

RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. FIFTH SEMESTER EXAMINATION, FEBRUARY 2022

THIRD YEAR [BATCH 2019-22]

CHEMISTRY (HONOURS)

Paper : XII [CC12]

Date : 28/02/2022

Time : 11 am – 1 pm

Full Marks : 50

[Attempt one question from each unit]

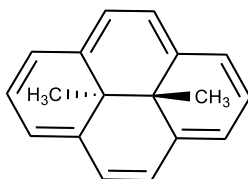
Unit –I

[13 Marks]

1. a) State the principal of proton magnetic resonance. [1]
- b) What is Larmor frequency? How does it change with applied magnetic field? [1+1]
- c) Explain how sharpness of NMR peak is related with spin lattice relaxation process. [1.5]
- d) In case of ^1H -NMR of PhCHO, two of the ring protons have resonance at 7.87 ppm, and other three resonance in the range from 7.5 to 7.6 ppm. Explain. [1.5]
- e) Derive the following equation and explain the role of magnetic analyzer in mass spectrometry. r is the radius of curvature; the M and Z is the mass and charge of the radical cation respectively. V is voltage and H is the magnetic field. [3]

$$\frac{m}{Z} = \frac{H^2 r^2}{2V}$$

- f) State the principle of formation of metastable ion in mass spectrometry. Calculate the expected apparent mass of the metastable ion produced when m/z : 77 decomposes by loss of $\text{CH}=\text{CH}$ to m/z : 51. [3]
- g) Explain why the methyl groups of the following molecule have resonance at -4.2 ppm? [1]



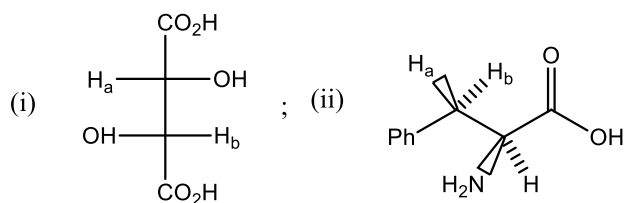
2. a) Explain the ^1H -NMR patterns and intensities of the isopropyl group in isopropyl iodide. [1.5]
- b) Chemical Shift of a proton in 60 MHz instrument is 5 ppm. Calculate the shift from TMS of the proton in 100 MHz instrument. [1.5]
- c) Explain how does ^1H - ^1H coupling constant in ^1H -NMR vary with dihedral angle? [1]
- d) Predict the appearance of the peak in ^1H - NMR spectrum of propyl bromide. [2]
- e) Explain the ratio of relative abundance of M , $(M+2)$ and $(M+4)$ peaks in the mass spectra of CH_2Cl_2 ? [2]
- f) Mass spectra of methyl butyrate (M.W. = 102) shows a peak at m/z : 74. How would you explain the formation of this peak? [2]

- g) State the working principal of (i) chemical ionization (ii) FAB and (iii) MALDI mass spectrometry. [3]

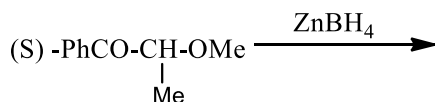
Unit -II

[13 marks]

3. a) Write down a scheme for the synthesis of the dipeptide, Ala-Leu, from L-aminoacids, using DCC promoted peptide bond formation. Give mechanism. [3]
- b) Carry out the following conversion: [3]
Glycine $\rightarrow$ Phenylalanine (using Erlenmeyer azlactone synthesis)
- c) Find out the topic relationship between the labelled atoms of the following molecules: [2]

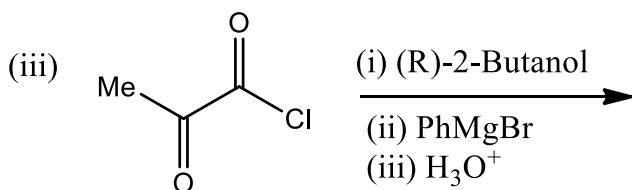
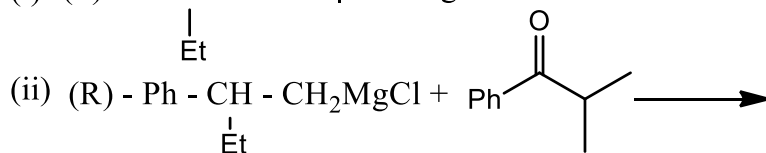
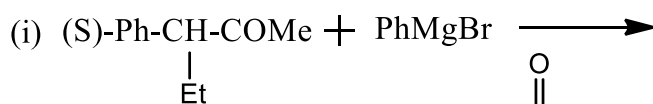


- d) Using Felkin-Anh model, predict the major product of the following reaction: [3]



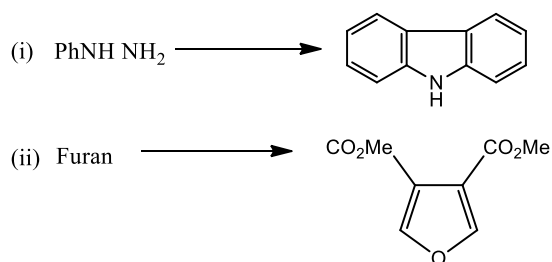
- e) Discuss the principle of enantioselective synthesis using a chiral auxiliary. [2]

