclo[3.2.1]octane ii) (2Z,4E)-2,5-dibromo-3-ethyl-4-methylhexa-2,4-diene
5. Rewrite the following structures in the Fischer formula



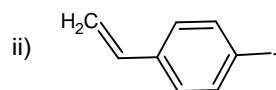
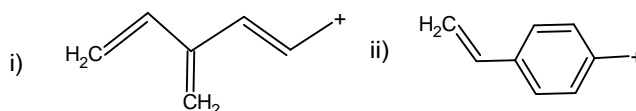
6. Write $\text{S}_{\text{N}}1$ mechanism. What is the stereochemical outcome of this reaction?
7. What is the effect of i) unsaturation at α carbon and ii) unsaturation at β carbon on the rates of $\text{S}_{\text{N}}1$ reactions?
8. How is m-chlorobenzenesulphonic acid synthesised from benzene?

PART B

Answer any **FOUR** questions. Each question carries **12** marks.

4x12=48

9. a) Draw the resonance contributors of the following ions and indicate the most stable among them in each set.

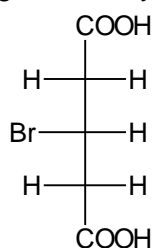


b) Give two methods of generation of carbon free radicals. Arrange the alkyl free radicals in the increasing order of their stability. Justify the order. (6+6)

10. a) Explain secondary kinetic isotope effects with suitable examples.

b) Plot the potential energy versus dihedral angle curve for butane and draw the conformations corresponding to the maxima and minima of this curve. Account for the energy differences between various conformers.

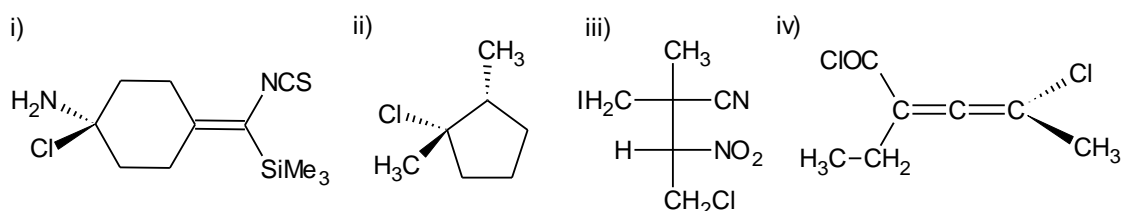
c) Identify any pairs of enantiotopic, homotopic, diastereopic or constitutionally heterotopic ligands in the following molecule. Assign pro-R/pro-S notation to enantiotopic ligands if any. (3+5+4)



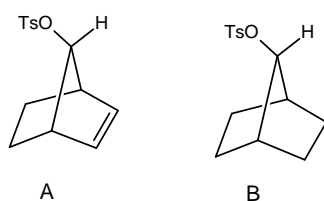
11. a) Write the structure for the i) most stable conformer of trans-1-isopropyl-3-methylcyclohexane ii) most stable conformer of 2-aminoethan-1-ol in Newman projection formula iii) chair form of cis-decalin iv) 1-tert-butyl-1-methylcyclohexane

b) Write in Fischer projection formula of all the isomers of heptane-3,4,5-triol. Identify the meso compounds among these. Identify the pseudoasymmetric centres and give configuration notations to these centres.

c) Give absolute configuration notation for the relevant chiral centres/axes in the following molecules. (4+4+4)



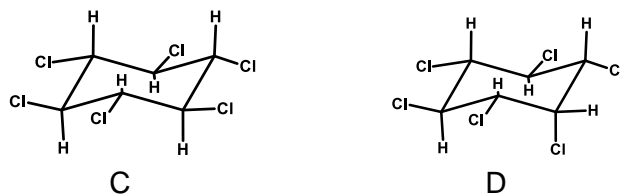
12. a) Compound A undergoes acetolysis 10^{11} times faster than compound B with retention of configuration. Explain this observation giving the mechanism of the reaction. What happens to the reactivity of A if electron withdrawing groups are present on the unsaturated carbons? Explain your answer.



b) What are ambident nucleophiles? Mention whether C-alkylation or O-alkylation will be preferred when phenoxide ion is the nucleophile in each of the following cases. Give reason to support your answer.

- i) in a polar aprotic solvent
 ii) when reaction conditions are S_N2 (6+6)

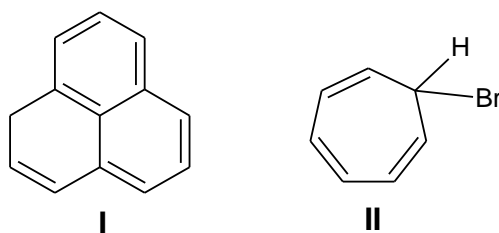
13. a) What are E1, E2 and E1cB reactions? Explain with the mechanism.
 b) Which of the following compounds will undergo E2 elimination (of HCl) faster? Give reason.



- c) Write the major product for the following reactions.
 i) bromination of p-methylbenzoic acid ii) bromination of p-chlorobenzoic acid
 iii) nitration of p-methoxybenzaldehyde. (6+3+3)

14. a) Discuss benzyne mechanism of nucleophilic substitution on aromatic rings. Give two evidences in favour of this mechanism.

b) Account for the observations of the compounds given below:

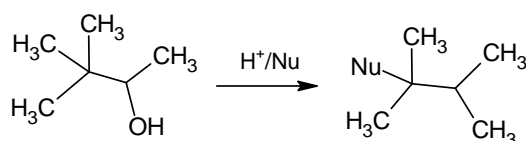


- i) Compound I reacts with potassium methoxide readily.
 ii) Compound II is an unusual alkyl halide that it is insoluble in non-polar solvents but it is soluble in water.
 c) Give the mechanism of von Richter rearrangement. (4+4+4)

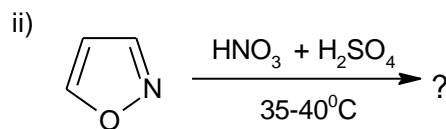
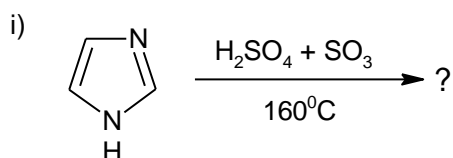
PART C

Answer any TWO questions. Each question carries 5 marks. 2x5 =10

15. a) Propose a mechanism for the following nucleophilic substitution reaction.



b) Write the major product in the following: (3+2)



16. Match the following reactions of *p*-substituted aryl compounds (Ar) given in column A with the Hammett reaction constant (ρ) values in column B.

Column A	Column B
a) $\text{Ar-CH}_2\text{-COOH} \rightleftharpoons \text{Ar-CH}_2\text{-COO}^- + \text{H}^+$	i) 1.00
b) $\text{Ar-COOH} \rightleftharpoons \text{Ar-COO}^- + \text{H}^+$	ii) 0.24
c) $\text{Ar-OH} \rightleftharpoons \text{Ar-O}^- + \text{H}^+$	iii) 0.50
d) $\text{Ar-CH}_2\text{-CH}_2\text{-COOH} \rightleftharpoons \text{Ar-CH}_2\text{-CH}_2\text{-COO}^- + \text{H}^+$	iv) 2.26

17. Indicate the relationship between the following pairs of molecules as enantiomers / diastereomers / constitutional isomers / identical / unrelated.

