

## U.G. 2nd Semester Examination - 2022

## CHEMISTRY

[HONOURS]

Course Code : CHEM-H-CC-T-04

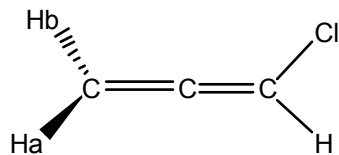
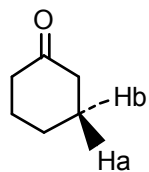
Full Marks : 40

Time : 2½ Hours

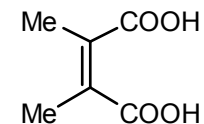
*The figures in the right-hand margin indicate marks.**Candidates are required to give their answers in their own words as far as practicable.*1. Answer any **five** from the following questions:

2×5=10

- a) Compare the acidity of  $\text{CH}(\text{CN})_3$  with  $\text{CH}(\text{NO}_2)_3$ .
- b) Designate  $\text{H}_a$  and  $\text{H}_b$  of the following molecules as Pro-R or Pro-S



- c) Give *Re-Si* descriptor to each ethylenic carbon face of the following molecule when viewed from the top.



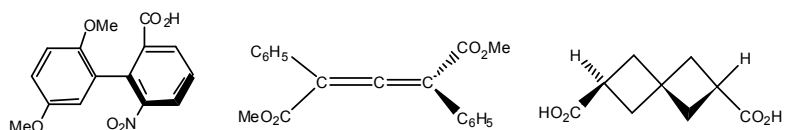
- d) In terms of *s*-character which N of guanidine is more likely to be protonated? Explain why guanidine is a strong base?
- e) Show the Transition State (TS) and products of pyrolysis of  $\text{Ph}_2\text{CHCH}_2\text{-O-(C=S)-S-Me}$ .
- f) Arrange the following in order of increasing nucleophilicity. Explain the order.  
 $\text{PhO}^-$ ,  $\text{EtO}^-$ ,  $\text{NO}_2^-$ ,  $\text{MeCO}_2^-$
- g) Explain whether the substitution reaction  $\text{Nu}^- + \text{R-N}_3 \rightarrow \text{Nu-R} + \text{N}_3^-$ , will follow  $\text{S}_{\text{N}}2$  path or not.
- h) Ethylacetoacetate has 10% enol content in ethanolic solution which increases to 46% in hexane— why?

2. Answer any **two** questions:

5×2=10

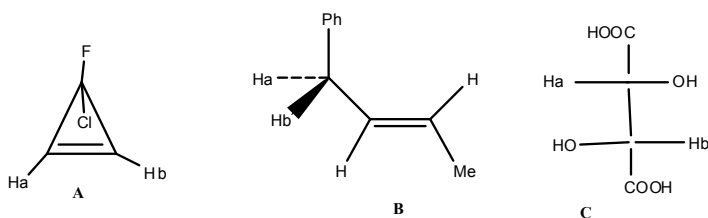
- a) i) Find out the R/S configurational descriptors to the following molecules.

[Turn Over]



ii) In an  $S_N2$  displacement, while bromine can be displaced by iodine in  $H_2O$  medium, the reverse reaction can be done in acetone medium– explain. 3+2=5

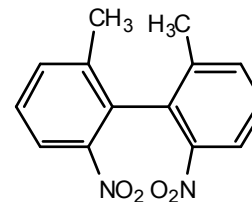
b) i) Indicate whether hydrogens marked  $H_a$  and  $H_b$  in each of the following compounds are homotopic, enantiotopic or diastereotopic.



ii) On the basis of SHAB theory give an example of a reaction of  $CH_3Br$  with an ambident nucleophile. 3+2=5

c) i) What is the necessary condition for a pair of conformational enantiomers to be isolable? Draw the enantiomers of the

following compound and explain the structural feature that makes their isolation possible.



ii) The hydrolysis of  $n\text{-BuCl}$  in aqueous ethanol is accelerated in presence of  $NaI$  – explain? (1+2)+2=5

d) i) Find out the absolute configuration of the chiral centre of the compound formed by the reaction of  $(R)\text{-3-hydroxybutanal}$  with  $CH_3MgBr$  where nucleophile attacks on  $>C=O$  function from the *Re* face.

