



Register Number:

Date: 25-10-18

ST. JOSEPH'S COLLEGE (AUTONOMOUS), BANGALORE-27
M.Sc. CHEMISTRY- I SEMESTER
SEMESTER EXAMINATION: OCTOBER 2018
CH 7218 : ORGANIC CHEMISTRY

Time- 2 ½ 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

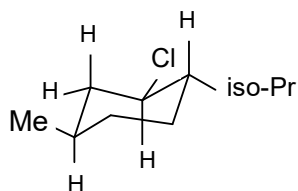
1. Draw the energy profile diagrams for the following reactions if i) the reaction product is B under kinetic control and C under thermodynamic control and ii) the product is B under both kinetic and thermodynamic controls.
2. State Curtin- Hammett principle.
3. Which of the following acids is stronger? Justify your answer.
 HOCH_2COOH NCCH_2COOH
4. Write $\text{S}_{\text{N}}1$ mechanism taking $\text{RCH}_2\text{SO}_2\text{Cl}$ as an example. What is the stereochemical outcome of this reaction?
5. Which of the following reactions will take place faster? Give reason.
i) $\text{MeBr} + \text{OH}^- \rightarrow \text{MeOH} + \text{HBr}$
ii) $\text{MeBr} + \text{H}_2\text{O} \rightarrow \text{MeOH} + \text{HBr}$
6. Draw line formulae and give IUPAC names of two isomeric 1,2-dibromobicycloheptanes.
7. What is a racemic conglomerate? How does its melting point vary when a pure enantiomer is added to it?
8. What is Gatterman-Koch reaction? What is the intermediate in this reaction?

PART B

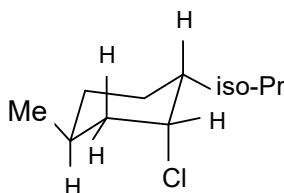
Answer any FOUR questions. Each question carries 12 marks. 4x12=48

9. a) What are i) nitrenes and ii) free radicals? Give an example, classification and one method of generation of each type.
b) Write Hammett equation which relates structure and reactivity. Show that this equation is a linear free energy relationship. When do we use σ^+ and σ^- values rather than σ in Hammett equation? (6+6)

10. a) Distinguish between isovalent and sacrificial hyperconjugation with an example each.
 b) Give the mechanism of pyrolytic elimination of amine oxides. Mention an advantage of this reaction.
 c) Explain the stereochemistry and regioselectivity of E2 elimination taking the following substrates as examples. Which one will react faster? Why? (3+3+6)

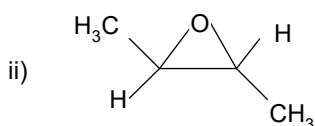
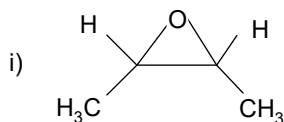


A



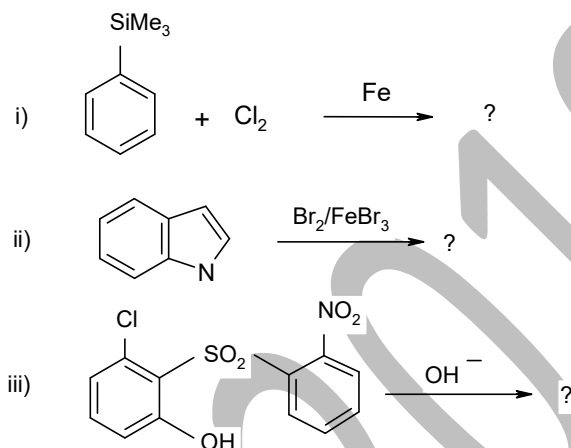
B

11. a) With proper reasoning explain how the following would affect the reactivity of the substrate in a S_N1 reaction.
 i) unsaturation at β - carbon ii) electron withdrawing groups at β -carbon
 b) Discuss neighbouring group participation of aromatic rings taking a suitable example. What happens to the rate of this reaction if i) electron withdrawing groups are present on the aromatic ring and ii) the solvent used for the reaction is a weak nucleophile?
 c) Write the BAC_2 mechanism for the cleavage of carboxylic esters. (3+6+3)
12. a) Draw enantiomeric pairs of examples in which i) a chiral axis is present and ii) a chiral plane is present. Give the configuration notations for the examples of enantiomers with chiral axis.
 b) Write Fischer projection formulae for the stereoisomers of 2,3,4-tribromopentane in which there is/are pseudoasymmetric centre/s present and give the configuration notation/s to the centre/s.
 c) Write the Newman projection formula for the most stable conformer in the following cases. i) ethane-1,2-diol ii) $2R,3R$ - 2,3-dichlorobutane iii) *meso*-2,3-butanediol. (6+3+3)
13. a) *Cis-tert*-butylcyclohexanol undergoes chromic acid oxidation faster than the corresponding *trans* isomer. Explain this observation with the mechanism of the reaction. Give the energy profile diagram for the reaction.
 b) Identify the topicity relationship between $-CH_3$ groups in the compounds given below and assign *pro-R/pro-S* configuration notations wherever applicable.



- c) Predict the major mononitration products of the following compounds.
 i) 2-bromobenzoic acid ii) naphthalene iii) 3-chlorotoluene (6+3+3)

14. a) 7-bromocycloheptatriene (tropylium bromide) completely dissociates in water and gives a precipitate of AgBr instantaneously with AgNO₃, unlike its open chain analogue. Give reason.
- b) What product/s is/are formed when o-methoxybromobenzene reacts with NH₂⁻ in liq.NH₃? Write the mechanism and give an evidence to support the formation of the intermediate. What will be the product/s if m-methoxybromobenzene reacts under the same conditions? Justify.
- c) Write the major product of the following reactions. (3+6+3)

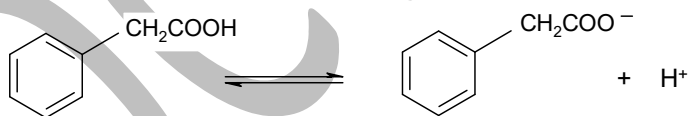


PART C

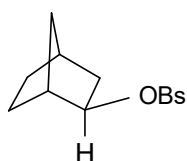
Answer any TWO questions. Each question carries 5marks.

2x5=10

15. a) The value of Hammett reaction constant, ρ , for the following ionization is +0.5. Will the value of reaction constant be higher/lower/same when i) a -CH₂ group is inserted between the aromatic ring and -CH₂COOH group ii) the substituent on the aromatic ring is -OH instead of -CH₂COOH? Explain.



- b) Draw four-membered rings showing all C-C double bonds, unshared pairs of electrons and charges that would result in aromatic ions. (3+2)
16. Exo-2-norbornyl brosylate (structure shown below) reacts 350 times faster than its endo isomer to give a racemic mixture of two exo-acetates on acetolysis. Explain this observation with a suitable mechanism.



17. a) Fumaric acid ((*E*)-2-butenedioic acid) is converted to 2-hydroxybutanedioic acid by the enzyme *fumarase*. The hydroxyl group is added stereospecifically from the *si-si* face and hydrogen from the opposite face of the double bond. Draw perspective formula of the product formed and assign configuration to the chirality centre. What is the topicity relationship between two trigonal faces in fumaric acid?
- b) Identify the relationship between the following pairs of molecules as enantiomers/diastereomers/identical/unrelated. (3+2)

