NEW

Part–III 3-Tier

2019

CHEMISTRY

(Honours)

PAPER—VI

Full Marks : 90

Time : 4 Hours

The figures in the right-hand margin ir.dicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Use separate scripts for Group-A and Group-B

Group—A

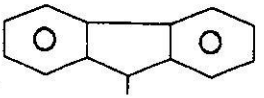
(Organic)

Group—A(a)

Answer any *one* question. 1×15

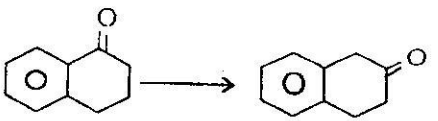
1. (a) Compare the λ_{max} value of s-cis and s-trans-1,3-butadiene and explain. 2

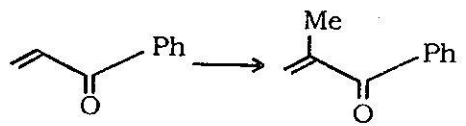
(b) What happens when the following compound is heated with piperidine in DMF ? 2



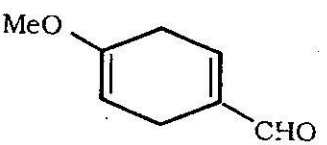
CH_2-OCONH-CH(CH_3)-COOOH

(c) How will you convert ? 2×2

(i) 

(ii) 

(d) Write down the two sets of diene and dienophite of the following adduct. Which set is more appropriate and why ? 1+1+1



(e) How will you prepare 4-Nitropyridine from pyridine ? 2

(f) Explain the "Anomeric effect with the help of M.O. theory. 2

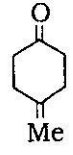
2. (a) A heptapetide on reaction with DNFB followed by hydrolysis produces N-DNP valine. The hydrolysis of peptide by carboxypeptidase enzyme releases glutamic acid. The partial hydrolysis product of peptide by 6(N) HCl are as follows :

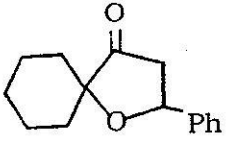
(i) Pro-Leu-Val (ii) Ala-Tyr-Pro

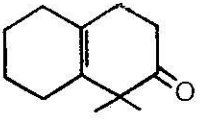
(iii) Leu-Val-Glu (iv) Val-glu.

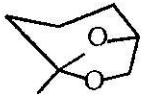
Identify the sequence of amino acids in the heptapeptide and explain. 1+1+1+1

(b) Write down the retro synthetic path and forward synthesis of the following compounds. (any *two*) 3×2

(i) 

(ii) 

(iii) 

(iv) 

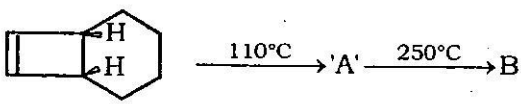
(c) Write down the basic principle of Sorenson's formal titration of amino acids. 2

(d) Write down the Skuarp synthesis of quinoline. 3

Group—A(b)

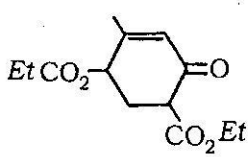
Answer any *two* questions. 2×10

3. (a) Predict the product with explanation 2+1



(b) How will you prove the ring size of glucose and fructose component present in cane sugar. 3

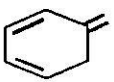
(c) Write retro synthesis and hence synthesis of 2



(d) Why furan-2 aldehyde undergoes Cannizaro reaction but pyrole-2-aldehyde does not ? 2

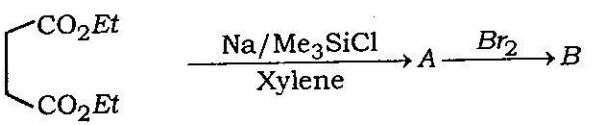
4. (a) Write a mechanism of colour reactions of amino acid with ninhydrine. Why proline behave differently ? 2+1

(b) Explain

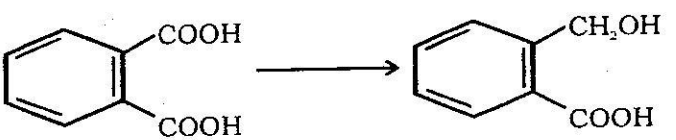
(i)  is stable at ordinary temperature. 1

(ii) Whether there will be any change in stretching wave number of O—H group of phenol when solvent is changed from carbon tetrachloride to benzene. Explain. 1

