RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

B.A./B.Sc. FIFTH SEMESTER EXAMINATION, DECEMBER 2014

THIRD YEAR

Date : 20/12/2014 **CHEMISTRY (Honours)**

Time : 11 am – 1 pm **Paper :** V (Gr. B) Full Marks : 50

(Answer <u>one question</u> from each Unit)

<u>Unit – I</u>

1. a) Predict the preferred conformation between cis and trans-1-phenyl-2-amino cyclohexanols. [3]

   b) Explain the effect of heat on the diastereoismers of 4-hydroxy cyclohexane carboxylic acid. [2]

   c) What would happen when cis-3 methoxy cyclohexane carboxylic acid is heated with acetic anhydride? [3]

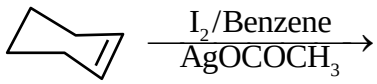
   d) Predict the predominant product of the following reaction— [3]

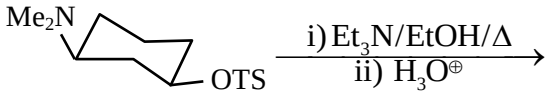
   (R)-3-phenyl-2-butanone $\xrightarrow[ii)\ H_3O^+]{i)\ LAH}$

   e) Indicate the symmetry elements in boat conformation of cyclohexane. [1]

2. a) Draw with proper labelling the energy profile for the flipping of chair conformation of cyclohexane. [3]

   b) Predict the product(s) in each of the following reactions with plausible mechanism in each case . [3+3]

   i) 

   ii) 

   c) Draw all possible chair conformations of *cis*-1, 3-dimethyl cyclohexane and comment on their relative stability and optical activity with reason. [3]

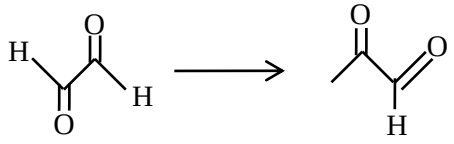
<u>Unit – II</u>

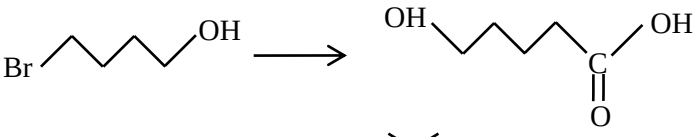
3. a) An aqueous solution containing alanine, glutamic acid and arginine is buffered at pH 6·0. If an electric current be passed through this solution, what would happen? [Given pi of alanine = 6, glutamic acid = 3·2 & arginine = 10·7] [3]

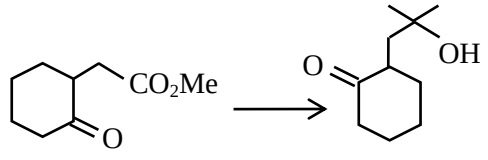
   b) Synthesise racemic phenyl alanine by azalactone method. [2]

   c) Outline the steps (protection, activation etc) to synthesize the dipeptide Phe-Ala. [3]

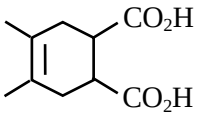
   d) How can you convert (**<u>any two</u>**): [2×2½]

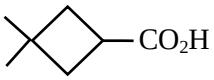
   i) 

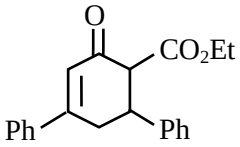
   ii) 

   iii) 

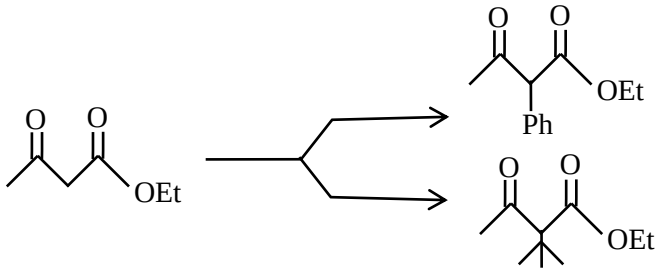
4. a) Give retrosynthetic analysis and one efficient synthesis of each of the following compounds (**any two**) : [2×3]

i) 

ii) 

iii) 

