



Register Number:

DATE: 7-01-2021

ST. JOSEPH'S COLLEGE (AUTONOMOUS), BANGALORE-27
M.Sc. CHEMISTRY-I SEMESTER
SEMESTER EXAMINATION: JANUARY 2021
CH/OCH 7218: ORGANIC CHEMISTRY-I

Time- 2 ½ hrs

Max Marks-70

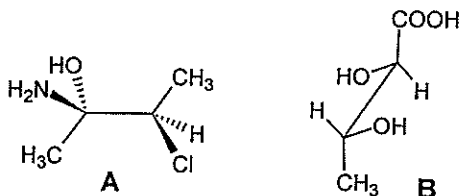
This paper contains FOUR printed pages and THREE parts

PART A

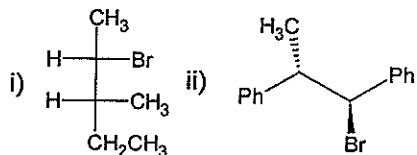
Answer any SIX questions.

2 x 6 = 12

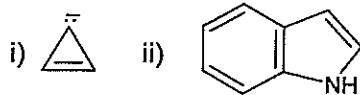
1. Write the hyperconjugative structures of 1-propene.
2. Illustrate Hammond postulate with a suitable energy profile diagram.
3. Convert A to a staggered Newman formula and B to a Fischer projection formula.



4. Which of the following is a better nucleophile in methanol?
i) H₂O or H₂S ii) I⁻ or Br⁻
5. Write S_Ni mechanism.
6. Write the structure of the major product formed when each the following compounds undergo E2 elimination.



7. Write the structure of the product formed when each of the following compounds are nitrated: i) *p*-nitrotoluene ii) *p*-methylphenol.
8. Classify the following ion/compound as aromatic/antiaromatic. Mention the number of π-electrons in each case.

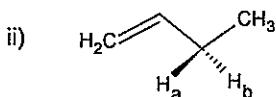
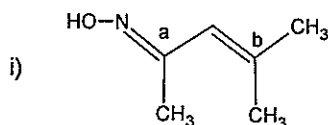


PART B

Answer any **FOUR** questions.

12 x 4 = 48

9. a) When do we use σ^+ and σ^- values in Hammett equation? Explain with examples. (3+3+6)
- b) The ρ value for alkaline hydrolysis of methyl esters of substituted benzoic acids is 2.38 and the rate constant for the hydrolysis of methyl benzoate under the conditions of interest $2 \times 10^{-4} \text{ m}^{-1} \text{ s}^{-1}$. Calculate the rate constant for the hydrolysis of methyl *m*-bromobenzoate. (Given, $\sigma_{m(\text{Br})} = 0.40$)
- c) Indicate the topicity relationship between the faces of the double bonds in (i) and between H_a and H_b in (ii). Give the relevant configuration notations (*Re/Si/pro-R/pro-S*) for the trigonal faces in (i) and for H_a and H_b in (ii), wherever applicable.



10. a) Draw Fischer projection formulae for all the stereoisomers of 2,3,4-trihydroxypentane-1,5-dioic acid and assign configuration notations to C-3 wherever applicable. (6+6)
- b) Give examples of i) an optically active allene ii) a biphenyl derivative which shows atropisomerism iii) a chiral cyclophane iv) an optically active spirane. Give the configuration notations of (i) and (ii).
11. a) The acetolysis of *cis*-4-*tert*-butyl cyclohexyl tosylate with axial tosylate group is about 3.4 times faster than that of the *trans* isomer. Give the mechanism of the reaction to explain this observation. (3+3+6)
- b) Write the tetrahedral mechanism for the base-catalyzed hydrolysis of carboxylic esters.
- c) With an example each explain the anchimeric assistance in aliphatic nucleophilic substitution by i) C=C bond (involving non-classical carbocations) and ii) C-C bond.
12. a) Give a method of generation of carbanions. Arrange the alkyl carbanions in the order of increasing stability. Justify the order. (4+4+4)
- b) What are secondary kinetic isotope effects? Give an example of a reaction involving secondary kinetic isotope effect. What would be the range of k_H/k_D ratio when such an effect is observed?
- c) With an example, illustrate the use of isotopic labelling experiments in elucidating reaction mechanisms.