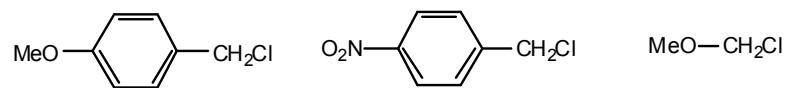
ii) Construct the energy diagram for the

exothermic reaction  $A \xrightleftharpoons[K_1]{K_1} B \xrightleftharpoons[K_{-2}]{K_2} C$  when  
a)  $K_1 > K_2$  and b)  $K_2 > K_1$ .

Indicate which step is faster and which is rate determining? 2+3=5

3. Answer any **two** questions:  $10 \times 2 = 20$

- a) i) With proper projection formulas draw the most plausible transition state leading to Hofmann and Saytzeff elimination products when  $\text{Me}_2\text{CH-CBrMe}_2$  is treated with an alkoxide. Comment on the relative ratio of the products as a function of size of the attacking bases.
- ii) What happens when 1,3-butadiene is treated with bromine at  $-15^\circ\text{C}$  and the reaction mixture is warmed to  $60^\circ\text{C}$ ? Explain the result with the help of potential energy diagram.
- iii) How are the topicities of methylene and carbonyl carbons are changed when they are separately converted into chiral centre?  $(2+2)+3+3=10$
- b) i)  $\text{PhCH}_2\text{CH}(\text{NH}_3^+)\text{COO}^-$  has two diastereotopic ligands. Label them as pro-R and pro-S.
- ii) Which mechanism  $\text{S}_{\text{N}}1$  or  $\text{S}_{\text{N}}2$  is favourable for reactions with each of the following substrates?



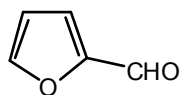
- iii) Give an example of a biphenyl molecule with enantiotopic ligands and prochiral axis.
- iv) Which mechanism  $\text{E}_2$  or  $\text{E}_{1\text{c}}\text{B}$  is operative in the reaction of  $\text{PhCH}_2\text{CH}_2\text{Br}$  with  $\text{NaOEt/EtOH}$ ? Give evidence in favour of your answer.  $2+3+2+3=10$
- c) i) Rate of hydrolysis of mustard gas ( $\text{ClCH}_2\text{CH}_2\text{-S-CH}_2\text{CH}_2\text{Cl}$ ) with aqueous  $\text{NaOH}$  is independent of hydroxide ions and is decreased by chloride ions. Suggest a mechanism consistent with this data.
- ii) Replacement of alcoholic hydroxyl group by  $\text{SOCl}_2$  always proceeds with retention of configuration however the same reaction in presence of pyridine takes place with inversion of configuration. Justify the statement.
- iii) Account for the fact that in benzene solution the active form of 2,3-dichlorobutane prefers skew conformation where dihedral angle between chlorine atoms is  $60^\circ$ .

iv) Suggest a structure of the product (with reason) when a concentrated aqueous solution of urea is treated with conc.  $\text{HNO}_3$  under cold condition .

$$3+3+2+2 = 10$$

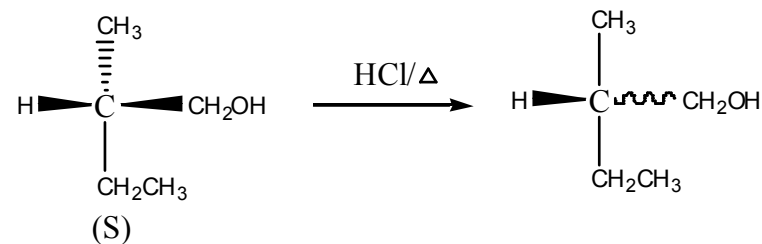
d) i) Why second dissociation constant of maleic acid is less than that of fumaric acid?

ii) Draw the s-cis and s-trans conformations of the following compound. How conformational equilibrium is affected in polar solvents and also in gaseous state



iii) State Hammond's postulates on the nature of transition states or intermediates of a reaction. Comment on the nature of the transition state of the chlorination and bromination of propane under photochemical condition.

iv) Assign the configuration (R/S) of the product in the following reaction.



$$2+(1+2)+(1+3)+1=10$$

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