

2016

CHEMISTRY

[Honours]

PAPER – VI (A+B)

Full Marks : 90

Time : 4 hours

The figures in the right hand margin indicate marks

Use separate books for Group – A and Group – B

GROUP – A

(Organic)

Group -- A(a)

Answer any one question : 15 × 1

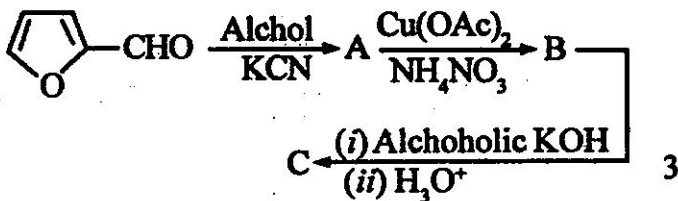
1. (a) Define logical and illogical synthons and label the synthons of C—C bond disconnection of glyoxal accordingly. . 2
- (b) Why double bonds of naphthalene remain almost fixed at 1, 2 position ? How will you prove it ?
1 + 2

(Turn Over)

(c) Synthesize chloroquinone from metachloro aniline. 2

(d) Prove that all methyl pyranosides of α -D-hexose series have same configuration at C-1 and C-5. 3

(e) Predict the products

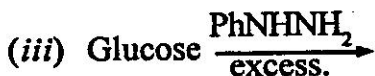
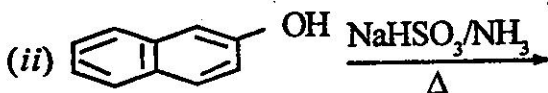
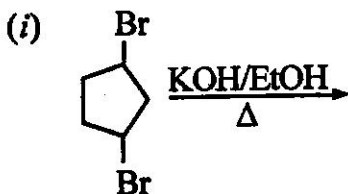


(f) What happens when alanine is heated with acetic anhydride and pyridine? Give mechanism of reactions. 2

2. (a) Outline the synthesis of phenylalanine using an active methylene compound. 2

(b) Why pyridine-2-carboxylic acid decarboxylate easily? What happens if decarboxylation is carried in presence of acetophenone. 1 + 1

(c) Predict the products of the following with mechanistic explanation (if any): 2 + 2 + 2



(d) Dickmann synthesis for cyclic ketones are less successful for ringsize less than five and above six – explain. 2

(e) Write structure of a nucleotide. 1

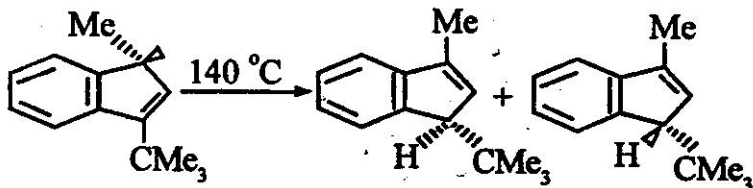
(f) Explain formation of different products of the following :



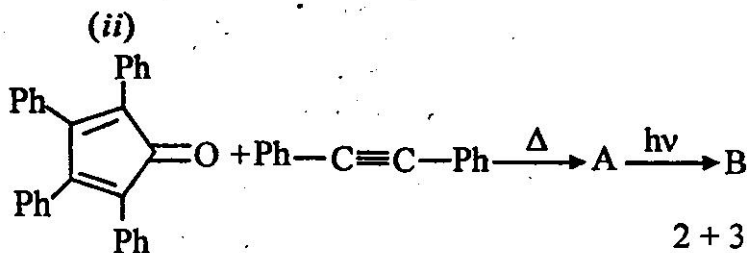
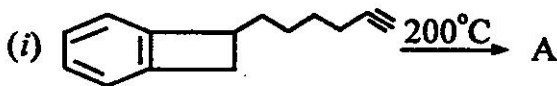
Group – A(b)

Answer any two questions : 10 × 2

3. (a) Explain following reaction products and indicate major and minor one. 2

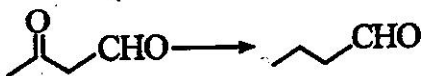


- (b) Predict the products using FMO approach



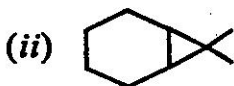
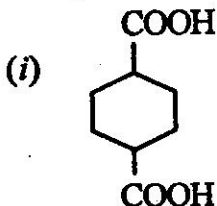
- (c) Why thiophene usually does not undergo Diels Alder Reaction? Explain. 1 + 1

(d) Convert :

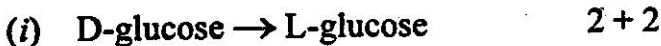


1

4. (a) Give retrosynthetic analysis of the following and synthesise : $2\frac{1}{2} + 2\frac{1}{2}$

