Register Number:
Date:

ST. JOSEPH'S COLLEGE (AUTONOMOUS), BANGALORE-27
M.Sc. CHEMISTRY– I SEMESTER
SEMESTER EXAMINATION: OCTOBER 2019
CH 7218 : ORGANIC CHEMISTRY

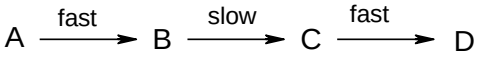
Time- 2½ hrs **Max Marks-70**

This paper contains FOUR printed pages and THREE parts

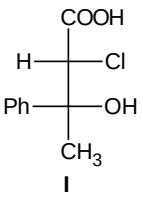
PART A

Answer any SIX questions. Each question carries 2 marks. 6x2=12

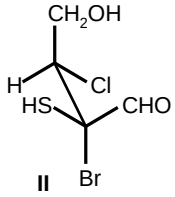
1. The mechanism of an exothermic reaction is shown below. Draw the energy profile diagram of the reaction.



2. Write Taft equation and explain the terms.
3. Rewrite structure I in sawhorse formula and II in Fischer formula.

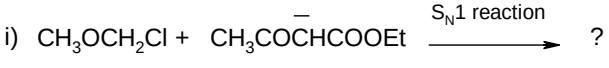


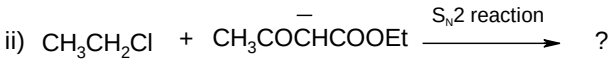
I



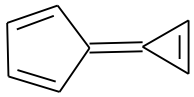
II

4. Write the structure of i) (*1Z,3E*)-1,4-dichlorobutadiene ii) bicyclo[2.1.1]hexane.
5. How does unsaturation at β carbon affect the rate of S_N1 mechanism? Illustrate with an example.
6. Write the major product of each of the following reactions:





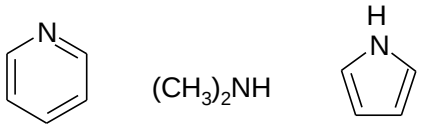
7. Which mechanism (E1/E2/E1cB) will be favoured under the following conditions?
   i) strong bases and higher base concentrations
   ii) good leaving groups
8. Account for the aromaticity and dipole moment of 5.2 D for the following compound.



PART B

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

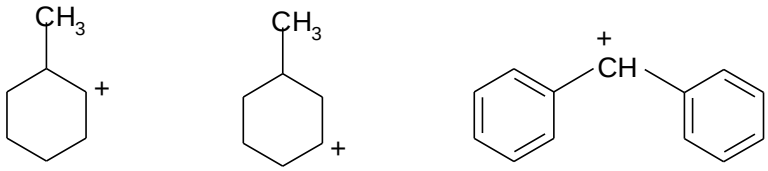
9. a) Arrange the following bases in the order of increasing base strengths. Justify the order.



b) Distinguish between primary and secondary kinetic isotope effects with suitable examples.

c) What is the significance of Hammett substituent constant, σ? Why is it necessary to use σ^+ and σ^- in some cases? Illustrate with examples. If the pK_a of *p*-methoxybenzoic acid is 4.46 and that of benzoic acid is 4.19, calculate the Hammett substituent constant, σ_p for methoxy group. (3+3+6)

10. a) Arrange the following carbocations in the increasing order of stability. Rationalize the order.



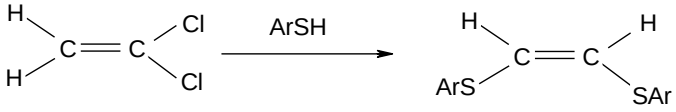
b) Write the structure of i) *cis*-decalin ii) stable conformer of 2-fluoroethanol in Newman formula iii) most stable chair conformer of *trans*-1-isopropyl-3-methylcyclohexane iv) least stable chair conformer of *cis*-1-*tert*-butyl-4-methylcyclohexane v) least stable conformer of n-butane in the sawhorse formula.

c) Write the structure of i) an ansa compound that is optically active ii) a compound that shows atropisomerism iii) an allene derivative that is optically active. Give the configurational notation for structures ii and iii. (3+5+4)

11. With suitable examples, explain the terms homotopic, enantiotopic and diastereotopic atoms/groups and faces.

12. a) Write the $B_{AC}2$ mechanism of ester hydrolysis.

b) Write the mechanism of the following conversion. Give an evidence for the mechanism.

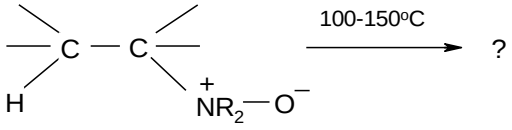


c) What is a non-classical carbocation? Give any two examples. (3+6+3)

13. a) Mention any two characteristics of E2C reaction mechanism. Write the structure of the transition state formed in this mechanism.

