RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

B.A./B.Sc. FIFTH SEMESTER EXAMINATION, DECEMBER 2019 THIRD YEAR (BATCH 2017-20)

CHEMISTRY (Honours)

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

(Answer one question from each Unit)

<u>Unit – I</u>

[12 marks]

[3]

[2]

[2]

[3]

- 1. a) Predict, with reasons, which of the following pairs will react faster with chromic acid. trans 4-t butylcyclohexanol and Cis-4-t-butylcyclohexanol.
 - b) Draw the preferred conformation of 1-methyl-1-phenylcyclohexane and justify your answer. [2]
 - c) In gaseous state, the diaxial conformation of trans -1,2-dibromo cyclohexane is much more stable than diequatorial conformation $(\underline{a},\underline{a}:\underline{e},\underline{e}=95:5)$. However in benzene, both the conformations are nearly equally stable (a,a:e,e=52:48). Explain the observation.
 - d) Apply Felkin-Anh model to explain the formation of major diastereomer of the following reaction. (S)-2-phenyl-3-pentanone LiAlH₄ [2]
 - e) Predict the products of the following reactions with plausible mechanism. [3]

(i) Ph
$$H \xrightarrow{\Theta} OH/Ag_2O$$
 (ii) Ph $OH \xrightarrow{\Theta} OH/Ag_2O$ Br

2. a) Comment on the optical activity of cis-1,2-dimethylcyclohexane.

: 16/12/2019

Date

- b) How can you identify the diastereomeric 1,2-dibromo cyclohexanes from their dipole moment measurement? [2]
- c) Complete the following reaction with proper explanation. [4]

- d) Both <u>cis</u>- and trans-isomers of 1,2-dibromocyclohexane produce cyclohexene when treated with KI in ethanol. Explain the observation. [2]
- e) Predict the products when trans-4-tertiary butylcyclohexylamine is treated with NaNO₂/dilute HCl at 0°-5°C. Also write down the relevant mechanism. [2]

 $\underline{\mathbf{Unit} - \mathbf{II}}$ [13 marks]

3. a) Give the forward and retro synthesis of the following molecule:(any one) [1×3]

(i)
$$Co_2Et$$
 ; (ii) Co_2Me

b) Describe the synthesis of Tyrosine applying Erlenmayer azlactone synthesis.

c) Carryout out the following conversions:

(ii)
$$H \longrightarrow OEt \longrightarrow OH$$

- d) Predict the product obtained between reaction of ninhydrin and proline which shows λ_{max} at 400 nm. Write down the colour of the product and also state the probable mechanism of the reaction. [3]
- 4. a) Show protection and deprotection strategies of the following molecules: [3]
 - i) Monohydric alcohol; ii) 1,2-Diol and (iii) 1,3-Diol
 - b) Give retrosynthetic analysis and an efficient synthesis of the following molecules. $[2.5\times2]$

c) Synthesise Leu. Ala. Phe using solid phase peptide synthesis method.

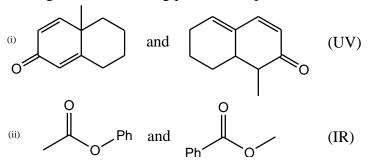
[4]

[3]

[4]

[3]

5. a) Distinguish the following pairs of compounds as indicated:



- b) Draw a clear diagram for PMR spectrum of CH₃CHBr₂ explaining the multiplicities of the proton signals. [2]
- c) A compound C₈H₈O shows the following spectral data:
 - i) IR:3100, 1700 (s), 1640, 1680 cm⁻¹.
 - ii) 1H NMR : $\delta 7.3 8.2$ (complex multiplet), $\delta 2.5(3H,s)$.

Identify the compound with proper justification.

- d) 2-Hydroxy-3-nitroacetophenone shows C=O stretching frequencies at 1692 and 1658 cm⁻¹ respectively. Explain. [3]
- 6. a) 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

- b) How would you differentiate between the members of each of the following pairs of compounds as specified: [4]
 - i) $CH_3 CH_2 C \equiv C H$ and $CH_3 C \equiv C CH_3$ [by 1HNMR spectroscopy]

- c) Cis-stilbene absorbs at shorter wavelength $(\lambda_{max} = 283 nm)$ compared to transstilbene $(\lambda_{max} = 295.5 nm)$. Give explanation for these observations. [2]
- d) Ethene is colourless but the polyene, $CH_3(CH = CH)_6 CH_3$ is yellow. Account for the observation. [2]
- e) How would you distinguish between the following pair of compounds using 'HNMR spectroscopy : CH₃COOCH₂CH₃ and CH₃CH₂COOCH₃ [2]

Unit - IV [13 marks]

[2]

 $[2\times3]$

[3]

[2]

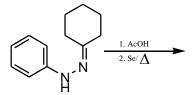
7. a) Explain the following observation:

 $(\mu = 1.58 D)$ and $(\mu = 1.81 D)$ H H

Also indicate the direction of dipole moment (μ) in the above mentioned compounds.

b) Carry out the following conversion:

- c) Outline Bardhan-sengupta synthesis of Phenanthrene.
- d) Write down the structure and one use of ranitidine.
- 8. a) Predict the product of the following reaction along with probable mechanism. [3]



(3)

b) Convert: [2]

$$\bigcap_{N} \longrightarrow \bigcap_{N}^{NO_2}$$

c)

$$\frac{\text{Na}_2\text{Cr}_2\text{O}_7 / \text{H}_2\text{SO}_4}{\text{(ii) H}_3\text{O}^{\oplus}} [S] \xrightarrow{\text{(ii) KOH/H}_2\text{O}} [T] \xrightarrow{\text{Heated}} [U]}{\text{in air}} [U]$$

$$[W] \xrightarrow{\text{Zn/Hg, Conc. HCl}} [V] \xrightarrow{\text{CrO}_3/\text{pyridine}} [S] [S] [T] \xrightarrow{\text{Heated}} [S] [S] [T]$$

Name the rearrangement reaction to convert [s] to [T]. Identify [S],[T],[U],[V] and [W]. [3]

- d) Why furan cannot be nitrated with a mixture of Conc. HNO₃ and Conc. H₂SO₄? Write the product and mechanism of reaction of furan with acetyl nitrate at $-10^{\circ}C$. [3]
- e) Draw the structure of Amlodipine and also give one use for it. [2]

