### M.Sc. CHEMISTRY THIRD SEMESTER ORGANIC CHEMISTRY-III

#### MSC-301

(Use separate answer scripts for Objective & Descriptive)

Duration: 3 hrs.

Full Marks: 70

## [ PART-A: Objective ]

Time: 20 min.

Choose the correct answer from the following:

Marks: 20 1x20=20

1. The correct structure of the compound 4,7-dihydrothieno[3,2-b]pyridine is:

a. NH

c. N

b. S

d. S

2. The nitration of pyridinium-N-oxide occurs regio-specifically at:

a. a-carbon

b. β-carbon

c. y-carbon

d. Non-regio-specific

3. Compound having maximum pKaH value in aqueous medium is:

a. Pyridine

b. Isoquinoline

c. Quinoline

d. 3-methylpyridine

**4.** Regio-selective nitration of indole at  $\beta$ -carbon can be obtained by using:

a. Conc. HNO<sub>3</sub> & Ac<sub>2</sub>O

b. PhCOONO<sub>2</sub>

c. Conc. HNO<sub>3</sub>

d. Mixture of Conc. HNO<sub>3</sub> & Conc. H<sub>2</sub>SO<sub>4</sub>

5. Chichibabin reaction of quinoline gives the product of:

a. α-C-alkylation c. α-C-amination

b. γ-C-alkylation

d. γ-C-amination

6. Porphyrin ring present in the hemoglobin is called:

a. Uroporphyrin III

c. Hematoporphyrin III

b. Mesoporphyrin III

d. Protoporphyrin III (IX)

7. The chemical formulae of Phthalocyanine is:

a. C<sub>32</sub>H<sub>18</sub>N<sub>8</sub>c. C<sub>32</sub>H<sub>14</sub>N<sub>8</sub>

b.  $C_{32}H_{16}N_8$ 

d. C<sub>32</sub>H<sub>18</sub>N<sub>6</sub>

8. Which of the following statement is not correct?

a. Starch is a mixture of two polymers.

**b.** Cellulose is a polymer of glucose linked by  $\alpha$ -1-4 glycosidic linkage.

c. Chitin is a polymer of N-acetyl glucosamine.

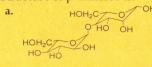
d. Glycogen is an animal sugar structurally similar to amylopectin.

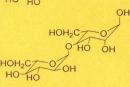
9. A given monosaccharide form the following osazone on treatment with excess of phenyl hydrazine.

- a. Glucose
- c. Galactose

- , the monosaccharide is:
- b. Mannose
- d. Both Glucose and Mannose

**10.** Structure of β-maltose is:





11. Oxidation of α-methyl D-glucopyranoside with HIO<sub>4</sub> will have the following result:

d.

- a. Consume 1 HIO<sub>4</sub> and produce 1 HCOOH
- b. Consume 2 HIO<sub>4</sub> and produce 1 HCOOH
- c. Consume 1 HIO<sub>4</sub> and produce 2 HCOOH
- d. Consume 2 HIO<sub>4</sub> and produce 2 HCOOH
- 12. The product of the following electrocyclic ring closing reaction



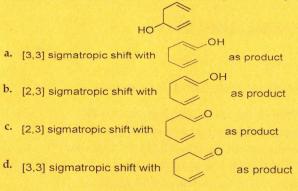
- d. None of these
- 13. Which of the following statement is not correct?
  - a. [2+2] cyclo-additions are photochemically allowed.
  - b. Thermal [1,3] sigmatropic shift is supra-antara.
  - c. Thermal [4+2] cycloaddition is supra-antara.
  - d. Pericyclic reactions involve a cyclic transition state.
- 14. The exited state HOMO of 1, 3, 5 hexatriene has:
  - a. m-plane of symmetry

b. C<sub>2</sub>-axis of symmetry

c. Both a & b

- d. None of these
- 15. The Cope rearrangement is:
  - a. [1,5] sigmatropic rearrangement
- b. [3,3] sigmatropic rearrangement
- d. [2,3] sigmatropic rearrangement c. [1,3] sigmatropic rearrangement

