

**U.G. 6th Semester Examination - 2022**

**CHEMISTRY**

[HONOURS]

Course Code : CHEM-H-CC-T-14

(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.*

**Answer all the questions.**

1. Answer any **five** from the following questions:

2×5=10

- a) How can you minimize the formation of undesired spirocyclic product in the Bardhan Sengupta synthesis of phenanthrene?
- b) Pyrrole-2-aldehyde does not undergo Cannizaro reaction whereas furan -2- aldehyde does. Explain why?
- c) How many destabilizing interactions are present in *cis*-1,2-dimethylcyclohexane? Is the molecule chiral? Explain your answer.
- d) Suprafacial [1,3] hydrogen shift is thermally forbidden but suprafacial [1,3] shift of an alkyl group can be thermally allowed. Why?

[Turn Over]

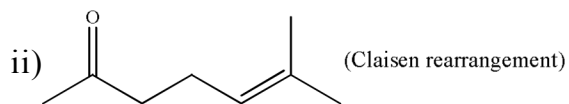
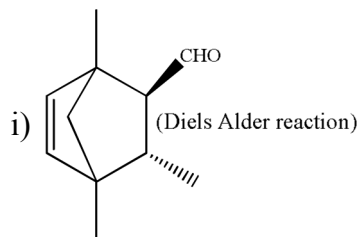
- e) Compare the rates of Diels Alder reaction of isoprene and 2-tert-butyl- 1, 3 – butadiene separately with tetracyanoethylene.
- f) Comment on the optical activity of the products when racemic alanine is strongly heated.
- g) Alkaline hydrolysis of RNA occurs faster than that of DNA. Why?
- h) How can you convert D-glucose into *meso*-tartaric acid?

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

- a)
  - i) How can you convert naphthalene into 9-methylanthracene?
  - ii) Furan and pyrrole react differently with maleic anhydride. Why? How pyrrole can be made to react with maleic anhydride in the same way as that of furan? 2+(2+1)=5
- b)
  - i) State with mechanism what happens when 2,3-dimethyl quinoline is treated with benzaldehyde in presence of alkali.
  - ii) Write down the most stable conformations of *trans*-1,2-dichlorocyclohexane in crystal and in the gaseous state. Explain your answer briefly. 2½×2=5

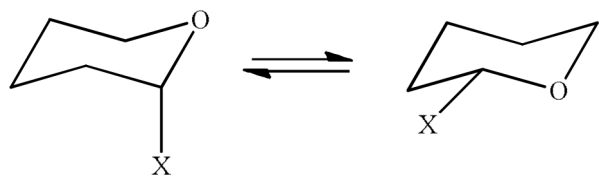
c) i) Acetolysis of optically active *trans*-2-acetoxy cyclohexyl tosylate gives optically inactive *trans*-1,2-diacetoxy cyclohexane but acetolysis of optically active *cis*-2-acetoxy cyclohexyl tosylate gives optically active *trans*-1,2-diacetoxy cyclohexane. Explain.

ii) How can you synthesize the following compounds by using the pericyclic reactions mentioned within parenthesis?



$$3+2=5$$

d) i) The following equilibrium favors left hand side for X = Cl and right hand side for X = pyridinium. Explain.



ii) What happens when L-alanine is heated with acetic anhydride in pyridine? Comment on the stereochemical aspects of the reaction with a plausible mechanism.  $2\frac{1}{2} \times 2 = 5$

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

a) i) When 1-nitronaphthalene is oxidized with permanganate, nitrogen is retained but when 1-amino naphthalene is oxidized with the same reagent, nitrogen is lost. Explain.

ii) State with mechanism when 1,2,3-trimethyl indole is treated with formaldehyde and dimethyl amine in presence of catalytic amount of acetic acid.

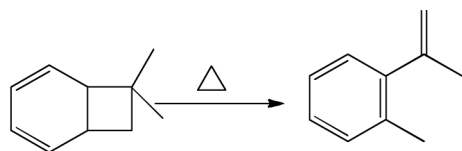
iii) Between *cis*- and *trans*- cyclohexane-1,3-dicarboxylic acids which one will undergo facile anhydride formation on heating? Justify your choice. Comment on the chirality of the anhydride that is formed easily.

iv) D-glucose reacts with hydroxylamine to give compound *A*. Heating of *A* with 1-fluoro-2,4-dinitrobenzene in aqueous sodium bicarbonate furnishes compound *B*. Identify *A* and *B* and formulate a

mechanism for the conversion of *A* to *B*.

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

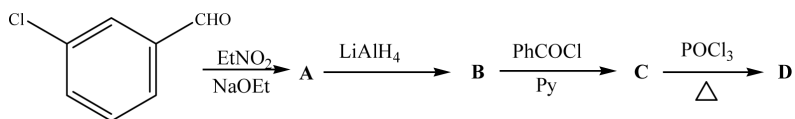
- b) i) Phenanthrene reacts with diazomethane but anthracene doesn't. Explain.  
 ii) State with mechanism what happens when pyridine is treated with dimethyl acetylene dicarboxylate.  
 iii) Formulate a mechanism for the following reaction clearly indicating the pericyclic steps involved therein.



- iv) How can you synthesize 'ala-phe-gly' using Merrifield protocol?  
 v) What is inversion of cane sugar?

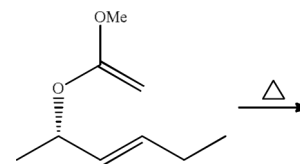
$$2+2+2+3+1=10$$

- c) i) Identify compounds (A-D) in the following sequence of reactions and suggest mechanism for the conversion of C to D.



- ii) Write down the zwitterionic structures of lysine and glutamic acid at their isoelectric points.

- iii) Under kinetically controlled conditions reaction between cyclopentadiene and maleic anhydride gives predominantly the *endo* cycloadduct despite its lower thermodynamic stability than the *exo* cycloadduct. Explain.  
 iv) Unlike glucose, arabinose shows abnormal mutarotation. Explain.  $4+2+2+2=10$   
 d) i) Explain the fate of the following reaction in terms of FMO theory.



- ii) Briefly explain how a DNA duplex is stabilized.  
 iii) For *trans*-2-chlorocyclohexanol both diaxial and diequatorial conformers are almost equally populated. Explain.  
 iv) D-Glucose but not D-galactose can be selectively methylated at C-3. Explain.

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