RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. FIFTH SEMESTER EXAMINATION, DECEMBER 2015

THIRD YEAR [BATCH 2013-16]

Date : 18/12/2015 **CHEMISTRY [Hons]**

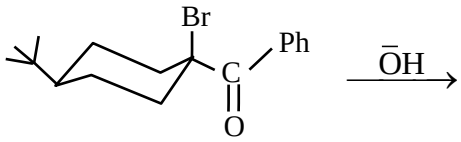
Time : 11 am – 1 pm **Paper : V [Group – B]** Full Marks : 50

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

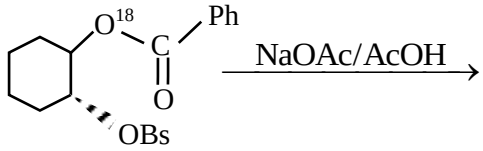
Unit - I

1. a) Draw all possible chair conformations of cis-1, 2-dimethylcyclohexane and trans-1, 2-dimethyl-cyclohexane and compare their relative stability. Also comment on their optical activity. [4]

   b) Give the product(s) in the following reaction with plausible mechanism. [2]



   c) Predict mechanistically the product(s) in the following reaction. [3]



   (Bs = *p*-bromobenzenosulphonate)

   d) Predict the predominant product of the following reaction with reason :

$$(R)-PhCOC(Me)(OH)Ph \xrightarrow{1.MeLi,\ 2.H^+}$$ [3]

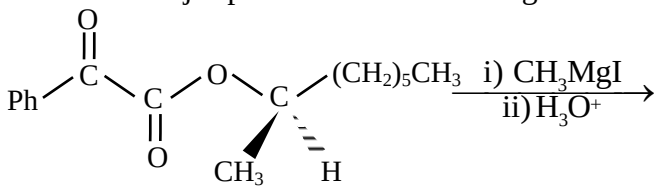
2. a) Predict with reasons which one of the following pair will undergo faster oxidation with chromic acid :

   trans-4-t-butylcyclohexanol and cis-4-t-butylcyclohexanol. [3]

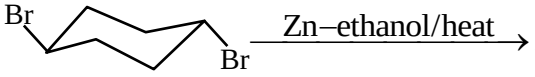
   b) Draw preferred conformation of 1-methyl-1-phenylcyclohexane and justify your answer. [2]

   c) Explain that in the reaction with Sodium Thiophenoxide (PhSNa) in aqueous ethanol, cis-t-butylcyclohexylbromide reacts about 60 times faster than the trans-isomer. [2]

   d) Predict the major product in the following reaction and justify your answer : [3]



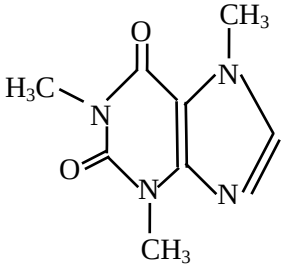
   e) Predict the product(s) of the following reaction with plausible mechanism. Explain the importance of the relative stereochemical relationship between the two leaving atoms. [2]



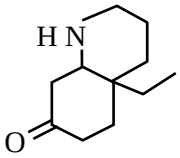
Unit - II

3. a) Give retrosynthetic analysis of the following and show their forward synthesis also (**any one**) : [4]

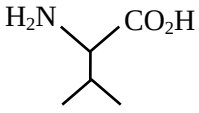
   i)



   ii)

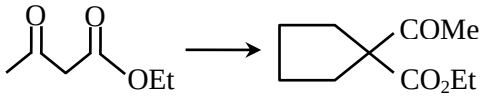


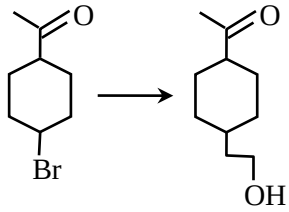
b) Using Merrifield solid phase method synthesize a tripeptide, Ala-Val-Phe. [3]



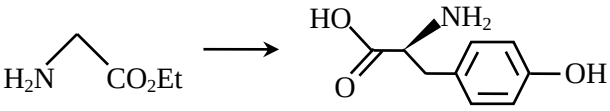
valine

c) How would you carry out the following transformation? [2+2]

i) 

ii) 

d) Carry out the following conversion : [2]

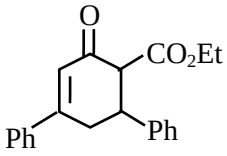


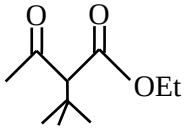
tyrosine

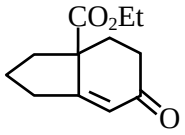
4. a) What are meant by 'illogical electrophile' and 'illogical nucleophile'? Give examples. [2]

b) Trace the route of synthesis of phenylalanine using diketopiperazine. [3]

c) Give retrosynthetic analysis and an efficient synthesis for the following : [3+2+3]

i) 

ii) 

iii) 