4. a) Write down the structure of the violet-coloured product from the reaction of an amino acid with ninhydrin. Explain the reaction with mechanism. [3]
- b) How can lysine be separated from glycine? [2]
- c) Justify or criticise : The carbonyl faces of (S)-2-phenyl propanal is diastereotopic. [2]
- d) Predict the major product of the following reactions: [3×2]



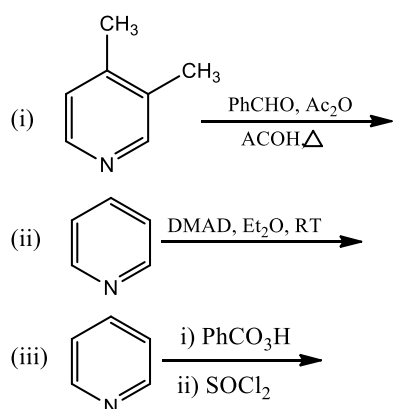
5. a) Carry out the following conversions:

[2×2]



b) Predict the product of the following reactions:

[3×2]

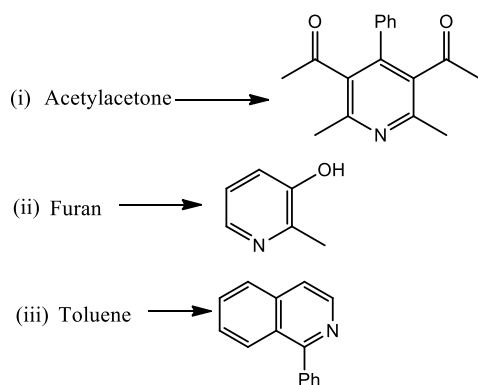


c) Outline the synthesis of Chloroquine.

[2]

6. a) Carry out the following conversions:

[3×2]

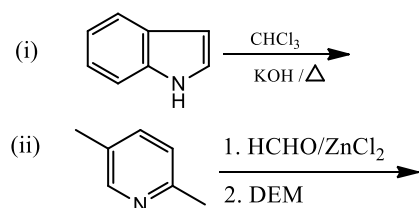


b) Draw the structure for Amlodipine and also give one use for it.

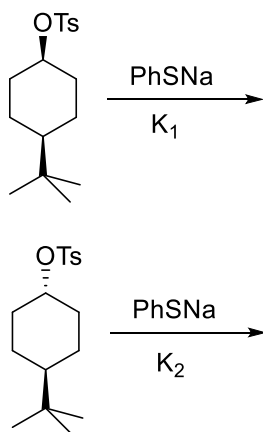
[2]

c) Write down the product of the following reactions:

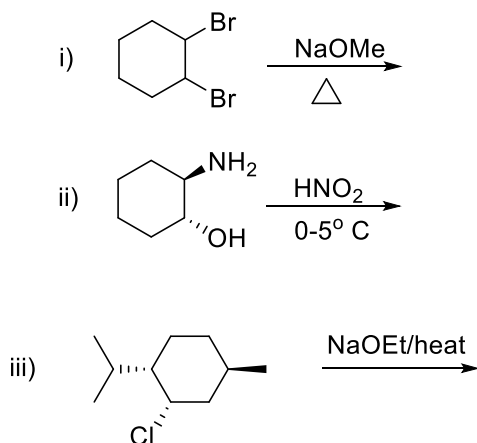
[2×2]



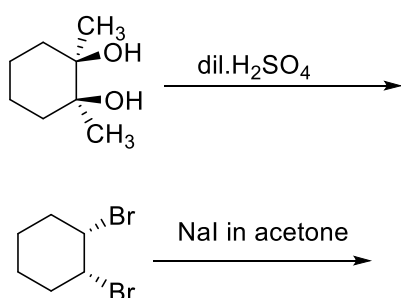
7. a) Write down the most stable conformation for cis-1,4-cyclohexanediol and trans-1,4-cyclohexanediol . [2]
- b) Compare the rate of substitution reactions for the following two molecules and also write down the structure of the products. [2]

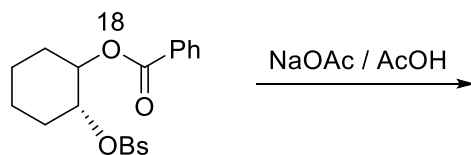


- c) Explain the products for the following reactions with mechanism. [3×2]



- d) Why twist boat form is lower in energy than true boat form? [2]
8. a) Draw the chair form of cis-1,3-dimethylcyclohexane in the Newman projection formula and how many gauche-butane interactions are present in the compound. Compare the stability of this cis-1,3-dimethylcyclohexane and trans-1,3-dimethylcyclohexane isomers. [3]
- b) Product with mechanism: [3×2]





c) Which of the following pair will undergo faster oxidation with chromic acid: trans-4-*t*-butylcyclohexanol and cis-4-*t*-butylcyclohexanol. [2]

d) Draw the preferred conformation of 1-methyl-1-phenylcyclohexane. [1]

_____ x _____