RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

B.A./B.SC. FIFTH SEMESTER EXAMINATION, DECEMBER 2013

THIRD YEAR

Date : 19/12/2013 **CHEMISTRY (Honours)**

Time : 11 am – 1 pm Paper : V-B Full Marks : 50

[*Answer **one** question from each unit***]**

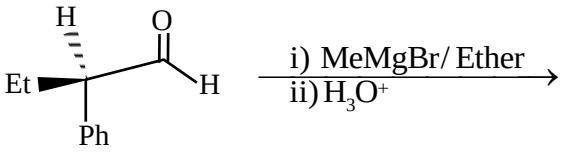
Unit - I

1. a) Draw the preferred conformation of 1-methyl-1-phenyl cyclohexane and justify your answer. [2]

   b) Predict with reasons, which one of the following pair will undergo faster oxidation with chromic acid. [3]

   trans-4-t-butylcyclohexanol and *cis*-4-t-butylcyclohexanol

   c) Use Felkin-Anh model to explain the formation of major product : [3]



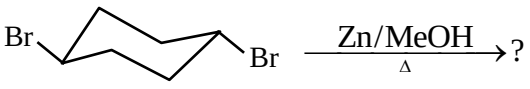
   d) Explain the fact that the ketone, Ph-CO-$CHMe_2$ on treatment with (S)-Ph-CHEt-CH_2MgCl, is reduced preprentially to the alcohol, (S)-PhCHOH-$CHMe_2$. [2]

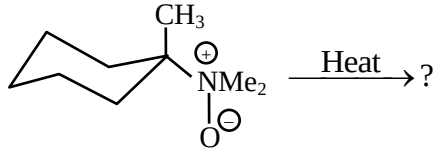
   e) Represent 1-methylcyclohexane in Newman projection formula and estimate the energies between two conformers. [2]

2. a) Draw the energy diagram for the ring inversion of cyclohexane following the C_2-pathway and explain the diagram. [3]

   b) Explain that *trans*-4-t-butylcyclohexyl tosylate undergoes elimination to give 4-t-butlcyclohexene with the base $\overset{(-)}{S}Ph$ although not with much stronger base $\overset{(-)}{O}Et$. [3]

   c) Predict the product(s) with mechanism : [3+3]

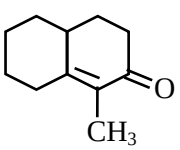
i) 

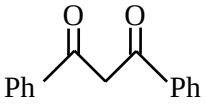
ii) 

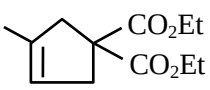
Unit - II

3. a) What is a synthon? Give one example of compounds that may form a^2 and d^1 types of synthons. [3]

   b) Give retrosynthetic analysis and efficient synthesis for each of the following (**any two**) : [2½×2]

i) 

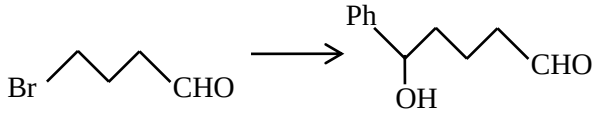
ii) 

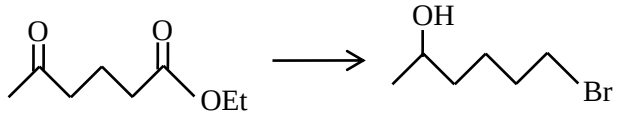
iii) 

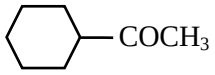
   c) What is Merrifield resin? Write the steps for the synthesis of the dipeptide gly-ala in the solid phase with the help of this resin. [3]

   d) Write the mechanism of ninhydrin reaction with an amino acid $R-NH-CH_2-CO_2H$ [2]

4. a) How would you carry out the following transformations? (**any two**) [2½×2]

i) 

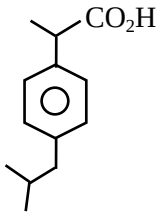
ii) 

