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KATHMANDU UNIVERSITY
End Semester Examination
August/September, 2017

Level : B. Sc./B. Pharm.
Year : II

Course : CHEM 203
Semester : II

Exam Roll No. :

Time: 30 min

F. M. : 20

Registration No.:

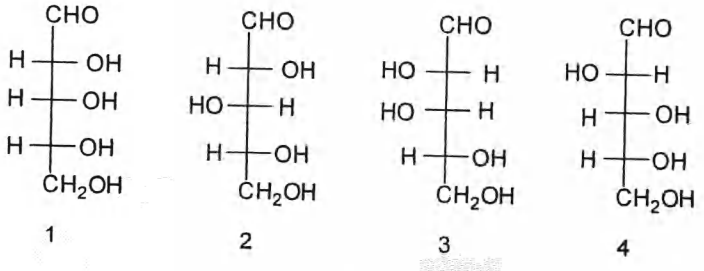
Date :

SECTION "A"
[20 Q × 1 = 20 marks]

Select the most appropriate answer.

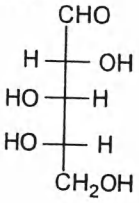
1. Which of the following best describes the polysaccharide amylose?
[ ] a 1,4-O-α-linked poly-D-glucose [ ] a 1,4-O-β-linked poly-D-glucose
[ ] an alternating 1,4-O-α/β-linked poly-D-glucose [ ] a 1,4-O-α-linked poly-D-mannose

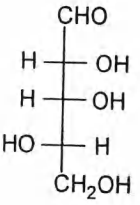
2. Two aldopentoses X and Y give the same osazone derivative. X is oxidized to an optically active aldaric acid by dilute nitric acid. Ruff degradation of Y gave a tetrose which was similarly oxidized to an optically active aldaric acid. Assign the structures of X and Y from the following list.

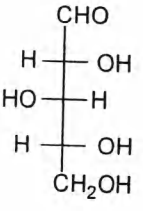


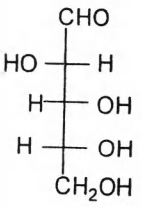
[ ] X=1 and Y=4 [ ] X=4 and Y=1 [ ] X=2 and Y=3 [ ] X=3 and Y=2

3. Which of the following gives an optically inactive aldaric acid upon oxidation with dilute nitric acid?

[ ] 

[ ] 

[ ] 

[ ] 

4. An ylide is a molecule that can be described as a
[ ] carbocation bound to a positively charged heteroatom
[ ] carbanion bound to a negatively charged heteroatom
[ ] carbocation bound to a carbon radical
[ ] carbanion bound to a positively charged heteroatom

5. For amino acids with neutral side chains, at any pH below the isoelectric point, the population of amino acids in solution will have
[ ] a net negative charge
[ ] a net positive charge
[ ] positive and negative charges in equal concentration
[ ] no net charge

6. A molecule with even number of *pi* bonds will undergo ----------type of electrocyclic reaction.
[ ] conrotatory, thermal
[ ] disrotatory, thermal
[ ] disrotatory, photochemical
[ ] conroratory, photochemical

7. In pyrrole and pyridine, the number of electrons that the N atom contributes to the *pi*-system is
[ ] pyrrole 1; pyridine 1
[ ] pyrrole 1; pyridine 2
[ ] pyrrole 2; pyridine 2
[ ] pyrrole 2; pyridine 1

8. Cationic polymerization is initiated by
[ ] a free radical [ ] an acid [ ] a base [ ] a peroxide

9. Which of the following statements is wrong?
[ ] The rate of the reaction of base-promoted α-halogenation of propanone depends upon the concentration of the base and acetone
[ ] The rate constant for the base-promoted α-halogenation of propanone decreases in the order $Cl_2 > Br_2 > I_2$
[ ] The base-promoted α-halogenation of propanone proceeds easily to give 1,1,1-trihalopropanone
[ ] The rate of the reaction of acid-catalyzed α-halogenation of propanone depends upon the concentration of the acid and acetone

10. Which one of the following is non-ionic detergent?
[ ] Sodium lauryl sulfate
[ ] Alkyl benzene sulfonic acid
[ ] Ethoxylate
[ ] Cetyltrimethylammonium bromide

11. Malonic ester upon treatment with sodium ethoxide/alcohol followed by replacement of one or more hydrogens by alkyl group gives
[ ] propanone
[ ] ethanol
[ ] ethanoic acid
[ ] ethyl ethanoate

12. Which statements are true about [4+2] cycloaddition reaction?
a. Thermal reaction occurs in supra, supra mode
b. Thermal reaction occurs in supra, antra mode
c. Photochemical reaction occurs in supra, supra mode
d. Photochemical reaction occurs in supra, antra mode
[ ] a,b [ ] b,c [ ] c,d [ ] a,d