(c) Predict the products with mechanism 2+1



(d) Convert



2

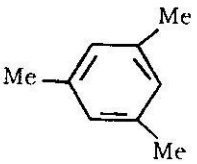
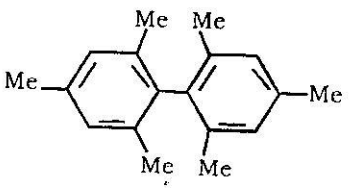
5. (a) Write mechanism of Fisher indole synthesis. 2½

(b) Predict the products with mechanism 3

$$\text{Pyridine} \xrightarrow[H_2O_2]{CH_3CO_2H} A \xrightarrow[(CH_3CO)_2O]{} B$$

(c) Convert : D-Glucose ⟶ D-3-0-Methyl Glucose 2

(d) Distinguish the following pair of compounds a directed

(i)  and 

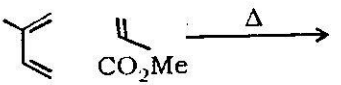
[by UV spectra] 1

(ii) $CH_3—O—CH_3$ and CH_3CH_2OH

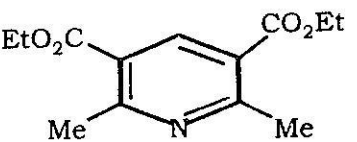
[by ^1H NMR spectra] 1½

(Continued)

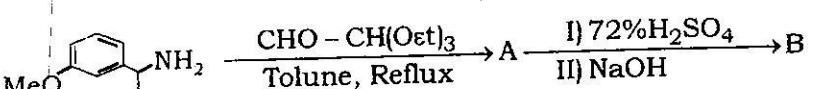
6. (a) Predict the products indicating minor and major using FMO approach for the reaction : 3



(b) Write retrosynthetic analysis and synthesis of 1½+1½



(c) Predict the product : 2

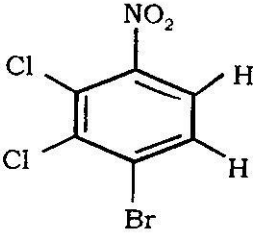


(d) How will protect amino group of an amino acid during dipeptide synthesis. 2

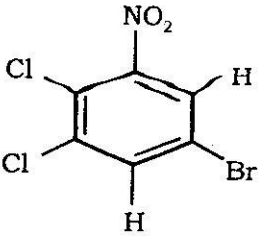
Group—A(c)

Answer any *five* questions. 5×2

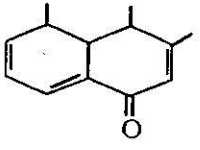
7. (a) Define coupling constant (J). Use the value of J to distinguish between 1+1



and

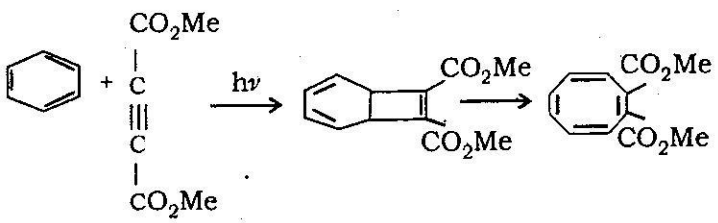


(b) Using Woodward's rule calculate λ max value of 2



(c) Mention one method for detection of c-terminal of a polypeptide 2

(d) Explain the formation of the products in the following reaction : 2



(e) Indole undergoes electrophilic substitution at C-3 but pyrorole at C-2. Explain. 2

(f) What is meant by bathochromic shift ? Why UV spectra of aniline is identical with benzene in acid medium ? 1+1

(g) Convert : D – glucose ⟶ D – Manose 2

Group—B

(Inorganic)

Answer any *one* question. 1×15

8. (a) A square planar arrangement of ligands can be formally *derived from an* octanedral array by removal

of two transligands. Explain by showing crystal field splitting diagrams. 2

(b) Both $[Ni(CN)_4]^{2-}$ and $[Ni(CO)_4]$ are diamagnetic but they have different Geometries. Explain. 2

(c) Give a scheme for the extraction of 'V' from its ore and write related chemical reactions. 3

(d) Why are small Fe-porphyrin complexes unable to bind O_2 reversible ? 2

(e) Give an outline of a possible mechanism for the Ziegler-Natta polymerization of ethene. 3

(f) Give two synthetic routes for preparations of ferrocene. 2

9. (a) Predict which of the complexes $[V(CO)_6]^-$, $Cr(CO)_6$ and $[Mn(CO)_6]^+$ has shortest C—O bond ? 2

