

2017

CHEMISTRY

[**Honours**]

PAPER – VI (A+B)

Full Marks : 90

Time : 4 hours

The figures in the right hand margin indicate marks

Use separate scripts for Group–A and Group–B

[**OLD SYLLABUS**]

GROUP – A

(-Organic)

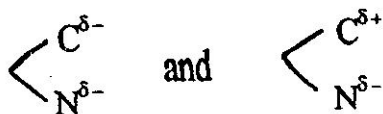
Group– A(a)

Answer any one question : 15 × 1

- 1. (a) Draw the structure of synthetic equivalent**

(Turn Over)

of the following synthon skeleton : 1 + 1



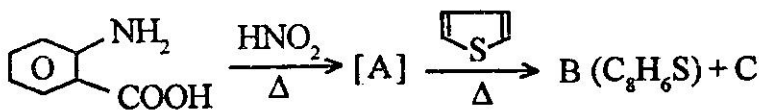
(b) Rationalise briefly the following facts : 2

"Phenanthrene reacts easily with diazomethane
Where as anthracene fails to record this reaction"

(c) What do you mean by "Antipyretic drug" ?
Out line the synthesis of paracetamol from
nitrobenzene. 1 + 2

(d) Hydrolysis of sucrose results equimolar
mixture of glucose and fructose. Specific
rotation of mixture and glucose are -20°
and $+52.5^\circ$. What is the specific rotation
of fructose ? 2

(e) Predict the products (A \rightarrow C) 1 $\frac{1}{2}$



(f) Write down the structure of an acidic amino acid at (i) $\text{pH} < 7$ (ii) $\text{pH} > 7$ (iii) isoelectric point. 1+1+1

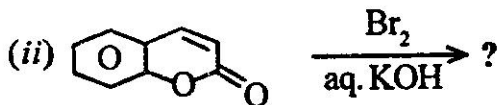
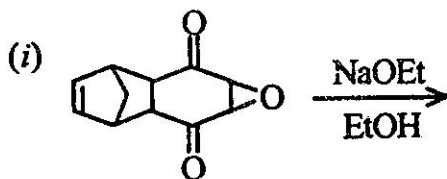
(g) Explain with appropriate reagent and mechanism of the reductive N-alkylation of primary amine. $1\frac{1}{2}$

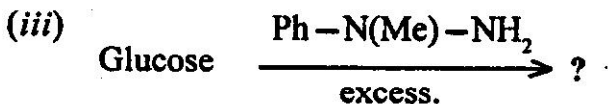
2. (a) Carry out the following conversion. 2

Glycine \rightarrow Phenylalanine (Using Erlenmeyer azalactone synthesis)

(b) "Furan can be regarded as a masked 1, 4- dicarbonyl compound" – Explain. 2

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

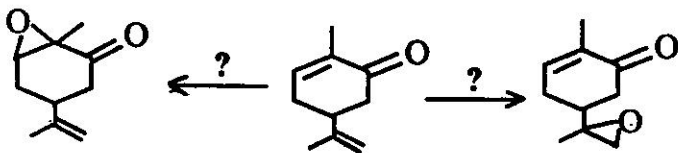




(d) What are the demerits of acyloin condensation in ring synthesis? How these problem can be overcome? 2+1

(e) Write down the structure of a *L*-amino acid which is a *R*-enantiomer. 1

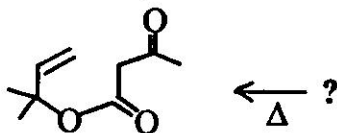
(f) Put the appropriate reagent. 1



Group— A(b)

Answer any two questions : 10 × 2

3. (a) Write down the product of the following reaction which follows [3, 3]-sigmatropic pathway and justify. 2



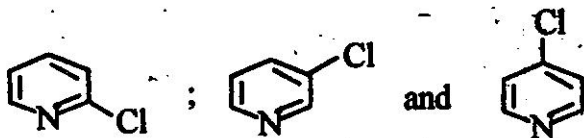
- (b) Predict the 1:1 adduct of the following reaction under thermal condition and explain. 2



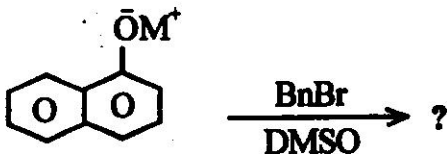
- (c) Carry out the following transformation using Diels-Alder reaction as one of the steps. 2