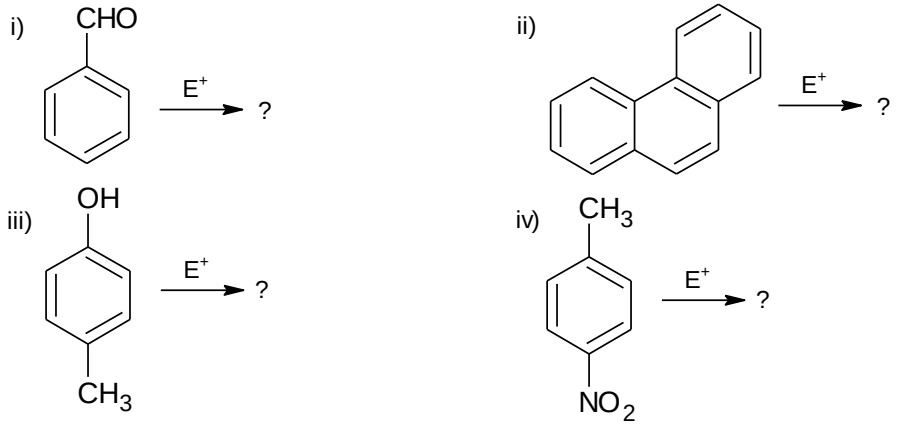
b) Why do *cis*-1-bromo-2-ethylcyclohexane and *trans*-1-bromo-2-ethylcyclohexane form different products when they undergo E2 elimination? What are the products formed?

c) Show the mechanism and complete the following reaction. Give an advantage of reactions of this type.



d) Which is the most preferred position for electrophilic substitution in imidazole? Explain your answer. (3+3+3+3)

14. a) Write the major product(s) formed in the following electrophilic substitution reactions?



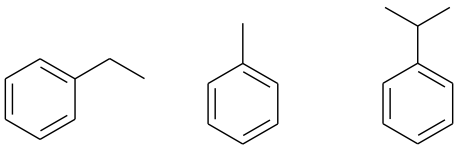
b) Write the $S_{RN}1$ mechanism. Give two evidences in support of the mechanism.

c) Write the mechanism of von Richter rearrangement. (4+4+4)

PART C

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

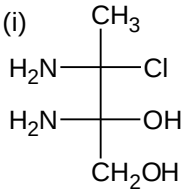
15. a) Using hyperconjugation, explain the relative order of nucleophilicity of the aromatic ring in the following molecules.

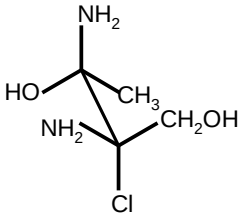


b) Predict the sign of Hammett reaction constant, ρ, for the reaction of $ArCOOC_2H_5$ with aq. NaOH. Explain your answer. (3+2)

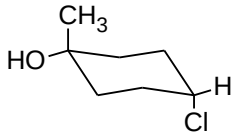
16. Indicate the relationship between the following pairs of molecules as enantiomers / diastereomers / constitutional isomers / identical / unrelated.

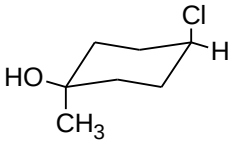
(i)



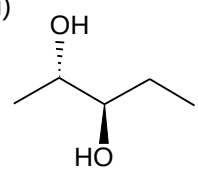


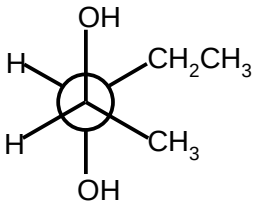
(ii)



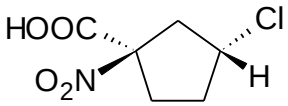


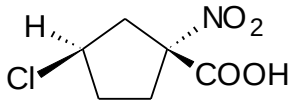
(iii)



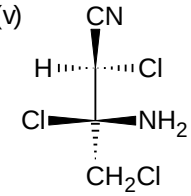


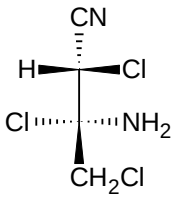
(iv)





(v)



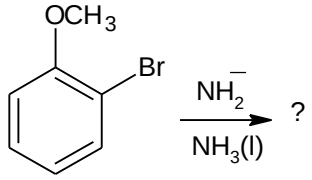


17. a) Percentage of product formed by k_{Δ} pathway in the solvolysis of *p*-$ZC_6H_4CH_2CH_2OTs$ in two different solvents is given below. Rationalize the relative percentage of the products formed.

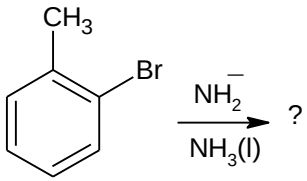
Z	Solvent	Percent by k_{Δ}
OMe	CH_3COOH	91
OMe	HCOOH	99

b) Write the major product of the following.

i)



ii)



(3+2)