16. The following molecule on heating undergo the changes, having



- 17. Isoelectric point is the pH at which a given amino acid exist in the:
  - a. Cationic form

b. Anionic form

c. Zwitterionic form

- d. All of the above
- 18. In the solution phase peptide synthesis of ala-gly, the amino group of alanine is protected
  - a. p-(chloromethyl)styrene
- b. ethyl chloroformate

c. benzyl chloroformate

- d. N-phthalimidomalonic ester
- 19. In Sanger degradation of the peptide gly-leu-phe, the peptide is treated with a reagent and the corresponding residue after the first cycle is:
  - The reagent is phenyl isothiocyanate and the residue is
  - The reagent is phenyl isothiocyanate and the residue is
  - The reagent is 2,4-dinitrofluorobenzene and the residue is
  - The reagent is 2,4-dinitrofluorobenzene and the residue is
- 20. The acidic and basic character of amino acids are due to:
  - a. -COOH and -NH2 group respectively
  - b. -NH<sub>2</sub> and -COOH group respectively
  - c. -COO- and -+NH3 group respectively
  - d. -+NH3 and -COO-group respectively

# PART-B: Descriptive

Time: 2 hrs. 40 min. Marks: 50

#### [Answer question no.1 & any four (4) from the rest]

- 1. a)  $\alpha$ -glucose show specific rotation of (+) 112° and  $\beta$ -glucose (+) 19°. Both these anomers of glucose exhibit mutarotation and specific rotation shown when the equilibrium is reached is (+) 52°. Calculate the percentage of  $\alpha$ -glucose and  $\beta$ -glucose at equilibrium.
  - **b)** For the Diels Alder reaction predict the product with appropriate geometry.

c) Write down the products (A & B) of the following reactions:

d) Identify A, B and C.

- e) Write a short note on disulfide linkages in peptides.
- a) An unknown disaccharide was methylated with methyl iodide and then hydrolysed. The two products obtained were – 2, 3, 4, 6tetramethyl-D-galactose and 2, 3, 6-trimethyl-D-glucose. Draw Haworth sructures and name the disaccharide and the glycosidic lincage.
  - b) Write down the reactions of oxidation of (i) maltose or (ii) sucrose with periodic acid.
  - c) Write down the structure of the products A, B,C & D.

Maltose 
$$\xrightarrow{Br_2 \text{ water}}$$
 A  $\xrightarrow{Me_2SO_4/\text{NaOH}}$  B  $\xrightarrow{H_2O/H}$  C + D

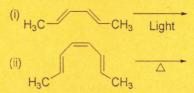
What information you can get from this result about the structure of maltose?

3. a) Match the following:

2x5=10

3+2+5=10

b) Predict the products with proper geometry of the following reactions. Also indicate the rotation of the terminal lobes of the  $\pi$ -system.



c) In the following sequence of pericyclic reactions reactions – predict X and Y.

- d) Write note on Claisen rearrangement.
- 4. a) Write down the product in the following sigmatropic shift. Mention 2+3+3+2=10 the order of the sigmatropic shift.

- b) Discuss the FMO theory of [1,5] sigmatropic shift.
- c) What do you understand by mutarotation? Explain why maltose undergoes mutarotation but not sucrose?
- d) Complete the following reactions:

(i) Glucose 
$$\xrightarrow{\text{MeOH/HCI}}$$
 ?

(ii) Glucose  $\xrightarrow{\text{Ac}_2\text{O}}$  ?

5. a) Write down the product of the following reaction with explanation.

3+4+3=10

2+3+2+3=10

b) Identify A & B with justification.

c) Write down the product with mechanism.

6. a) Write down the products A & B of the reactions.

B 
$$\leftarrow$$
 hv  $\rightarrow$  N O  $\rightarrow$  Toluene, reflux

b) Write down the suitable reagents for the following transformation. Give the reaction mechanism.

c) Identify the products A & B. Suggest the mechanistic route of the product formation.

- 7. a) Write the structure of uroporphyrinogen III. How does uroporphyrinogen III differ from uroporphyrinogen I, structurally? Discuss the Biosynthesis of uroporphyrinogen III.
  - b) Draw and discuss the titration curve for glycine.
  - c) Discuss the role of DCC in the Merrifield synthesis of peptides.
  - d) Discuss how you would use bromination followed by amination to synthesize leucine.
- 8. a) Discuss the Edman degradation of the peptide Ser-Phe-Cys.

2+3+2+2+1=10

5+2+2+1=10

3+3+4=10

- b) Discuss how the solution phase synthesis would be used to synthesis Valylalanylglycine from Valylalanine.
- c) Give a brief classification of proteins.
- d) Briefly describe the secondary structure of protein.
- e) What is protein denaturation?

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