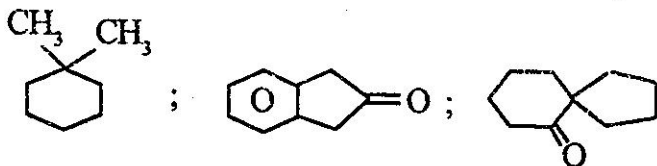
- (d) Compare the rate of alkaline hydrolysis of the following compounds and explain. 2



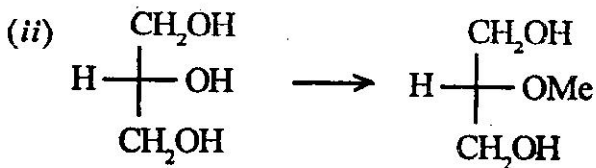
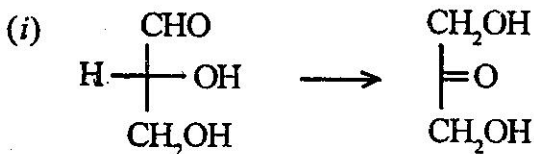
- (e) Predict the product(s) and explain why does a change from $\text{Li}^+ < \text{Na}^+ < \text{K}^+$ favour O-alkylation over C-alkylation. 2



4. (a) Give retrosynthetic and synthetic path of the following compound from suitable starting material. (any two):

 $2\frac{1}{2} + 2\frac{1}{2}$


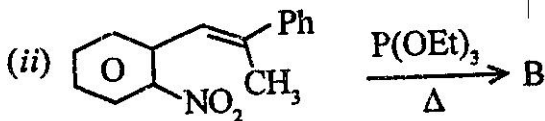
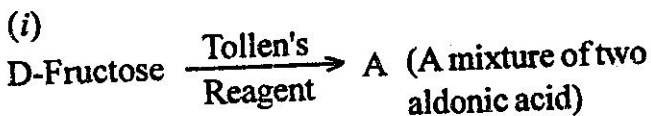
- (b) Convert:

 $1\frac{1}{2} + 1\frac{1}{2}$


- (c) What is isoelectric point? Find out the relation between pH; pK_{a1} and pK_{a2} of glycine at isoelectric point.

 $1 + 1$

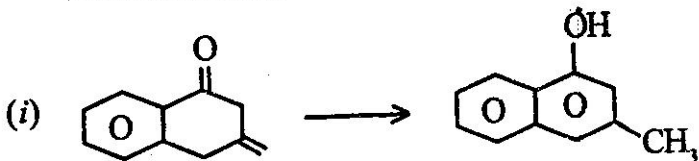
5. (a) Predict the product(s) (A→C) with mechanism. 3 × 2

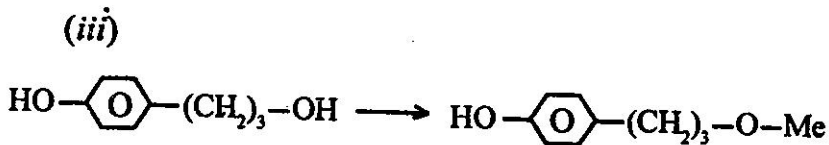
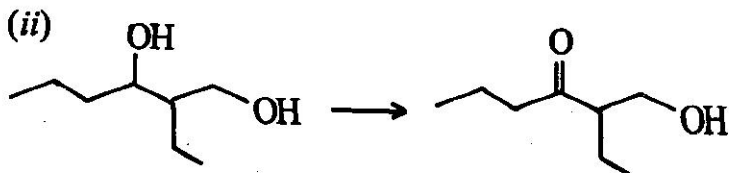


- (b) What is meant by specific base pairing in double helix structure of a DNA molecule? 2
- (c) How will you convert? 2



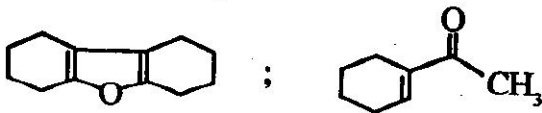
6. (a) Write suitable reagent(s) of the following transformations: 1+1+1





(b) How will you convert $\text{CH}_3\text{COCOCH}_3$ to CH_3COCH_3 using CH_3Li as one of the steps. 2

