

U.G. 6th Semester Examination - 2021

CHEMISTRY

[HONOURS]

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

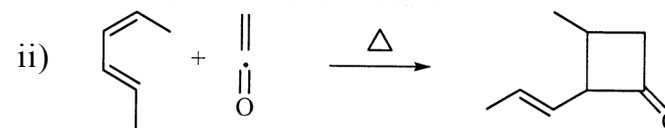
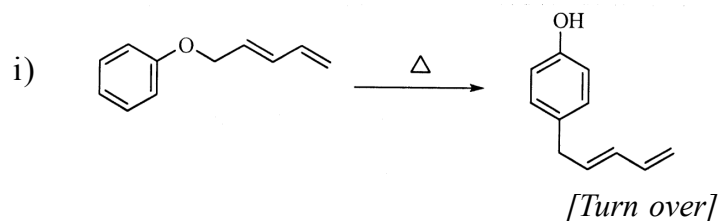
Full Marks : 40

Time : 2½ Hours

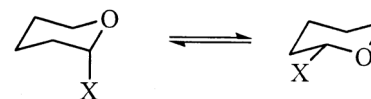
*The figures in the right-hand margin indicate marks.**Candidates are required to give their answers in their own words as far as practicable.***Answer all the questions.**1. Answer any **five** from the following questions:

2×5=10

- a) State with mechanism, how can you convert furan into 4-oxopentanoic acid (MeCOCH₂CH₂COOH).
- b) When treated with permanganate, 1-nitronaphthalene retains nitrogen but α-naphthylamine loses nitrogen. Explain.
- c) Properly designate the following pericyclic processes:



- d) Draw energy profile for conformational inversion of cyclohexane through the least energetic pathway.
- e) The following equilibrium favours left hand side for X = Cl and right hand side for X = NMe₃⁺. Explain.

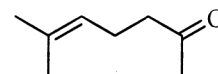


- f) (1R, 2S)-1,2-Dimethylcyclohexane exists as an inseparable dl-pair at room temperature. Explain.
- g) During peptide bond formation activation of COOH through conversion into COCl is not recommended when the -NH₂ group of amino acid is protected in the form of benzyl urethane. Why?
- h) How can you separate the components of a mixture of alanine, aspartic acid and lysine? Isoelectric points of alanine, aspartic acid and lysine are 6.1, 3.0 and 9.5 respectively.

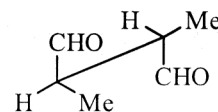
2. Answer any **two** questions from the following:

$$5 \times 2 = 10$$

- a) i) How can you minimize the formation of undesired spirocyclic product in the Bogert Cook synthesis of Phenanthrene?
ii) Count the number of destabilizing interactions present in all the conformers of *Cis*-1,3-dimethyl cyclohexane. Comment on the chirality of these conformers.
- b) i) Acetyl nitrate and nitronium fluoroborate nitrate furan *via* different mechanistic pathway but nitration of pyrrole with these two reagents takes place through the same mechanistic pathway. Offer an explanation.
ii) Tollen's oxidation of D-fructose yields a mixture of D-gluconic acid and D-mannonic acid. Explain with a suitable mechanism.
- c) i) State with mechanism, what happens when L-alanine is heated with acetic anhydride in presence of pyridine. Comment on the configuration of the product.
ii) How can you synthesize the following compounds as directed?



(via Claisen rearrangement)



(Using electrocyclic ring closure as one of the steps)

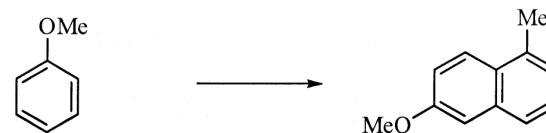
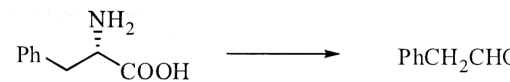
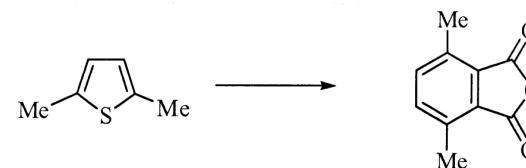
$$2 + \frac{1}{2} (1 + 1 \frac{1}{2})$$

- d) i) Briefly explain the factors responsible for the stabilisation of a DNA duplex.
ii) For *trans*-2-chlorocyclohexanol, both the axial and the equatorial isomers are almost equally populated. Explain.

3. Answer any **two** from the following questions:

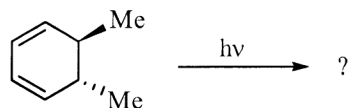
$$10 \times 2 = 20$$

- a) i) How can you accomplish the following transformations?



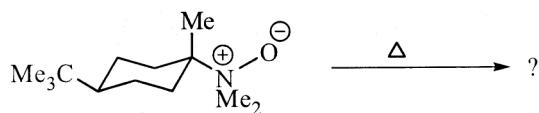
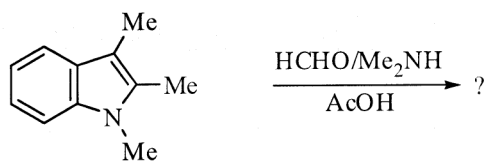
ii) Periodic acid oxidation of *cis*-isomer of 1,2-cyclohexanediol occurs 22 times faster than that of the *trans* isomer. Explain.

iii) Rationalise the fate of the following reaction in terms of FMO theory:



$$(2\frac{1}{2} + 1 + 2\frac{1}{2}) + 2 + 2$$

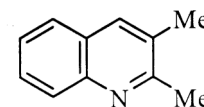
b) i) Predict the products in the following reactions and suggest plausible mechanism in each case. Also indicate the major product wherever necessary.



ii) How can you synthesize ala-phe-gly using Merrifield protocol?

iii) For D-glucose the percentage of α anomer in aqueous solution is 36 whereas for D-mannose the percentage of β -anomer in aqueous solution is 36. Offer an explanation. $(2\frac{1}{2} + 2\frac{1}{2}) + 3 + 2$

c) i) State with mechanism, how can you synthesize the following compound:



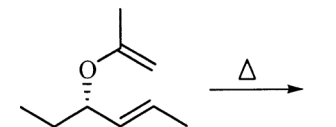
ii) Phenanthrene reacts with diazomethane but anthracene does not. Explain.

iii) For 4-*tert*-butyl cyclohexyl bromide the *cis* isomer reacts about 60 times faster than the *trans* isomer with PhSNa in aqueous EtOH. Explain with mechanism.

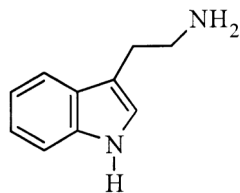
iv) Compare the rates of acid hydrolysis of adenosine and Guanosine with reason.

$$3 + 2 + (2\frac{1}{2} + 2\frac{1}{2})$$

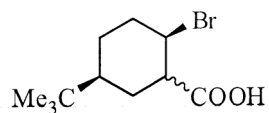
d) i) Comment on the stereochemical aspects of the following reaction:



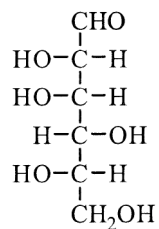
- ii) How can you convert indole into the following compound?



- iii) One of the diastereomers of the following compound loses COOH when treated with a base but the other does not. Why?



- iv) How can you convert D-glucose into the following sugar?



- v) G-C base pairing is stronger than A-T base pairing. Why? 2×5