Unit - III

5. a) How would you differentiate between the members of each of the following pairs of compounds as specified. [3×2]

i) $CH_3-CH_2-C\equiv CH$ and $CH_3-C\equiv C-CH_3$ (by ^{1}HNMR spectroscopy)

ii) $CH_3-\underset{\underset{O}{||}}{C}-O-CH=CH_2$ and $CH_2=CH-\underset{\underset{O}{||}}{C}-O-CH_3$ (by IR spectroscopy)

iii) trans-stilbene and cis-stilbene (by UV spectroscopy)

b) 4-Methyl-3-penten-2-one has two absorption bands in its UV spectrum, one at 236 nm and one at 314 nm.

i) Why are there two absorption bands?

ii) Which band shows the greater absorbance? [2]

c) How many signals will you expect in the ^{1}H-NMR spectrum of o-dinitrobenzene? Assign the signals and arrange them in the increasing order of their chemical shifts. State the splitting pattern of the signals. How can you distinguish it from p-dinitrobenzene from their ^{1}H-NMR spectra? [3]

d) In ^{1}H NMR spectrum of ordinary ethanol one signal disappears while ethanol is shaken with D_2O. Which one and why? [1]

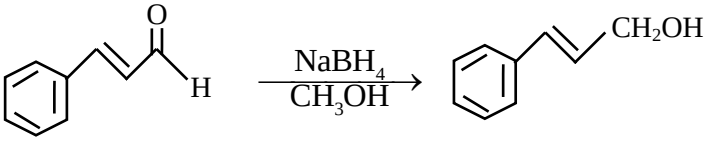
6. a) An organic compound with molecular formula $C_6H_{12}O$ gives positive iodoform test. Its UV, IR and ^{1}HNMR spectral data are given below :

UV : λ_{max} 282 nm, $\in_{max}$ 22

IR : ν_{max} 1710 cm^{-1}.

^{1}HNMR : δ 2·1 (3H, S) and 1·1 (9H, S) . Deduce the structure of the compound with proper explanation. [4]

b) Describe how the IR spectrum of the product would differ from that of the reactant in the following reaction. Give approximate frequencies for distinctive peaks in the IR spectrum of the reactant and also that of the product. [2]



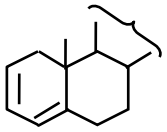
cinnamaldehyde cinnamyl alcohol

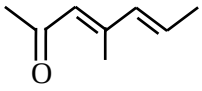
c) Sketch the expected ^{1}H NMR spectra of the following compounds taking TMS as the standard reference : [2×2]

i) $(CH_3)_2CH-CH_3$

ii) $H_3C-CH(Cl)-COCH_3$

d) Calculate λ_{max} (UV) values for the following compounds. [2]

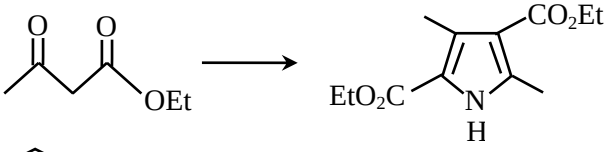
i) 

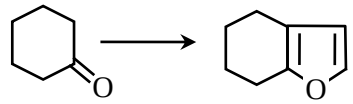
ii) 

Unit - IV

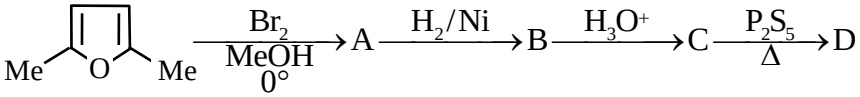
7. a) Outline Bardhan-Sengupta Synthesis of phenanthrene. [3]

b) Carryout the following conversions : [2×2]

i) 

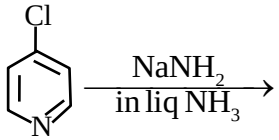
ii) 

c) Identify A, B, C, D in the following sequence of reactions : [2]



d) Show the steps for conversions of benzene to 1-phenylnaphthalene. [2]

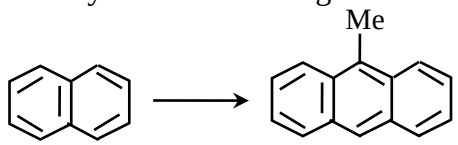
e) Write the product(s) in the following reaction with mechanism. [2]



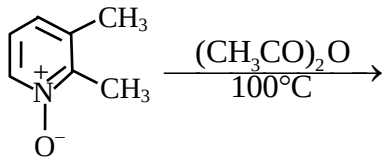
8. a) A mixture of cyclohexanone and phenylhydrazine on heating with poly phosphoric acid at 100°C affords an indole derivative. Give the structure of the product and explain the mechanism involved. Provide at least one experimental evidence in support of the mechanism. [3]

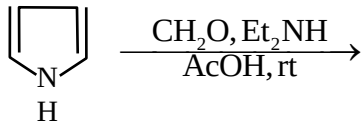
b) At low temperatures, phenanthrene undergoes $C_9 - C_{10}$ addition with Br_2. At high temperatures, Br substitution at C_9 occurs. Outline the mechanism of addition and substitution to phenanthrene. [2]

c) How would you carry out the following conversion? [2]



d) Write the product(s) in the following reactions with mechanism. [2+2]

i) 

ii) 

e) Write down the structure of amlodipine and make retrosynthetic analysis to furnish starting materials. [2]

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