(c) Write retrosynthesis and forward synthesis of the following : 2+2

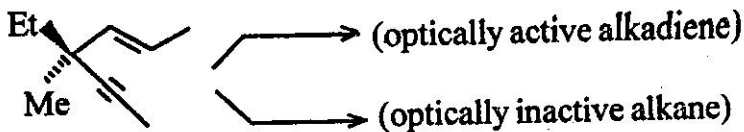


(d) What are metallo enzymes ? 1

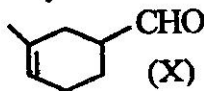
Group— A(c)

Answer any five questions : 2 × 5

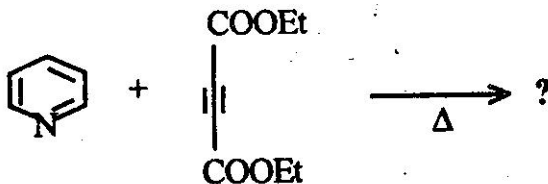
7. (a) Put the appropriate reagent.



- (b) Write down the role of t-RNA and r-RNA in protein synthesis.
- (c) What happens when pyridine N-oxide is refluxed with acetic anhydride?
- (d) A student wrote the following Diels-Alder adduct (X) from isoprene and acrolein. Is it correct? Why?



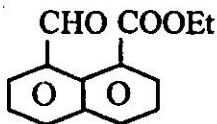
- (e) How can you determine the C-terminal residue of a peptide chain?
- (f) How will you distinguish D-glucose and D-fructose chemically?
- (g) Predict the product with mechanism:



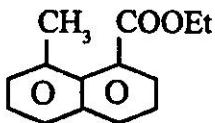
- (h) Find out the pericyclic path(s) of the following conversion :



- (i) Compound 'A' undergoes alkaline hydrolysis at faster rate than compound 'B'.— Explain.

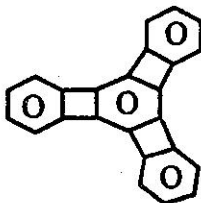


A



B

- (j) On partial reduction by Ni/H_2 , the middle benzene ring of 'P' undergoes reduction at faster rate than terminal one-- Explain.



'P'

GROUP – B

(Inorganic)

Group – B(a)

Answer any one question : 15 × 1

8. (a) Why $K_3[CuF_6]$ is paramagnetic while $K[AgF_4]$ is diamagnetic. 2
- (b) The complex $[Cu(H_2O)_6]^{2+}$ is susceptible to Jahn-Teller distortion more than $[Ti(H_2O)_6]^{3+}$ – Explain. 2
- (c) What is the 'Co-operative effect' in the oxygen transport phenomena? 2
- (d) Explain briefly the principle of separation of lanthanides by ion exchange method. 3
- (e) Starting from $K_2[PtCl_6]$ how would you prepare Zeise's salt? 2
- (f) Will oxidation of Cp_2Fe to $[Cp_2Fe]^+$ produce a substantial change in Metal-Carbon (M–C) bond length? 2

- (g) Mention the conditions for orbital contribution to spin only magnetic moment value. 2
9. (a) Give the preparation and uses of $(\eta^5-C_5H_5)_2TiCl_2$. 3
- (b) $[NiCl_4]^{2-}$ is tetrahedral while $[PdCl_4]^{2-}$ and $[PtCl_4]^{2-}$ are square planar— Explain. 2
- (c) $cis-[Co(en)_2F_2]^{\oplus}$ is more intensely coloured than trans. 2
- (d) What is the role of globin chain in hemoglobin oxygenation? 2
- (e) The N—O distance in $[Co(diars)_2NO]^{2+}$ is 168 pm and the $\angle Co-N-O$ bond angle is 180° . Reaction of the complex with SCN^{\ominus} forms $[Co(diars)_2(NCS)NO]^+$ in which N—O distance is 185 pm and $\angle Co-N-O$ bond angle is 135° — Explain.
[diars = 1, 2-bis(dimethylarsino) benzene] 3

- (f) Name the metal ion(s) present in the active site of the following biomolecules : 2
- (i) Carbonic Anhydrase
- (ii) Rubredoxin.
- (g) Explain why $V(CO)_6$ is readily reduced to the monoanion. 1

Group – B(b)

Answer any two questions : 10 × 2

10. (a) Define oxidative addition reaction. What type of compounds generally undergo this type of reaction ? 2
- (b) $K_2Ba[Cu(NO_2)_6]$ has distorted octahedral structure but $K_2Pb[Cu(NO_2)_6]$ has regular octahedral. 2
- (c) To remove Pb^{2+} from human body it is better to use $Na_2Ca(edta)$ than $Na_2H_2(edta)$ — Explain. 2

(d) Draw a plot of $1/\chi_M$ vs temperature T(K) for materials which obey 2

(i) Curie law.

