

RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

B.A./B.Sc. FIFTH SEMESTER EXAMINATION, DECEMBER 2018

THIRD YEAR (BATCH 2016-19)

CHEMISTRY (Honours)

Paper : V (Gr. B)

Date : 21/12/2018

Time : 11 am – 1 pm

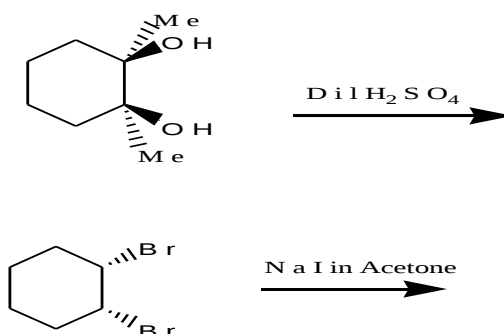
Full Marks : 50

(Answer one question from each Unit)

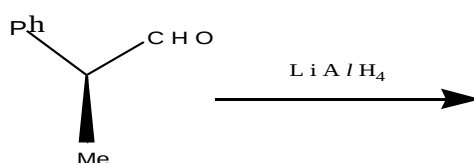
Unit – I

[12 marks]

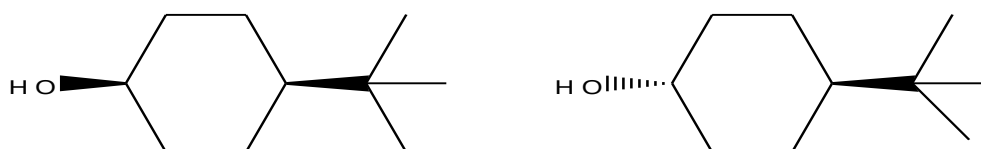
1. a) Conformation free energy values of Chlorine and Iodine atoms are almost identical, even though the size of iodine is larger than chlorine. Offer an explanation. (2)
- b) Between cis and trans 1,2-dimethylcyclohexane which one is more stable and why? Comment on their optical activity. (3)
- c) The ratio of saponification of *trans*-4-*t*-butylcyclohexane carboxylate to the *cis*-4-*t*-butylcyclohexane carboxylate is formed to be $K_{trans} : K_{cis} = 20:1$. Explain the observation. (2)
- d) Write the product of the following transformation with detailed mechanism. (3)



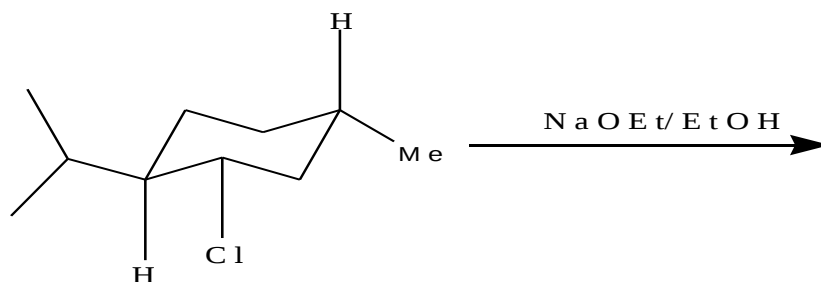
- e) Apply Felkin-Anh model to explain the formation of major diastereomer of the reaction. (2)



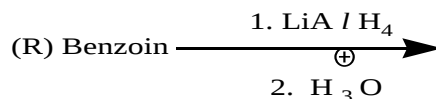
2. a) What do you mean by the term "pseudorotation"? Hence draw the energy profile diagram of ring inversion of chair form of cyclohexane through C_2 pathway clearly indicating the intermediates and transition states in the diagram. (1+2)
- b) Write down the stable conformations of the following molecules: (3)
 - (i) Cyclohexane-1,4-dione
 - (ii) 1,2,2,6,6-Pentamethyl-4-Hydroxy-4-phenylpiperidine
 - (iii) *trans*-1,3-Ditertiarybutylcyclohexane
- c) Which one of the following pair will undergo oxidation with chromic acid at a faster rate and why? (2)



d) Give the product of the following reaction with plausible mechanism. (2)



e) Applying Cram's rule, write down the major product of the following reaction: (2)



Unit – II

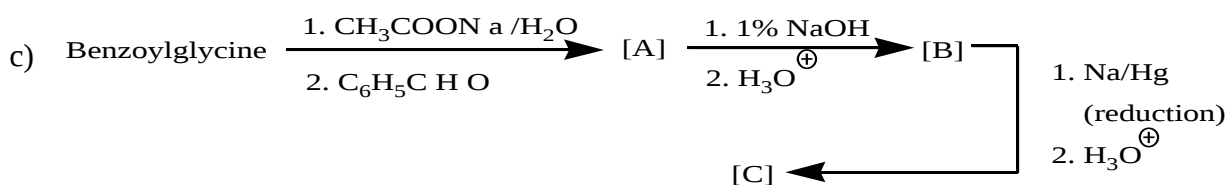
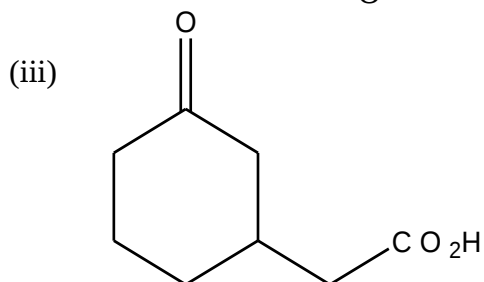
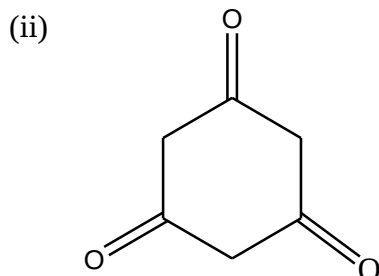
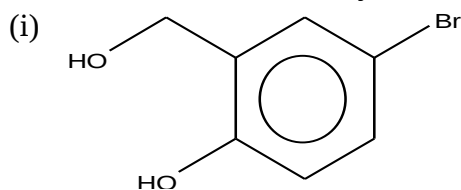
[13 marks]

3. a) Answer the questions as instructed.

(i) Give two examples of illogical electrophile.

(ii) A suitable reagent to convert RCH_2OH to RCHO . (2)

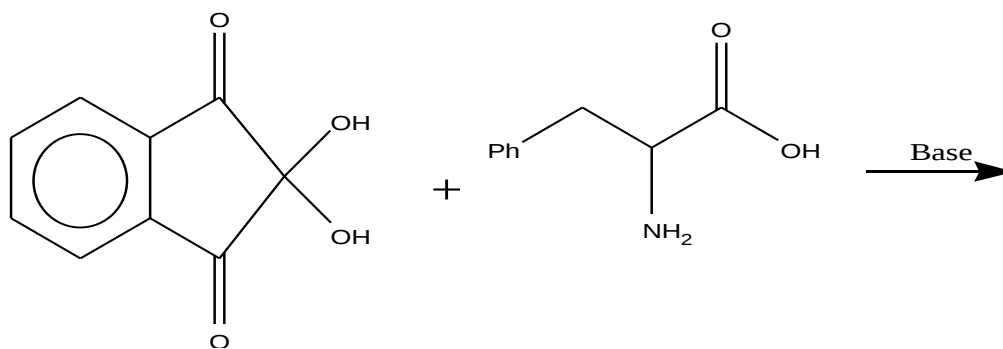
b) Outline retro and forward synthesis of the following molecules (**any two**): (3+3)



Give the mechanism of formation of [A]. (3)

d) Synthesis gly-ala in the solution phase using DCC as the activating agent. (2)

4. a) Predict the product of the following reaction and give mechanism: (3)



b) Write down the name and structure of amino acids with: (2)

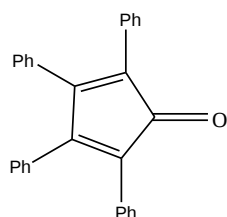
(i) acidic side chain

(ii) basic side chain

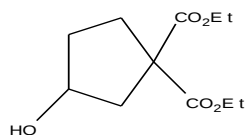
c) Describe the synthesis of phenylalanine using Strecker method. (2)

d) Outline the synthesis of following compounds by showing retrosynthetic analysis (**any two**): (2×3)