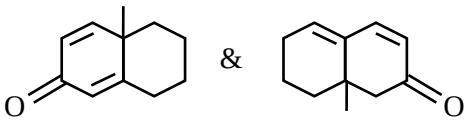
b) Carryout the following transformations showing steps : [2+2]



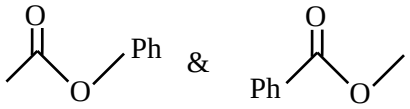
c) Write the structure of the violet-coloured product formed by reaction between alanine and ninhydrine showing steps. [3]

Unit – III

5. a) How can you distinguish between the given pairs, by— [2+2]

i) 

(U.V)

ii) 

(I.R)

b) Explain the terms in connection with NMR spectroscopy (**any two**) : [2]

i) Magnetic anisotropy ii) Coupling constant iii) Integration

c) How many carbonyl stretching bands would you observe for ortho hydroxy-metanitro-acetophenone? [2]

d) For a compound of molecular formula $C_5H_{10}O_2$, the following spectral data are obtained :

IR : 1200 cm^{-1}(s), 1740 cm^{-1}(s), 3000 cm^{-1}(m); PMR : Two quartets at $\delta 4{\cdot}1$ & $\delta 2{\cdot}3$, Two triplets at $\delta 1{\cdot}3$ & $\delta 1{\cdot}2$; Integration ratio (downfield to upfield) : 2 : 2 : 3 : 3

From these informations, assign a structural formula to the compound. [4]

6. a) Explain why a polar solvent usually shifts the $\pi \rightarrow \pi^*$ transition to longer wave lengths. [2]

b) Give the characteristic absorption bands in the IR spectrum of benzaldehyde. What changes do you observe in the absorption bands if benzaldehyde is oxidised to benzoic acid? [3]

c) A compound having molecular formula $C_6H_{10}O$ shows a 6H singlet at 2·30 ppm, a 1H singlet at 6·09 ppm and 3H singlet at 2·27 ppm in the NMR spectrum. The compound shows absorption at 1705 cm^{-1} in IR spectrum.

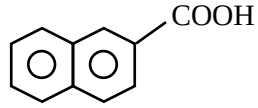
Identify the structure of the compound with proper assignment of the NMR and IR signals. [4]

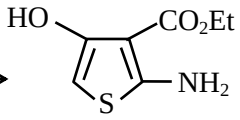
d) Define with one example each : [1½+1½]

i) Bathochromic shift ii) Hypochromic effect

Unit – IV

7. a) Outline the steps to carry out the following transformations (**any one**) : [3]

i) Naphthalene 

ii) Ethyl cyanoacetate $\longrightarrow$ 

b) Name an antimalarial drug and give its synthesis. [3]

c) Convert with showing mechanism (**any two**) : [3+3]

i) Pyridine $\rightarrow$ 4-nitropyridine

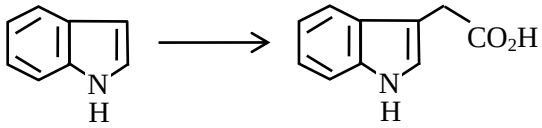
ii) Anthranilic acid $\rightarrow \alpha$ -naphthol

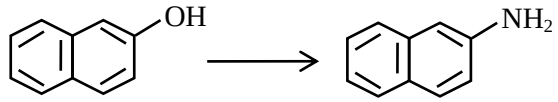
iii) m-anisidine $\rightarrow$ 7-methoxyquinoline

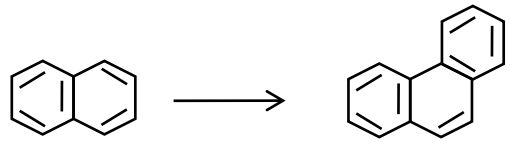
d) Pyridine is more readily attacked by nucleophiles than electrophiles —explain. [1]

8. a) Work backword to derive a phenyl hydrozone needed to synthesize 3-ethyl-2-methylindole by Fischer method showing the synthesis and show the isomeric product that is also isolated. Cite one experiment to ascertain which nitrogen of the phenyl hydrazone is lost during the reaction. [3+1+2]

b) Carryout the following transformations (**any two**) : [2+2]

i) 

ii) 

iii) 

c) Outline the synthesis of ranitidine. Mention one use of it. [3]

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