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-$POCl_3$.

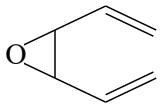
(c) Draw the most stable chair conformation of 1-methyl-1-phenylcyclohexane.

(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?

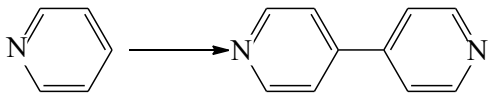
(f) Name a reagent by which D-glucose and D-fructose can be distinguished chemically.

(g) Write down the product of thermal sigmatropic 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. 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 :

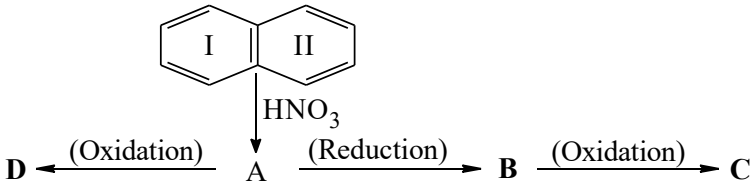
3-Methylindole (Fischer indole synthesis)

(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 $NaNO_2$ and dilute HCl gives cyclopentane carboxaldehyde while its *cis*-isomer gives mixture of products. — Explain.

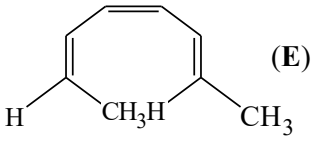
(b) Explain why *cis*-4-hydroxycyclohexanecarboxylic acid lactonises on heating but the *trans*-isomer does not. 3+2

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

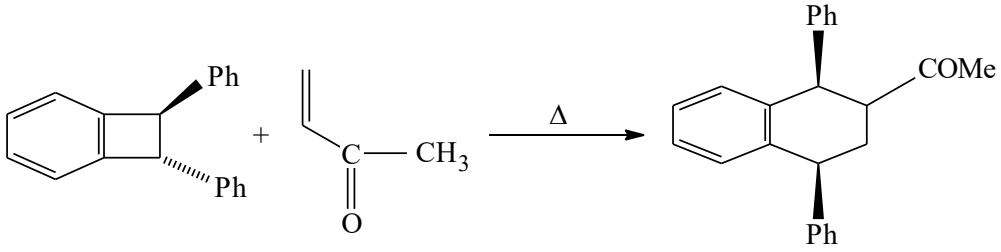
6. (a) Predict the fate of the following compound **E** in the case of photochemical electrocyclic ring closure and explain the reaction on the basis of FMO theory :



(**E**)

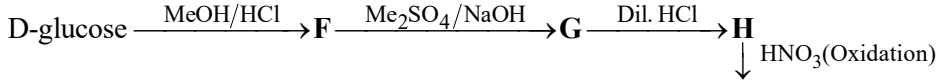
(b) Thermal [1, 5] – H shift is facile but thermal [1, 3] – H shift is not observed. — Explain. 3+2

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

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



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

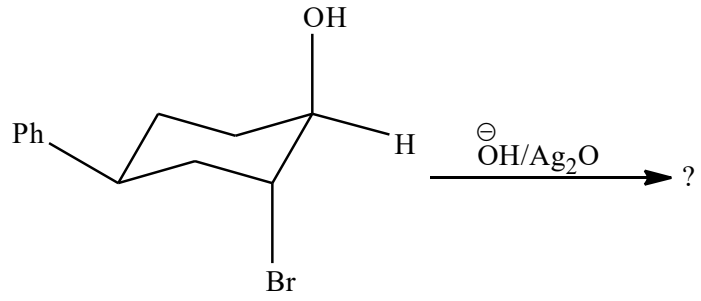
10. (a) Write down a scheme for the synthesis of Gly-Ala using DCC promoted peptide bond formation. Give mechanism for the DCC coupling reaction step.

(b) In an electric field, towards which electrode, would an amino acid migrate at a

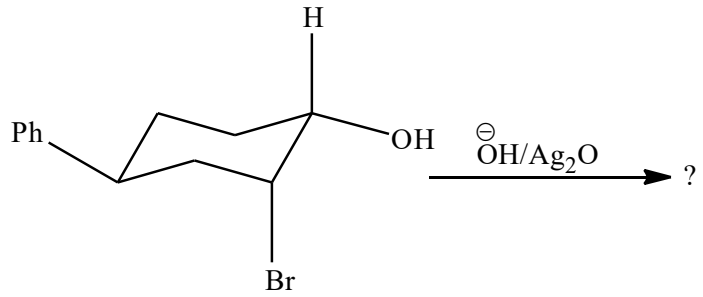
(i) pH < pI, (ii) pH > pI. Explain. 3+2

11. (a) Write down the products of the following reactions with plausible mechanism :

(i)



(ii)



(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