

U.G. 2nd Semester Examination - 2024

CHEMISTRY**[HONOURS]****Course Code : CHEM-H-CC-T-04****(Organic)****[CBCS]**

Full Marks : 40

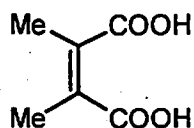
Time : $2\frac{1}{2}$ Hours*The figures in the right-hand margin indicate marks.**Candidates are required to give their answers in their own words as far as practicable.*

1. Answer any five from the following questions:

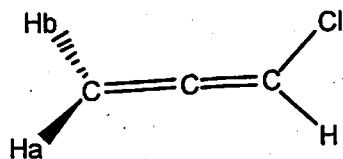
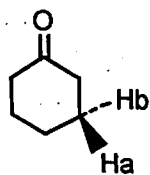
2×5=10

- $(\text{Me}_3\text{CO})_3\text{CH}$ exists almost in keto form — why?
- Explain whether the substitution reaction $\text{Nu}^- + \text{R}-\text{N}_3 \longrightarrow \text{Nu}-\text{R} + \text{N}_3^-$, will follow $\text{S}_{\text{N}}2$ path or not.
- Give *Re-Si* descriptor to each ethylenic carbon face of the following molecule when viewed from the top.

[Turn Over]



- d) Compare the acidity of $\text{CH}(\text{CN})_3$ with $\text{CH}(\text{NO}_2)_3$.
- e) Write the structure of a molecule with a chiral centre and also with a pro-R and a pro-S ligands.
- f) What are nucleophilic and electrophilic catalysts? Give one example of each.
- g) Arrange the following in order of increasing nucleophilicity. Explain the order.
 PhO^- , EtO^- , NO_2^- , MeCO_2^-
- h) Designate H_a and H_b of the following molecules as Pro-R or Pro-S



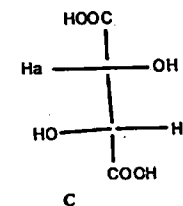
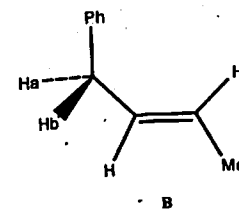
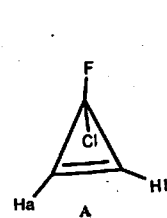
2. Answer any two questions: 5×2=10

- a) i) Compare with reasons the ease of nucleophilic substitution reactions in 2,6-dimethyl-4-nitrochlorobenzene and 3,5-dimethyl-4-nitrochlorobenzene.

- ii) Draw the energy profile for a three step reaction in which the first step is fastest and the last step is slowest.

- iii) Give an example of a molecule with S-configuration having a pair of homomorphous ligands but one is pro-R and other is pro-S. 2+1+2

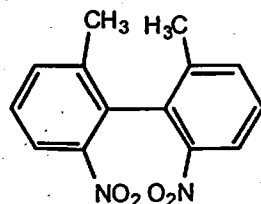
- b) i) Indicate whether hydrogens marked H_a and H_b in each of the following compounds are homotopic, enantiotopic or diastereotopic.



- 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

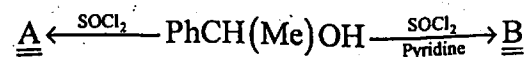
possible.



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

- d) i) 1, 3-Dichloro allene is chiral although it does not contain any asymmetric atom. Explain.

- ii) Predict the products A and B of the following reactions.



- iii) Predict the configuration of the product when the pro-R hydrogen of butanal is replaced by chlorine. 2+2+1

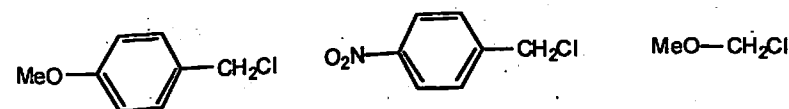
3. Answer any two questions: 10×2=20

- a) i) What happens when 1,3-butadiene is treated with bromine at -15°C and the reaction mixture is warmed to 60°C ? Explain the result with the help of potential energy diagram.

- ii) 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.

- iii) How are the topicities of methylene and carbonyl carbons are changed when they are separately converted into chiral centre? $3+(2+2)+3=10$

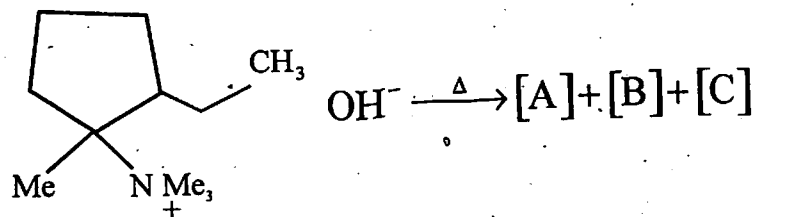
- b) i) Which mechanism $\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$ is favourable for reactions with each of the following substrates?



- ii) $\text{PhCH}_2\text{CH}(\text{NH}_3^+)\text{COO}^-$ has two diastereotopic ligands. Label them as pro-R and pro-S.

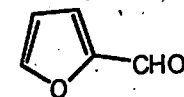
- iii) Give an example of a biphenyl molecule with enantiotopic ligands and prochiral axis.

- iv) Which mechanism $E-2$ or $E1_cB$ is operative in the reaction of $\text{PhCH}_2\text{CH}_2\text{Br}$ with NaOEt/EtOH ? Give evidence in favour of your answer. 3+2+2+3=10
- c) i) Assign *Re-Si* descriptor to the face of acetaldehyde to which HCN will add to produce the corresponding (*R*)-cyanohydrin.
- ii) Draw the energy profile diagram of 1-propyl chloride as a function of rotation about $\text{C}_1\text{-C}_2$ bond and label the maxima and minima with proper conformations.
- iii) Account for the fact that addition of HCl to 1-butene or 2-butene involves the same intermediate but the reaction of 1-butene is faster than that of 2-butene.
- iv) Identify the structures of the products of [A], [B] and [C] for the following reaction. Arrange the products in order of decreasing relative amounts of formation with proper explanation.

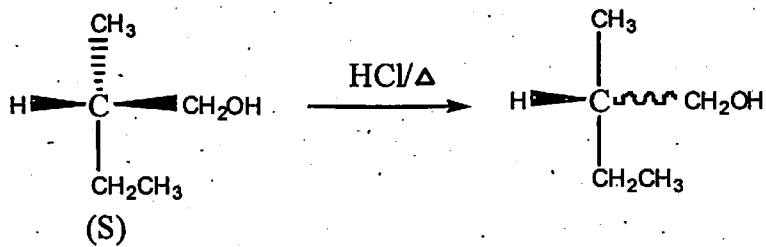


2+3+2+3

- d) i) 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



- ii) Why second dissociation constant of maleic acid is less than that of fumaric acid?
- 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.



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