(b) Discuss the quadruple bonding in $[ReCl_8]^{2-}$. 2

(c) What are photosystem I and II ? Explain their role in photosynthesis using "Z-diagram". 4

(d) Sketch different bonding modes of nitrosyl ligand. 2

(e) The isoelectronic ions VO_4^{3-}, CrO_4^{2-} and MnO_4^- all have intense charge transfer transition where MnO_4^- having absorption at the longest wavelength. Suggest a reasons for this trend. 2

(f) Comment on the observation that octahedral Ni(II) complexes have magnetic moments in the range $2.9-3.4\,u_B$, tetrahedral Ni(II) complexes have moments upto $\approx 4.1\mu_B$ and square planar Ni(II) complexes are diamagnetic. 3

Group—B(b)

Answer any *two* questions. 2×10

10. (a) For $[Ti(OH_2)_6]^{3+}$, a value of Δ_{oct} can be determinal directly from λ_{max} in the electronic spectrum. Why is this not possible for $[V(OH_2)_6]^{3+}$, and for most other octahedral ions ? 2

(b) Addition of sodium ethanoate to aqueous solution of Cr(II) gives a red diamagnetic product. Draw the structure of the product noting any features of interest. 3

(c) A standard five-day BOD test is run using a mix consisting of four parts distilled water and one part waste water (no seed). The initial DO of the mixture is 9.0 mg/L and the DO after five days is determined to be 1.0 mg/L. What is BOD_5. 2

(d) Classify the following ligands as σ-donot, Π-donor or Π-acceptor F^-, CO and NH_3. 3

11. (a) Comment with reasoning, on how you expect the trend in radii for the lanthanoid M^{3+} ions between La^{3+} and Lu^{3+} to vary. 2

(b) Why is the change from deoxyhaemoglobin to the oxy-Form accompanied by a decrease in the observed magnetic moment ? 2

(c) In $[Fe(CN)_6]^{3-}$, does the CN^- ligand act as a Π donor or a Π acceptor legand ? Explain how the ligand properties lead to $(Fe(CN)_6]^{3-}$ being low-spin. 2

(d) Show the variation of ionic radii of M^{2+} ion of the 3d-block elements. 3

(e) Show that $[Mn(CO)_5]^-$ obeys the 18-electron rule. 1

12. (a) Write a note on metal ion transportation across the biological membrane. 3

(b) The Racah parameter B is 460 cm^{-1} in $[Co(CN)_6]^{3-}$ and 615 cm^{-1} in $[CO(NH_3)_6]^{3+}$. Consider the nature

of bonding with the two ligands and explain the difference in nephelauxetic effect. 2

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

(d) Complete the following reaction sequence with explanation and identify A and B

$$[Pt[NH_3)_4]^{2+} \xrightarrow{HCl} A \xrightarrow{HCl} B$$ 2

13. (a) Explain why $[FeF_6]^{3-}$ is colourless whereas $[CoF_6]^{3-}$ is coloured but exhibits only a single band in the visible. 2

(b) State the reaction of ferrocene with 2

(i) N_2O_4 and

(ii) n-BuLi

(c) The high-spin complex $Cr(H_2O)_6]^{2+}$ is labile, but low-spin complex $[Cr(CN)_6]^{4-}$ is inert. Explain. 3

(d) An octahedral d^8 complex show d-d absorption bands at 10739, 17489 and 28217 cm^{-1}. Assign the bands from orgel diagram and calculate $10D_q$. 3

Group—B(c)

Answer any *five* questions : 2×5

14. (a) What is Z-R reagent ? Explain the role of this solution in the permanganometric titration of Fe^{2+}.

(b) 'The magnetic moment of $VO(acac)_2$ is 1.7 BM'. Discuss.

(c) Discuss the role of Zn^{2+} in the active site of the carbonic anhydrase.

(d) Explain the structure for the simplest dinuclear carbonyl compound of cobalt.

(e) Draw a polarogram and identify different parts.

(f) What happens when Co(II) acetate is treated with ammonium thiocyanate in presence of mercuric chloride in aqueous solution.

(g) The spectrum of $[Ti(H_2O)_6]^{3+}$ shows a broad peak with a shoulder. Explain.

(h) The NO stretching frequency in $[Fe(CN)_5NO]^{2-}$ and $[Fe(H_2O)_5NO]^{2+}$ appears at 1939 cm^{-1} and 1745 cm^{-1} respectively. Comment.

(i) How many isomers are possible for $[Co^{II}(bpy)_2(NCS)Cl]$? Give reasons for your answer.