2020

CHEMISTRY — HONOURS

Paper : CC-12

Full Marks : 50

The figures in the margin indicate full marks. Candidates are required to give their answers in their own words as far as practicable.

Answer question no. 1 (compulsory) and any eight questions from the rest.

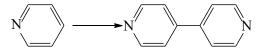
1. Answer any ten questions :

 1×10

- (a) Write down the most stable conformation of *trans*-1, 4-dimethylcyclohexane.
- (b) Write the structure of the product when 2-methylfuran is treated with DMF-POCl₃.
- (c) Draw the most stable chair conformation of 1-methyl-1-phenylcyclohexane.
- (d) Show the number of hydrogen bonds present in a guanine-cytosine base pair.
- (e) What is the effective structural unit necessary for osazone formation?
- (f) Name a reagent by which D-glucose and D-fructose can be distinguished chemically.
- (g) Write down the product of thermal signatropic reaction of the following molecule :



- (h) Draw the most stable chair conformation of methyl-D-glucopyranoside.
- (i) Write appropriate reagent for the following conversion :



- (j) Define pericyclic reaction.
- (k) [2+2] Cycloaddition reaction is not a thermally favourable process— why?
- (l) Draw the complete structure of the peptide Gly-Phe-Ser.
- (m) Anthracene is more reactive at what positions and why?
- 2. (a) How will you prepare 3-nitropyrrole exclusively from pyrrole?
 - (b) Carry out conversion of pyridine to 4-nitropyridine.

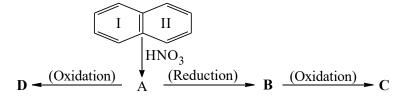
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3+2

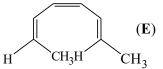
3. (a) Identify the starting materials and show the mechanism of the reaction to obtain the following product involving reaction indicated in the parantheses :

3-Methylindole (Fischer indole synthesis)

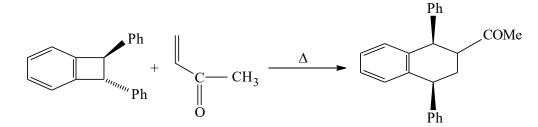
- (b) Quinoline-2,3-dicarboxylic acid smoothly forms only quinoline-3-carboxylic acid via a selective decarboxylation. Explain. 3+2
- 4. (a) *Trans*-2-aminocyclohexanol on treatment with aqueous NaNO₂ and dilute HCl gives cyclopentane carboxaldehyde while its *cis*-isomer gives mixture of products. Explain.
 - (b) Explain why *cis*-4-hydroxycyclohexanecarboxylic acid lactonises on heating but the *trans*-isomer does not. 3+2
- 5. (a) Complete the following series of reactions and indicate at what conclusion would you achieve from it regarding the structure of naphthalene :



- (b) How would you synthesise anthracene taking Diels-Alder reaction as one of the steps involved in the synthesis? 3+2
- 6. (a) Predict the fate of the following compound E in the case of photochemical electrocyclic ring closure and explain the reaction on the basis of FMO theory :



- (b) Thermal [1, 5] H shift is facile but thermal [1, 3] H shift is not observed. Explain. 3+2
- 7. (a) Rationalise the following reaction by FMO, showing the steps of the reaction :



(b) Using frontier orbital overlap, explain why Diels-Alder reaction between 1, 3-butadiene and ethylene is thermally allowed but not catalysed by UV light. 3+2

3+2

8. (a) Determine whether D-glucose possesses a furanose or a pyranose ring structure from the final product in the following reaction sequence :

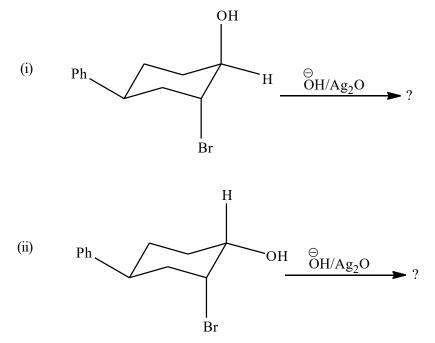
(3)

D-glucose
$$\xrightarrow{\text{MeOH/HCl}} \mathbf{F} \xrightarrow{\text{Me}_2\text{SO}_4/\text{NaOH}} \mathbf{G} \xrightarrow{\text{Dil. HCl}} \mathbf{H}$$

 $\downarrow \text{HNO}_3(\text{Oxidation})$

2, 3-Dimethoxysuccinic acid + 2, 3, 4-Trimethoxyglutaric acid

- (b) The mutarotation of D-glucose in an aprotic solvent does not occur in the presence of pyridine alone or cresol alone; when both cresol and pyridine are present together, mutarotation of glucose takes place. Explain the observation with mechanism. 3+2
- **9.** (a) How would you determine the N-terminal residue of a peptide following Edman's degradation method? Why is the method preferred over Sanger's method?
 - (b) Guanosine is hydrolysed more rapidly than adenosine in dilute acid solution. Explain why. 3+2
- (a) Write down a scheme for the synthesis of Gly-Ala using DCC promoted peptide bond formation. Give mechanism for the DCC coupling reaction step.
 - (b) In an electric field, towards which electrode, would an amino acid migrate at a
 (i) pH < pI, (ii) pH > pI. Explain.
- 11. (a) Write down the products of the following reactions with plausible mechanism :



(b) Explain the fact that *trans*-4-*tert* butylcyclohexyl tosylate undergoes bimolecular elimination with the bases bromide and thiophenolate, although not with the much stronger base ethoxide. 3+2