(ii) Curie-Weiss law.

(χ_M = Magnetic susceptibility)

(e) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ forms two isomers. One isomer gives $[\text{Pt}(\text{NH}_3)_2(\text{tu})_2]^{2+}$ on treatment with thiourea (tu); the other isomer gives $[\text{Pt}(\text{tu})_4]^{2+}$ on similar treatment. Identify the isomers. 2

11. (a) The position of CO in the spectrochemical series is higher compared to CN^\ominus . 2

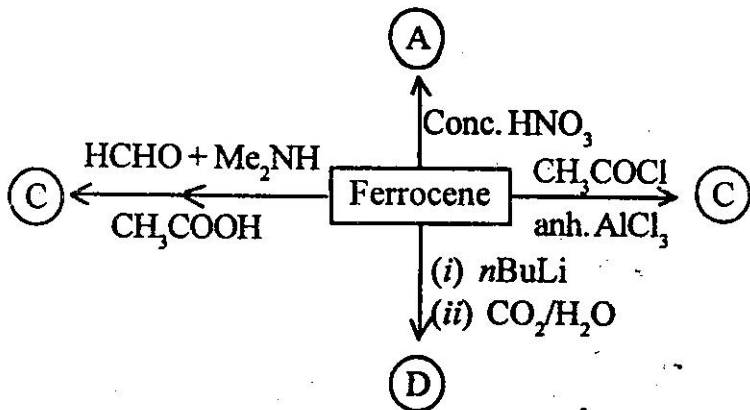
(b) Discuss about the Laporte selection rule for electronic spectral transitions. 2

(c) Write down the mechanism through which the nerve cells maintain Na^+ and K^+ concentrations inside and outside of the cell. 3

(d) Copper (II) formate tetrahydrate have a magnetic moment value of 1.67 BM. 2

- (e) Give one example of optically active square planar complex. 1
12. (a) Lanthanides exhibit +3 oxidation state in general while actinides can show variable oxidation state—Explain. 3
- (b) Draw the catalytic cycle for hydroformylation reaction. 3
- (c) A deep blue solution containing Co(II) in concentrated HCl gradually turns pale pink on addition of excess water. 2
- (d) What do you mean by TDS and COD of a sample of water ? 2
13. (a) State the role of PS-I and PS-II in photosynthesis using z-scheme. 3
- (b) Give the flow-sheet diagram of extraction of pure Uranium metal from Pitchblende. Write the related chemical reactions. 3

- (c) Identify A, B, C and D in the following reaction scheme : 2



- (d) Compute Δ_0 and B' for the CrF_6^{3-} from the given absorption energies 34, 400, 22700 and 14900 cm^{-1} . 2

Group – B(c)

Answer any five questions : 2 × 5

14. (a) Compare the coordination sphere of cytochrome a with that of cytochrome C. 2
- (b) Draw the all possible isomers of $[\text{Co}(\text{NH}_3)(\text{OH})_2\text{Cl}_3]^{2-}$. 2

- (c) What happens when zinc uranyl acetate is added to an aqueous solution of NaCl? Give equation. 2
- (d) The C—C bond length in the co-ordinated olefin is greater than that in the free olefin. 2
- (e) Electronic Absorption spectra of lanthanides consists of sharp lines whereas those of the transition metal ions consist of broad bands — Explain. 2
- (f) Name one gold drug and state its therapeutic application. 2
- (g) Find the values of x assuming validity of the $18e^{\ominus}$ rule. 2
- (i) $\text{Co}_2(\text{CO})_x(\text{C}_2\text{H}_2)$
- (ii) $\text{Fe}(\eta^5 - \text{Cp})(\eta^1 - \text{Cp})(\text{CO})_x$
- (h) What do you mean by half-wave potential in polarography? 2