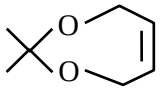
iii) $CH_3COCH_2CO_2Et \rightarrow$ 

b) Explain, with mechanism, the role of dicyclohexylcarbodiimide in the formation of the peptide linkage between two different suitably blocked amino acids. [3]

c) Trace the route of synthesis of R-$CH(NH_2)$-CO_2H from phthalimide. [2]

d) Give retrosynthetic analyses of the following and show their forward synthesis also : (**<u>any one</u>**) [3]

i) 

ii) 

Unit - III

5. a) Define chemical shift and explain the terms—
(i) downfield and (ii) upfield shifts as used in NMR spectroscopy. [3]

b) How would you distinguish between the members of each of the following pairs of compounds as indicated. [2×3]

i) *trans*-stilbene and *cis*-stilbene (by uv spectroscopy)

ii) *ortho*-chloronitrobenzene and *para*-chloronitrobenzene (by NMR spectroscopy)

iii) *ortho*-hydroxyacetophenone and *para*-hydroxyacetophenone (by IR spectroscopy)

c) Draw the ^{1}HNMR signals of CH_3CH_2OH (ordinary grade) showing relative chemical shifts, integration and spin-spin coupling patterns. [3]

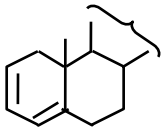
6. a) An organic compound [B] having molecular formula C_4H_8O absorbs at 274 nm ($\in_{max} = 17$) in uv spectroscopy. In IR, a strong absorption band is found at 1715 cm^{-1}, and medium absorption band are formed at 2940 – 2860 cm^{-1}(m) and 1460 cm^{-1}(m). The signals in NMR spectrum are (i) δ 2·48 (quartet), (ii) δ 2·12 (s) and (iii) δ 1·07 (t).

Assign the structure of [B], explaining the spectroscopic observations. [4]

b) In n-hexane, mesityl oxide [Me_2C = CHCOMe] shows two absorption peaks at λ_{max} 230 nm and 270nm. Identify the electronic transition for each of them. Explain how these λ_{max} values shift if water is used as solvent instead of n-hexane. [3]

c) Why TMS is used in NMR spectroscopy? [2]

d) Calculate λ_{max} in uv spectrum for the following compound using Woodward-Hofmann's rule. [3]

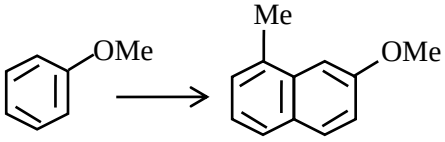


Unit - IV

7. a) Indole undergoes electrophilic substitution primarily at C–3 but pyrrole does at C–2. Explain. [2]

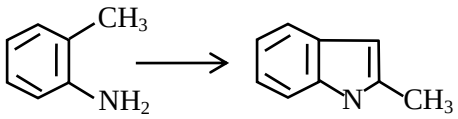
b) How can you convert naphthalene to 2-aminonaphthalene? [3]

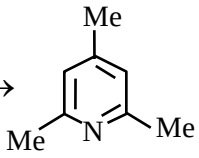
c) Write the structure of the product showing the steps of reaction, when β-phenylethylamine is heated with acetyl chloride in presence of $POCl_3$ and the resulting product is heated with palladium-charcoal. [3]

d) Convert :  [2]

e) Outline the synthesis of ranitidine and mention one use of it. [3]

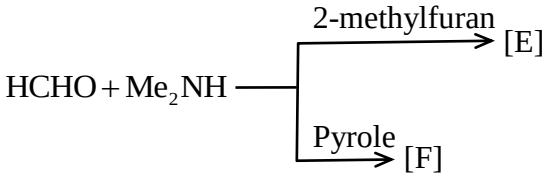
8. a) Carryout the following conversions. Write down the reaction conditions and the reagents involved. [2×2]

i) 

ii) $CH_3COCH_2CO_2C_2H_5 \rightarrow$ 

b) Convert : Phthalic acid $\rightarrow$ 9-methylanthracene. [2]

c) Identify the products [E] and [F] in the following reactions and explain the reaction scheme : [4]



[4]

d) Outline the synthesis of nifedipine. Mention one use of it. [3]