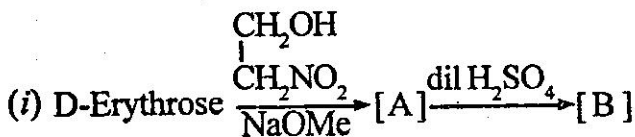


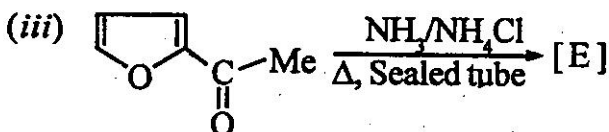
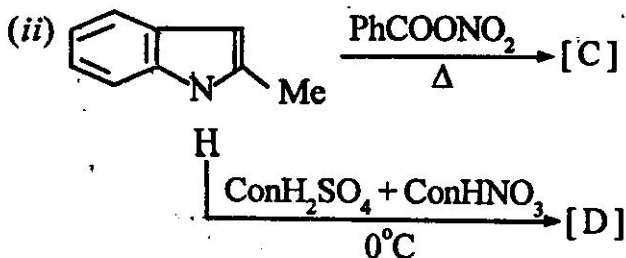
(b) Convert :



(c) Define epoenzyme. Give an example. 1

5. (a) Predict the products with mechanism



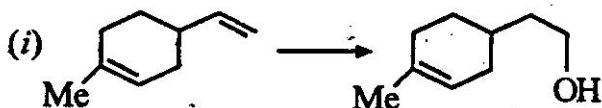


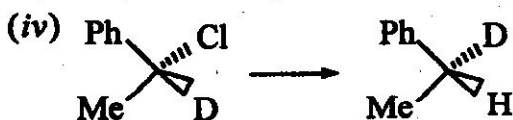
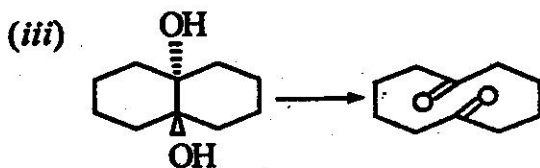
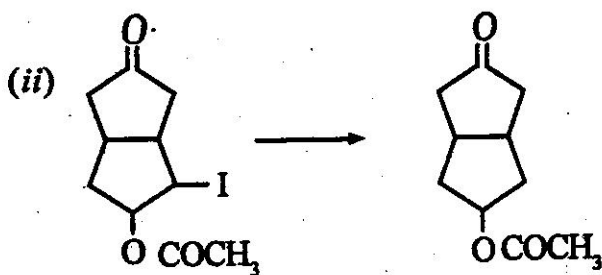
2 + 3 + 2

(b) How will you determine N-terminal amino acid residue of a polypeptide. 2

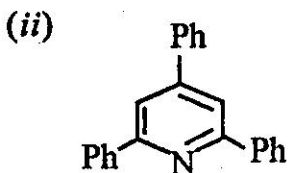
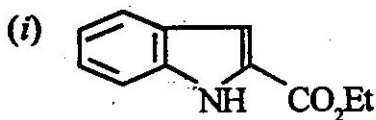
(c) How will you protect alcoholic hydroxyl group. 1

6. (a) Write suitable reagents of the following conversions : 1 × 4

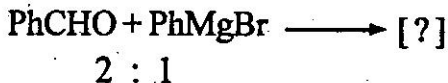




(b) Write retrosynthesis and synthesise the following: $2\frac{1}{2} + 2\frac{1}{2}$



(c) Predict the products of the following : 1



Group – A(c)

7. Answer any *five* questions : 2 × 5

(a) Write factors stabilising the double helix structure of DNA.

(b) Why excess diazomethane is used during Erndt Ester synthesis of carboxylic acid.

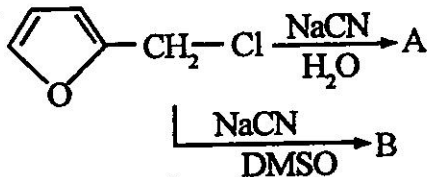
(c) Pyridine-N-oxide undergo electrophilic as well as nucleophilic substitution at 2-and 4-positions.

(d) Give example of a spray reagent for detection of amino acid. Write mechanism of the reaction.

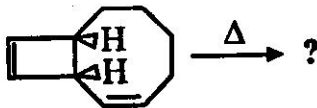
(e) Write the role of DCC in peptide synthesis with mechanism.

(f) Why all reducing sugars undergo mutarotation ?

