

U.G. 2nd Semester Examination - 2023

CHEMISTRY

[HONOURS]

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

(Organic)

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.*

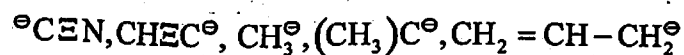
1. Answer any five from the following questions:

2×5=10

- Compare the acidity of 2, 6-dihydroxy benzoic acid and 2-hydroxybenzoic acid.
- Which one of phloroglucinol (1,3,5-trihydroxy benzene) and phenol is an ambident nucleophile?
- Write the structure of a molecule with a chiral centre and also with a pro-R and a pro-S ligands.
- What are nucleophilic and electrophilic catalysts? Give one example of each.

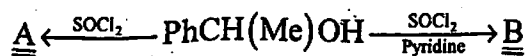
[Turn Over] ...

- e) Draw the most stable conformation of 1,2-difluoroethane and ethylene glycol with proper justification.
- f) $(\text{Me}_3\text{CO})_3\text{CH}$ exists almost in keto form — why?
- g) Indicate the *pro-R* methyl group and *Re*-face in isobutyraldehyde.
- h) Arrange the following carbanions in order of decreasing nucleophilicity:



2. Answer any two questions : $5 \times 2 = 10$

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



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

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

- b) i) Compare with reasons the ease of nucleophilic substitution reactions in 2,

6-dimethyl-4-nitrochlorobenzene and 3,5-dimethyl-4-nitrochlorobenzene.

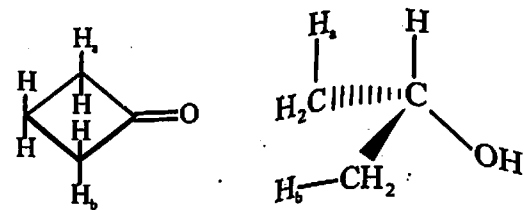
- ii) Give an example of a molecule with *S*-configuration having a pair of homomorphic ligands but one is *pro-R* and other is *pro-S*.

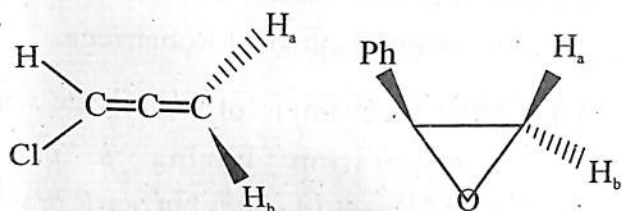
- iii) Draw the energy profile for a three step reaction in which the first step is fastest and the last step is slowest. $2+2+1$

- c) i) Find out the absolute configurations of the chiral centres of the compound(s) formed when Br_2 is added to *Re-Re* and *Si-Si* faces of fumaric acid.

- ii) Hydrolysis of $\text{EtSCH}_2\text{CH(Me)Cl}$ gives two products. Predict the major product with proper explanation. $2\frac{1}{2} + 2\frac{1}{2}$

- d) i) Indicate whether the hydrogen atoms marked H_a and H_b in each of the following compounds are homotopic, enantiotopic and diastereotopic. (any three)

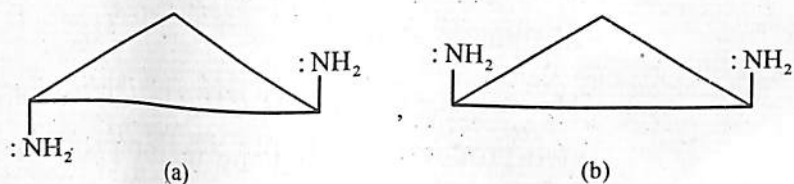




- ii) Bromination of propane is regio selective while chlorination is not — Justify the statement. 3+2

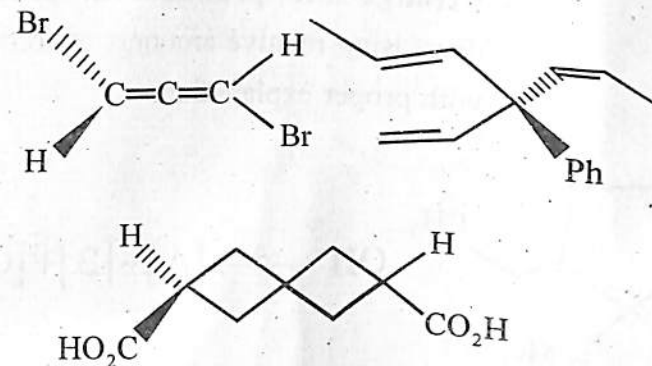
3. Answer any **two** questions: 10×2=20

- a) i) Which of the following compounds (a) and (b) is more basic and why?