13. a) Choose the mechanism that is favoured (from the ones shown inside brackets) in each of the following cases. Give reason. (6+3+3)

i) presence of electron withdrawing groups at the β -carbon (E1/E2/E1cB)

ii) positively charged leaving group (E1/E2/E1cB)

iii) β -branching (elimination or substitution)

b) Explain any two factors governing regioselectivity of a reaction involving an ambident nucleophile.

c) Write the structures of i) *cis*-1,3-cyclohexanediol (most stable conformer) ii) *erythro* 3-bromobutan-2-ol (in eclipsed Newman formula) iii) *cis*-4-*tert*-butylcyclohexanol (most stable conformer)

14. a) Illustrate the effect of substrate structure on the position of nucleophilic attack in benzyne mechanism taking *m*-dichlorobenzene as an example. Give an evidence for benzyne mechanism. (6+6)

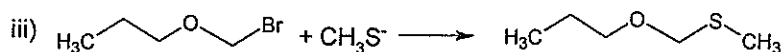
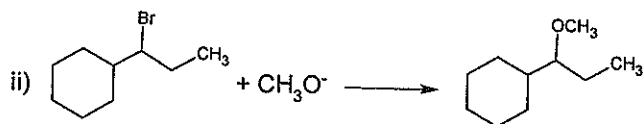
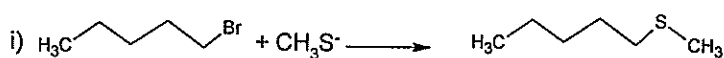
b) Draw the resonance contributing structures of the intermediates obtained from electrophilic aromatic substitution at the 2-position and at the 3-position of pyrrole. Use the resonance contributing structures to explain why substitution at the 2-position is preferred.

PART C

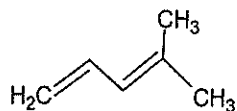
Answer any TWO questions.

5 x 2 = 10

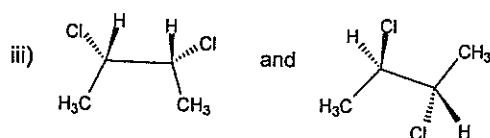
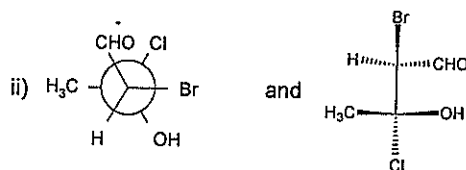
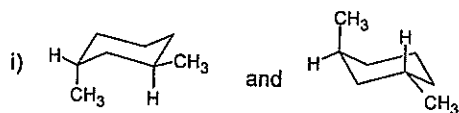
15. a) Identify the reaction/s that will go faster if the concentration of the nucleophile is increased? (2+3)



b) Write the products formed when the following compound undergoes addition reaction with HCl. Indicate the kinetic product and the thermodynamic product.

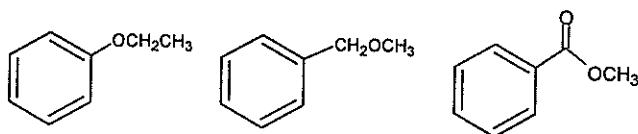


16. a) Indicate the relationship between the following pairs of compounds as enantiomers/diastereomers/identical/constitutional isomers/unrelated: (3+2)



b) Write the structure of the product obtained from the reduction of (2*S*,3*R*)-2,3-dichlorocyclobutanone with LiAlH_4 when H^- attacks the carbonyl carbon on *Re* face. Mention the configuration notation of the new chiral centre generated.

17. a) Among the following substituted benzenes, indicate i) the one that would be the most reactive and ii) the one that would be the least reactive and iii) the one that would yield the highest percentage of meta product in electrophilic substitution reactions. (3+2)



b) Write the major product formed in the following reactions:

