RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. FIFTH SEMESTER EXAMINATION, MARCH 2021
THIRD YEAR [BATCH 2018-21]
CHEMISTRY [HONOURS]
Paper : V [Gr.B]

Date : 16/03/2021
Time : 11.00 am – 1.00 pm
Full Marks : 50

Attempt **one question** from **each unit**

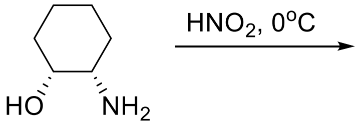
Unit I

[12 marks]

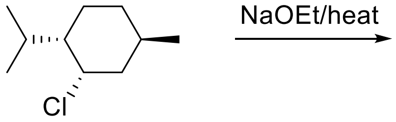
1. a) Draw and explain the energy profile diagram of ring inversion of chair form of cyclohexane through C_2 pathway with intermediates and transition states in the diagram. [3]

   b) Predict the products for the following reactions also explain with mechanism: [2×2]

   i)

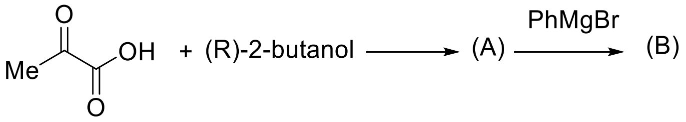


   ii)



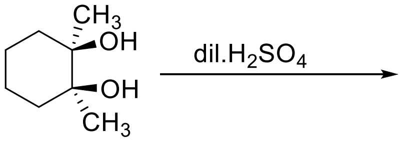
   c) The conformational free energies of Cl,Br, I are same (when attached to cyclohexane) – explain. [2]

   d) Predict the products (A) and (B, major) of the following reaction sequence: [3]



2. a) Predict the products for the following reactions also explain with mechanism: [2×2]

   i)



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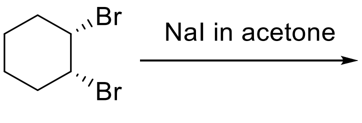
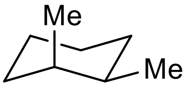


   b) Which of the following pair will react faster with chromic acid:

   trans-4-t-butylcyclohexanol and cis-4-t-butylcyclohexanol [2]

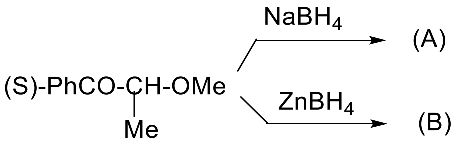
   c) Show the stereochemical relationship between (A) and its flipped form. [2]



(A)

   d) Draw the stable chair form of cis-1,3-dimethylcyclohexane in the Newman projection formula. [1]

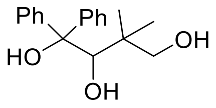
e) Predict the major product (A) and (B) of the following reaction sequence: [1.5×2]



Unit II [13 marks]

3. a) Give retrosynthetic analysis and an efficient synthesis of the following compounds: [3×2]

i)



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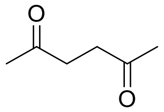
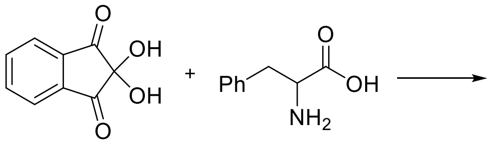
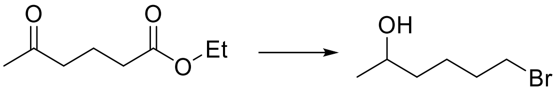


b) Describe the synthesis of Tyrosine applying Erlemeyer azalactone synthesis. [2]

c) Predict the product of the following reaction. Give mechanism. [3]



d) Convert: [2]

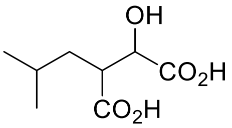


4. a) During deprotection of benzyloxycarbonyl group from a N-protected peptide, usually additives like anisole or dimethyl sulphide is used - explain the role of these additives. [2]

b) Synthesise Ala-Phe-Gly using solid phase peptide synthesis method. [2]

c) Outline the total synthesis of the following molecules showing retrosynthetic analysis. [3]

i)



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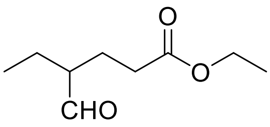
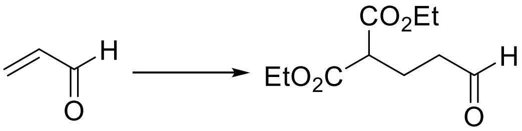
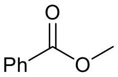
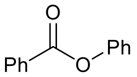


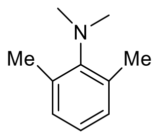
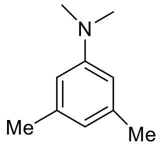
d) Carry out the following conversion: [2×3]

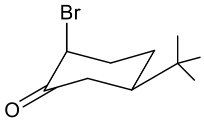
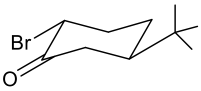


Unit III [12 marks]

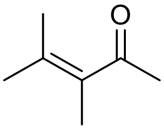
5. a) How would you distinguish between the following compounds by spectroscopic method: [3×2]

i)  and  (by IR spectroscopic method)

ii)  and  (by UV spectroscopic method)

iii)  and  (by IR spectroscopic method)

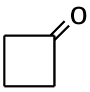
b) Calculate the value for λ_{max} for the molecule [2]

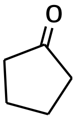


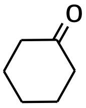
c) Discuss the effect of dilution by CCl_4 on IR absorption position of O-H stretching frequency of EtOH. [2]

d) Saturated acyclic ketones usually gives three absorption bands in their UV spectra at around 160 nm, 190 nm and 280 nm. Assign them in terms of electronic transition and also predict with proper reason which one will be recorded as most intense absorption. [2]

6. a) Arrange the following molecules with increasing order of increasing C=O stretching frequency with proper reason: [3]


I

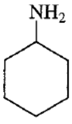

II

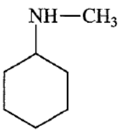

III

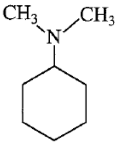
b) The UV spectrum of α, β–unsaturated ketone shows absorption bands at 230 and 321 nm in isooctane. Assign them in terms of electronic transition. How does the absorption band change their position with the change of solvent from isooctane to water? [3]

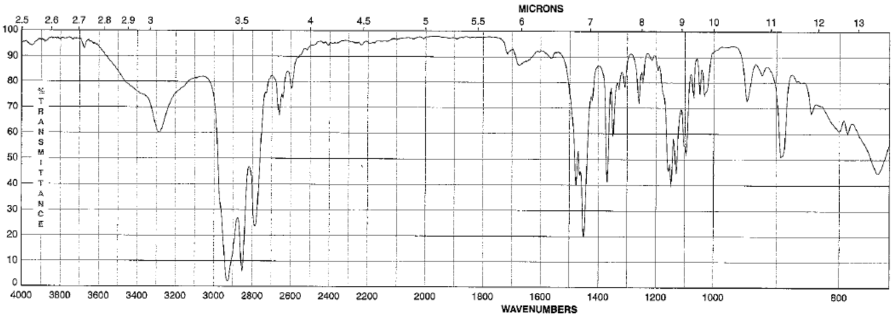
c) Identify the following compound (A, B, C) from the corresponding given IR spectra and also give explanation for your answer. [2×2]

(i)


A


B


C



d) Explain the following observation: [2]

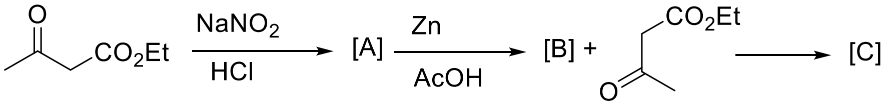
i) 1,3-butadiene shows the UV absorption maxima at 217 nm (ε 21000) while 1,3,5-hexatriene exhibits maxima 258nm (ε 35000).

ii) The UV absorption spectrum of o-nitophenol has λ_{max} 350 nm in a 0.1 M HCl but in 0.1 NaOH its shifted to λ_{max} 415 nm.

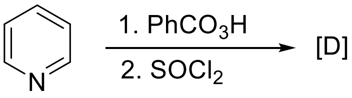
Unit IV [13 marks]

7. a) Predict the products from (A) to (H) in the following reactions: [3+2+2+1+2]

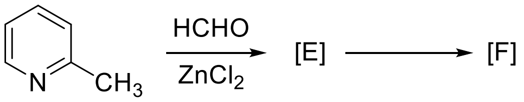
i)



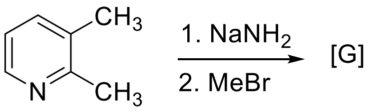
ii)



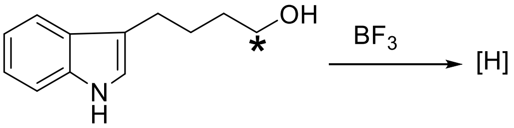
iii)



iv)



v)

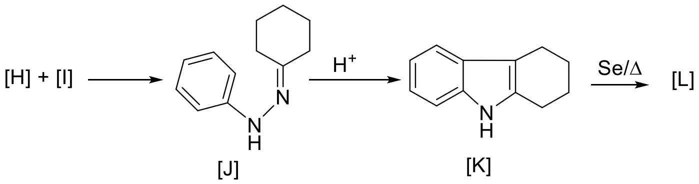


Give mechanism for the formation of (H).

b) Predict the products from (A) and (B) in the following reactions; also give mechanism for the formation of (B). [3]

$$\text{Phenanthrene} \xrightarrow[\text{Zn, AcOH}]{O_3} \text{A} \xrightarrow{\text{Cat. KCN}} \text{B}$$

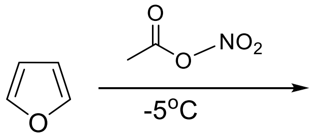
8. a) Complete the following reaction sequence:



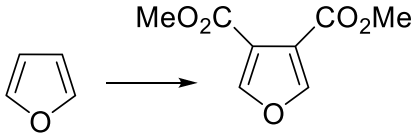
Identify [H], [I] and [L] in the reaction and show the mechanism of formation of [K] from [J]. [3]

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 mechanism: [2]



d) Convert: [2]



e) Apply Diels-Alder reaction for the synthesis of anthracene. Starting from anthracene how would you obtain 9-bromoanthracene? Explain the reaction with mechanism. [3]

f) Give a chemical reaction to distinguish anthraquinone from phenanthroquinone. [1]

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