2022

CHEMISTRY — HONOURS

Paper : CC-12

(Organic Chemistry)

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*** (**8**) questions from the rest (***question no.*** **2** to **12**).

1. Answer ***any ten*** questions : 1×10

(a) Why 2, 3-ditertiarybutyl-buta-1, 3-diene does not undergo Diels-Alder reaction?

(b) Why 9 or 10 position of anthracene is more reactive than any other position?

(c) Designate the structures of possible dipeptides which on hydrolysis afford one mole of glycine and one mole of alanine.

(d) Why do glycosides not react with either Fehling's or Tollens' reagent?

(e) What are the bases common both in DNA and RNA? (Structures not needed).

(f) Why indole-3-aldehyde cannot undergo Cannizzaro reaction?

(g) Why is conrotatory ring closure of $(4n + 2)\pi$ system photochemically allowed?

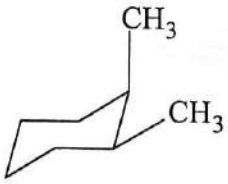
(h) Give an example of a substituted cyclohexane system where the conformation with axial substituent is more stable than the equatorial one.

(i) Furan undergoes Diels-Alder reaction, but pyrrole does not. Explain.

(j) Write down the structure of one pyrimidine base present in RNA only.

(k) Why 1,2-bond of naphthalene is shorter than 2,3-bond?

(l) What are the number of gauche-butane interactions present in the following compound?



2. (a) Explain why anthracene cannot be prepared from naphthalene by Friedel-Crafts reaction with succinic anhydride.

(b) Write down the mechanism of bromination of phenanthrene. 3+2

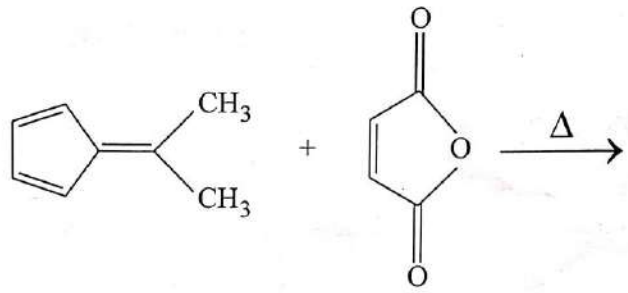
3. (a) *cis*-cyclohexane-1,3-diol is oxidised by HIO_4 more rapidly than corresponding *trans*-isomer. Explain.

(b) What happens when *cis*- and *trans*- isomers of 3-hydroxycyclohexanecarboxylic acid are heated separately? 3+2

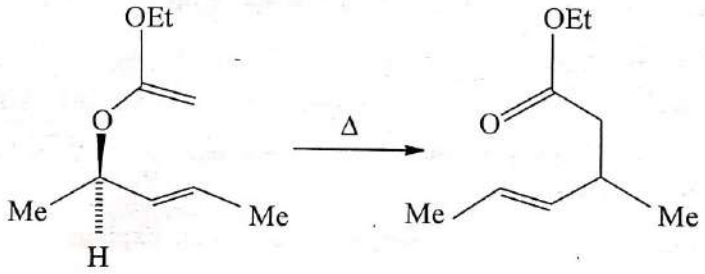
4. (a) Convert open chain structure of D-galactose to β-D-galactopyranose and explain which form is more stable between $^4C_1$ and $^1C_4$.

(b) Why specific rotation of β-D-galactopyranose changes rapidly when dissolved in water? 3+2

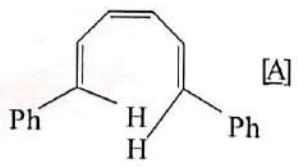
5. (a) Predict the product of the following reaction and justify the formation in terms of FMO interaction.



(b) Suggest mechanism for the following transformation and depict the stereochemistry of the chiral centre. 3+2



6. (a) Write the products when [A] is cyclised thermally and photochemically separately. Show FMO interaction and Woodward-Hoffman rule to explain the formation of products.

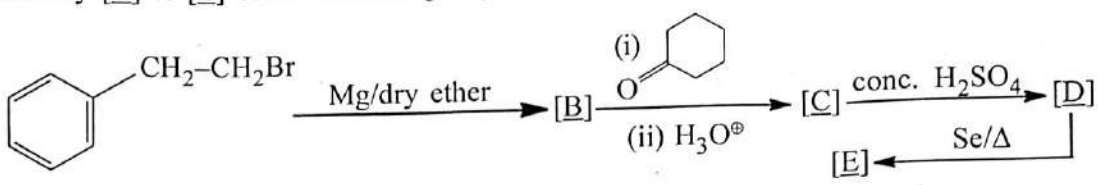


(b) Write down the product of the following reaction with plausible mechanism.

Indole-2-acetic acid $\xrightarrow{\text{Acidulated water}}$

3+2

7. (a) Identify [B] to [E] of the following sequence of reactions



(b) What happens when pyridine-N-oxide is heated with acetic anhydride followed by hydrolysis of the product? 3+2

8. (a) Write down Sanger's degradation method for the N-terminal amino acid determination of the tripeptide ala-gly-phe.

(b) Write down the reaction of proline with ninhydrin. 3+2

9. (a) Synthesise glutamic acid *via* phthalimidomalonic ester synthesis.

(b) Provide the structures of the nucleosides of

(i) Deoxyribose with cytosine

(ii) Ribose with guanine. 3+2

10. (a) (i) Account for the formation of diketal from the reaction of D-glucose with acetone in sulphuric acid.

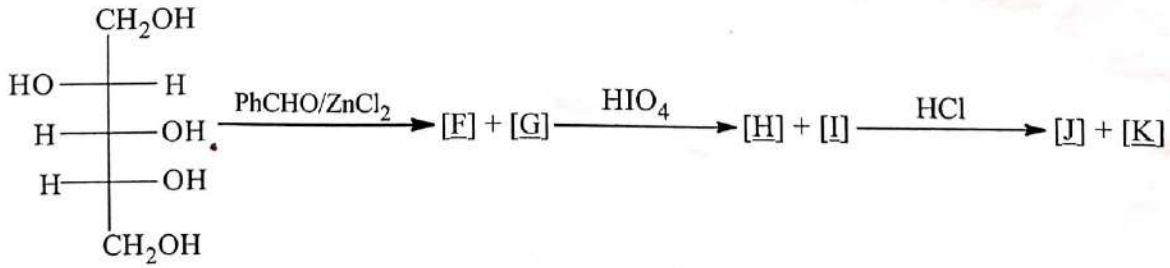
(ii) Using the above technique convert D-glucose to D-3-benzylglucose.

(b) Convert D-arabinose to D-mannose. 3+2

11. (a) Write down the mechanism of hydrolysis of adenosine and uridine. Which one undergoes more rapid hydrolysis in aqueous acid? Give reason in favour of your answer.

(b) Write down the structure of cyclic AMP. When it is treated with aqueous sodium hydroxide, the major product is adenosine-3′-monophosphate rather than adenosine-5′-monophosphate. Explain the observation. 3+2

12. (a) Give the structures of [F] to [K] of the following :



(b) Provide an explanation for the fact that under the same condition (NaOEt/EtOH at 75°C), the *cis*-isomer of 4-tertiarybutylcyclohexyl tosylate undergoes a facile E2 elimination reaction, but the *trans*-isomer does not. 3+2