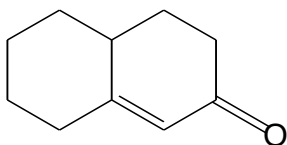
(i)



(ii)



(iii)



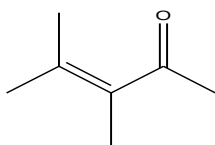
Unit – III

[12 marks]

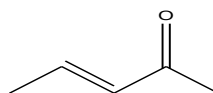
5. a) Define the following terms each with one example: (2)

(i) Anochrome, (ii) Hyperchromic effect

b) Which one of the following molecules should show $\pi \rightarrow \pi^*$ electronic transition at higher wave length? Also find out the $\lambda_{\max}$ value for molecule [D]. (2)

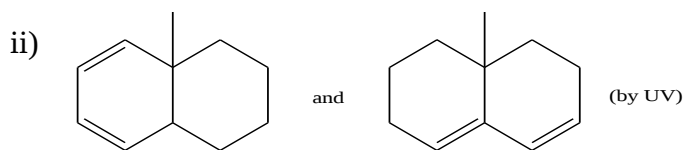
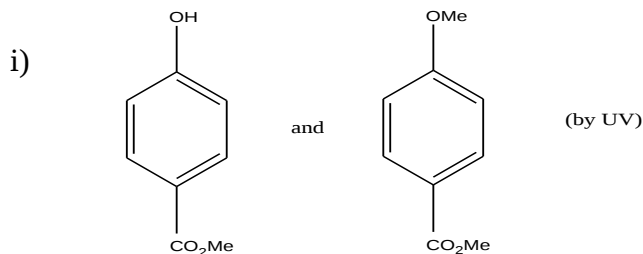


[D]

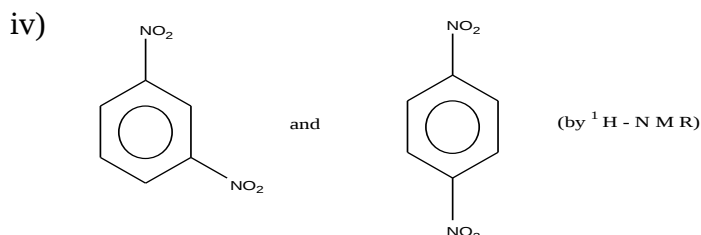


[E]

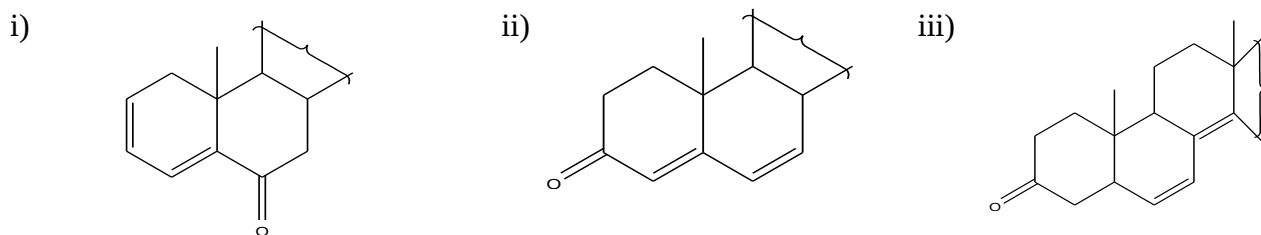
c) How could you distinguish the following compounds (**any three**): (3 × 2)



iii) Methylbenzoate and Phenylacetate (by IR spectroscopy)



- d) A compound with molecular formula C₅H₁₀O had a band at 1715 cm⁻¹ in IR spectrum and Two singlet in ¹H-NMR (a triplet and a quartet) – predict the structure of the molecule. (2)
6. a) The following polyenones have λ_{max} at 284 nm (ε = 28,000), 315 nm (ε = 7000) and 355 nm (ε = 26,500) in ethanol. Identify each of the compounds applying Woodward–Fieser rules. (3)