- ii) How do you explain the statement that the rotation about the C-C bond in ethane at ordinary temperature is neither completely free nor frozen but only restricted?
- iii) Treatment of alkyl iodides with AgCN yields alkyl isocyanides as the major product whereas alkyl iodides give mainly alkyl cyanides on treatment with KCN—explain. (4)

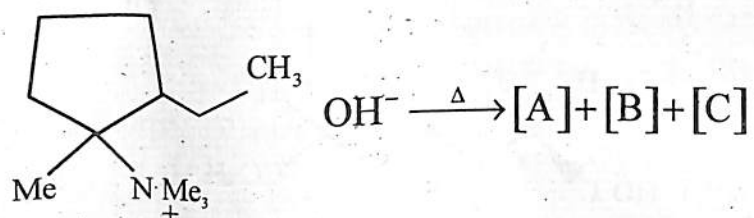
- iv) Assign *R/S* configurational descriptors to the following molecules (any **two**):



2+3+3+2

- b) i) Draw the energy profile diagram of 1-propyl chloride as a function of rotation about C₁-C₂ bond and label the maxima and minima with proper conformations.
- ii) Assign *Re-Si* descriptor to the face of acetaldehyde to which HCN will add to produce the corresponding (*R*)-cyanohydrin.
- 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.

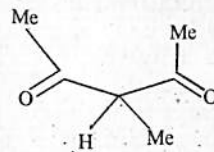
- iv) Identify the structures of the products of [A], [B] and [C] for the following reaction. Arrange the products in order of decreasing relative amounts of formation with proper explanation.



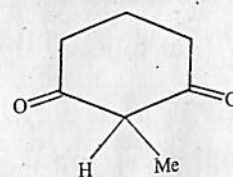
3+2+2+3

- c) i) Explain the stereoisomerism of 6,6'-dinitrophenyl -2, 2'-dicarboxylic acid and draw the energy profile diagram for racemization of its (*R*)-enantiomer.
- ii) Arrange the following compounds in increasing order of enol contents with reasons: $\text{PhCOCH}_2\text{COCH}_3$, $\text{CH}_3\text{COCH}_2\text{COCH}_3$, $\text{CH}_3\text{COCH}_2\text{COOEt}$, $\text{CH}_2(\text{CO}_2\text{Et})_2$
- iii) Define an intermediate. Draw the energy profile diagram for a two step reaction with an unstable intermediate.

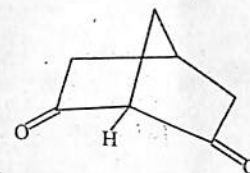
- iv) Of the following three diketones A, B and C, compounds A and B are acidic but C is not— explain.



A



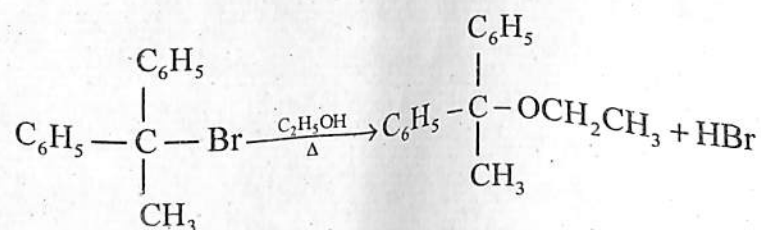
B



C

3+3+2+2

- d) i) How could you predict the intramolecularity of a reaction? Explain with a suitable example.
- ii) The *threo* form of a substrate undergoes 1,2-elimination reaction *via* the E-2 pathway more readily than the *erythro* form under identical reaction conditions. Explain with an example.
- iii) Answer the questions below for the following $\text{S}_{\text{N}}1$ reaction :



- A. What is the rate expression of the reaction ?
- B. What would be the effect on the rate of the reaction if the concentration of 1-bromo-1,1-diphenyl ethane is doubled?
- C. Will the rate of the reaction change significantly on addition of water to the solvent (C_2H_5OH) ?
- iv) A stereoisomer of 2-methyloxirane reacts with aqueous NaOH to give (R)-isomer of 1,2- propanediol. Identify the absolute configuration of the starting oxirane.

2+3+3+2