13. What reagent is used in the Edman degradation for N-terminal group analysis of peptides?
[ ] Phenyl isothiocyanate
[ ] Dicyclohexylcarbodiimide
[ ] 2,4-Dinitrofluorobenzene
[ ] Benzyl chloroformate

14. Which of the following statements are correct?
a. [1, 3] sigmatropic migration of carbon occurs with inversion of configuration
b. [1, 3] sigmatropic migration of carbon occurs with retention of configuration
c. [1, 5] sigmatropic migration of carbon occurs with inversion of configuration
d. [1, 5] sigmatropic migration of carbon occurs with retention of configuration
[ ] a,c [ ] a,d [ ] b,c [ ] b,d

15. During the biosynthesis of fatty acid, malonyl-S-ACP reacts with acetyl–S-ACP (ACP is acyl carrier protein) to give
[ ] butyryl-S-ACP [ ] crotonyl-S-ACP
[ ] hydroxybutyryl-S-ACP [ ] acetoacetyl-S-ACP

Fill in the blanks with appropriate words/symbols.

16. Pyrrole on hydrogenation yields _____

17. Minimum number of carbon required to form a monosaccharide is _____

18. One of the optically inactive natural amino acid is _____

19. Hydrolysis of methylated amylase during end group analysis yields _____ which is around 0.3% of the total product.

20. CH_3MgBr reacts with ethanal followed by hydrolysis to give _____ (write structural formula)

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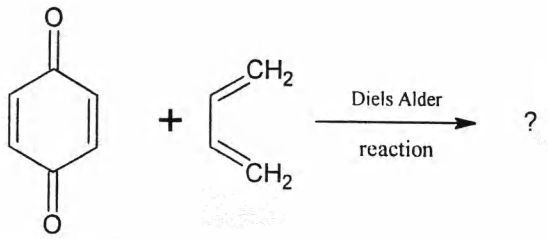
SECTION "B"

Attempt *ALL* questions.

1. Give the mechanism for the following reactions. [5 × 2 = 10]
   a. Crossed aldol condensation
   b. Coordination polymerization
   c. Edman degradation
   d. [2+2] cycloaddition reaction in a photochemical condition
   e. Alkali with aldoses

2. Explain the following statements (*ANY FIVE*). [5 × 2 = 10]
   a. [1,5] carbon shifts in sigmatropic reaction occurs with retention of configuration.
   b. Electrophilic substitution in pyrrole takes place at 2-position.
   c. Decarboxylation of CH_3-CO-CH_2-COO^- is faster than from simple carboxylate ion ($RCOO^-$).
   d. (+) Maltose is a reducing sugar.
   e. Protection/deprotection of required functional groups of amino acid is performed in peptide synthesis.
   f. Pyridine is more basic than pyrrole.

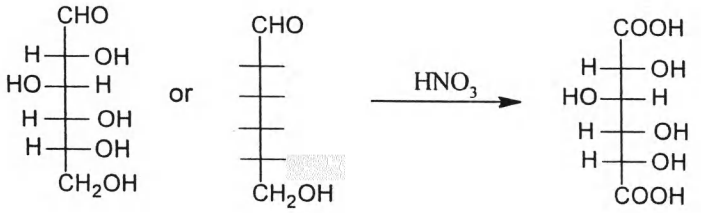
3. Give the chemical reactions involved in the following processes *(ANY SIX)*. [6 × 2 = 12]
   a. D (+) Glucose with acetic anhydride
   b.



   c. Methylmagnessium bromide with carbon dioxide followed by acidic hydrolysis
   d. Preparation of sodium lauryl sulfate
   e. Thermal cyclization of trans,cis,trans-2,4,6-Octatriene
   f. CH_3CHO with Ph_3P=CRR'
   g. Methylated amylase with HCl

4. a. How would you synthesize $CH_3COCH(CH_3)_2$ starting from acetoacetic ester? [2]
   b. Write down the full forms, structural formulae and uses of DNFB and DCC which are commonly employed in protein chemistry. [2]
   c. What is a chain transfer in polymerization reaction and why is it performed? [2]

d. Oxidation of given below two hexoses gives the same product. Assign the configuration of unknown hexose. [2]



e. What is the role of NH_2 group of isoleucine and COOH of aspartic acid in the enzymatic activity of chymotrypsin? [2]

f. Write down chemical reaction which demonstrates nucleophilic substitution in pyridine. Where does the substitution take place and why? [3]

5. Write short notes on (*ANY FOUR*). [2.5 × 4 = 10]

a. Biosynthesis of fatty acid
b. Cyclodextrins
c. Step-reaction polymerization
d. Halogenation of ketones
e. Cyclic structure of D (+) glucose