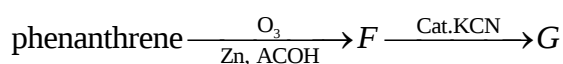


- b) How can you distinguish between *cis*-cyclohexane-1,2-diol and *cis*-cyclohexane-1,3-diol by IR spectroscopy? (2½)
- c) What will be the change in UV spectrum of 4-nitro-N,N-dimethylaniline when it is made acidic from a neutral medium? (2½)
- d) Assign the given δ_H (in ppm) values for the aromatic protons present in the following molecules with explanation. (2+2)
- i) Anisole: δ 7.17 (2H,m), δ 6.86 (1H,m), δ 6.81 (2H,m)
- ii) Benzaldehyde: δ 7.8 (2H,m), δ 7.6 (1H,m), δ 7.5 (2H,m)

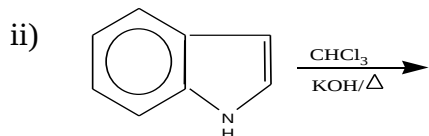
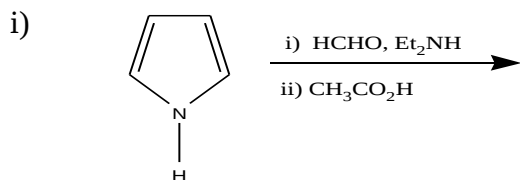
Unit – IV

[13 marks]

7. a) Carryout the following transformation (no mechanism needed): (2+2)
- i) Naphthalene → phenanthrene
- ii) O-Fluorobromobenzene → α-Naphthol
- b) In the following reaction, identify the molecule F and G. Also give mechanism for formation of G from F. (3)



c) Write down the product for the following reaction with mechanism:



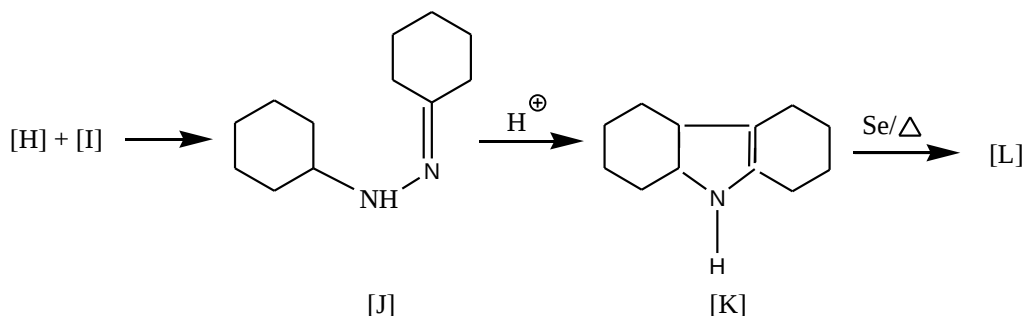
(2)

d) Write down the structure of Nifedipine along with two uses of it in medicine.

(2)

8. a) Complete the following reaction sequence:

(3)



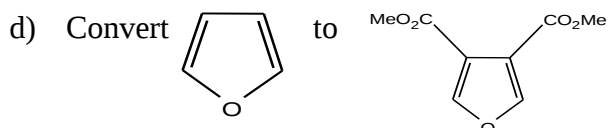
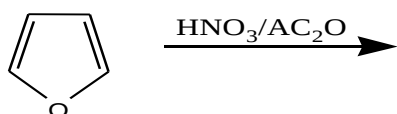
Identify [H],[I] and [L] in the reaction and show the mechanism of formation of [K] from [J].

b) Pyrrole is a π -excess molecule while pyridine is a π -deficit one. Explain the statement.

(2)

c) Predict the product of the following reaction with plausible mechanism:

(2)



(2)

e) How is naphthalene synthesised using Friedel-Craft reaction as one of the steps.

(2)

f) Draw the structure for Amlodipine and also give one use for it.

(2)

_____ x _____