- (g) Why tributyl tin hydride is not a suitable reagent for reduction of halide attached to chiral centre.
- (h) Prove that naphthalene contains two fused benzene rings.
- (i) Predict the product of the following :



- (j) Write stereochemistry of the product of



GROUP - B

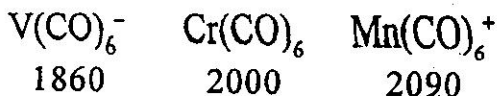
(Inorganic)

Group - B(a)

Answer any one question :

15 × 1

8. (a) Comment on the CO stretching frequencies (ν_{CO} cm^{-1}) in the following compounds 2



- (b) $\text{VO}(\text{acac})_2$ has a magnetic moment of 1.7 B.M but $\text{V}(\text{acac})_3$ is 2.8 B.M. (acac = acetyl acetate anion) – Explain. 2

- (c) What is 'Lanthanide Contraction' ? 2

- (d) What is the difference between the structures of hemoglobin and myoglobin ? Which one can carry oxygen more and why? 3

- (e) Normally Co^{3+} is powerful oxidising agent in $\text{Co}^{3+}/\text{Co}^{2+}$ system. However, if excess CN^- is added then Co^{2+} turns into a powerful reducing agent – Comment. 3

- (f) $\text{Mn}^{2+}(\text{aq})$ is faintly coloured whereas aqueous solution of MnO_4^- is highly coloured – Explain. 3

9. (a) Although Ni(O) and Zn(II) are isoelectronic, Ni(CO)₄ exists but [Zn(CO)₄]²⁺ does not why? 2
- (b) What are fluxional molecules? Give one example. 2
- (c) Give a flow diagram for the extraction of 'V' from its ore. Write the related chemical reactions. 4
- (d) What is the effect of common ion in gravimetric analysis. 2
- (e) Name the metal ion(s) present in the active site of the following biomolecules : 2
- (i) Nitrogenase
- (ii) Cytochrome-C-oxidase.
- (f) Starting from (NH₄)₂[PtCl₄] how will you synthesize *cis*- and *trans*-platin. 3

Group - B(b)

Answer any two questions : 10 × 2

10. (a) Using Orgel diagram, explain the electronic

spectral transitions of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ion in weak octahedral field indicating the spectroscopic ground state. 4

(b) 'An inner metallic ligand is essentially a chelating ligand, but the reverse is not true' – Justify. 2

(c) Predict whether CO_3O_4 is normal spinel or inverse spinel. 2

(d) Explain the principle of chelation therapy with reference to the removal of arsenic. 2

11. (a) The high-spin complex $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ is labile but the low-spin complex $[\text{Cr}(\text{CN})_6]^{4-}$ is inert – Explain. 3

(b) Cu, Ag and Au have the stable oxidation states +2, +1 and +3 respectively. Give reasons. 2

(c) What metal indicator is used for the complexometric estimation of Ca^{2+} by EDTA titration? Discuss its indicator action. 3

- (d) $[Co(H_2O)_6]Cl_2$ is pale pink but turns in to deep blue when concentrated HCl is added in excess – Why? 2
12. (a) Discuss the nature of John-Teller-distortion for an octahedral Cu(II) complex ion. 4
- (b) What is an insertion reaction? Give two examples for this. 3
- (c) $KMnO_4$ is an oxidant in both acidic and alkaline medium but $K_2Cr_2O_7$ is an oxidant in acidic medium – Explain. 3
13. (a) Discuss the active site structure of the enzyme carbonic anhydrase. 2
- (b) Co(II) complex with high spin state shows magnetic moment 4.8 – 5.2 B.M. in the octahedral field, while in tetrahedral field it is 4.0 – 4.4 B.M. Explain this observation. 2
- (c) Discuss the basis of Ziegler-Natta polymerization? 2

- (d) CO has negligible donor properties toward simple acceptors such as BF_3 , but can form strong bonds to transition metal atoms – Explain. 2
- (e) What do you mean by masking agent? Give an example. 2

Group – B(c)

14. Answer any five questions : 2 × 5

- (a) Cobaltocene is much readily oxidised than Ferrocene – Explain.
- (b) How do you determine BOD of *potable water*? Give reactions.
- (c) Starting from hydrated nickel (II) chloride how will you prepare $\text{K}_2[\text{Ni}(\text{CN})_4]$?
- (d) Why prior to titration of Fe^{2+} by standard KMnO_4 solution in HCl medium a small volume of Zimmermann-Reinhardt solution is added?

- (e) Draw the structures of all the possible isomers of the complex ion $[\text{Co}(\text{en})_2\text{Cl}(\text{NO}_2)]^+$ where $\text{en} = \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$.
- (f) Write down the chemical equation involved when H_2O_2 is added to a solution of titanium (IV) sulphate in presence of H_2SO_4 .
- (g) Chromium (II) acetate monohydrate is diamagnetic yet it possess d^4 system – Explain.
- (h) Write the IUPAC name of the following compounds :

