2015

CHEMISTRY

[Honours]

PAPER – VI

Full Marks : 90

Time : 4 hours

The figures in the right hand margin indicate marks

Write answers of the questions of each Group in separate scripts

(*Organic*)

[*Marks* : 45]

Time : 2 hours

GROUP – A (a)

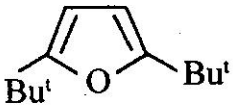
Answer any **one** question :

1. (*a*) β-D-Glucopyranose undergoes oxidation with Br_2/H_2O at a faster rate than α-D-glucopyranose. – Explain. 2

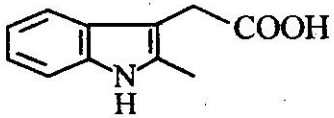
(*b*) What are sulpha drugs ? Give the synthesis of sulphanilamide from aniline. 1 + 2

(*c*) Give retrosynthetic analysis and an efficient synthesis of any *two* of the following compounds : $2\frac{1}{2} \times 2$

(*i*)



(*ii*)



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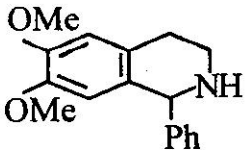
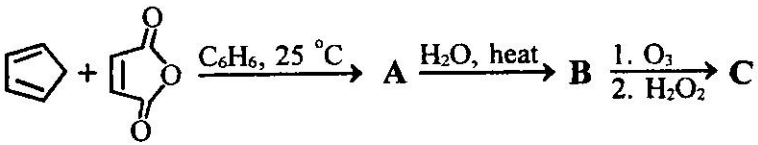


(*d*) Identify the products with proper stereochemistry : 3

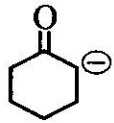


(*Continued*)

(*e*) Buta-1, 3-diene does not undergo Diels -Alder reaction when tert-butyl groups are present at the 2 and 3-positions. – Explain. 2

2. (*a*) Explain with proper examples the meaning of the term "Two Group C-X Disconnection". 2

(*b*) Give synthetic equivalents corresponding to the following synthons : 2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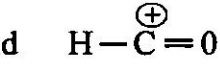
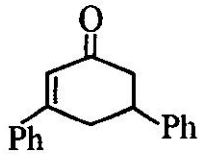


(*c*) Describe the synthesis of any two of the following compounds with proper retro-synthetic analysis : $2\frac{1}{2} \times 2$

(*i*)


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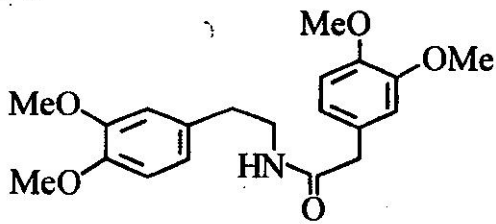
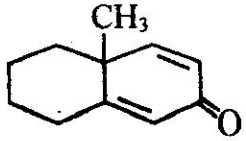
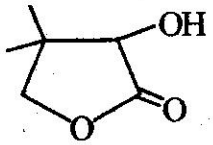


(*iii*) 

(*iv*) 

(*d*) Write the structure of L-Proline. 1

(*e*) Chymotrypsin is an important hydrolytic enzyme. What are the structures and names of two α-amino acids responsible for the hydrolysis reaction ? 2

(*f*) What happens when ; $1\frac{1}{2} \times 2$

(*i*) an ether solution diazomethane is slowly added to a warm solution of the acid chloride (RCOCl).

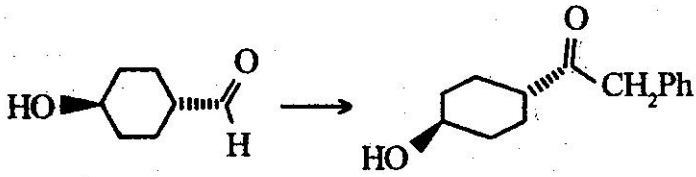
(*ii*) a cold solution of the acid chloride (RCOCl) is added slowly to diazomethane in cold ether solution.

(*Continued*)

GROUP – A (b)

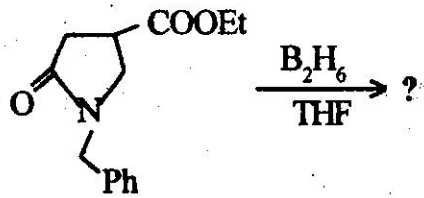
Answer any **two** questions :

3. (*a*) How would you carry out the following transformation using Me_3SiCl as one of the reagent ? 3

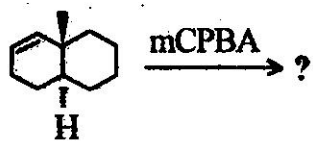


(*b*) Predict the product with plausible mechanism : 2 × 2

(*i*)



(*ii*)



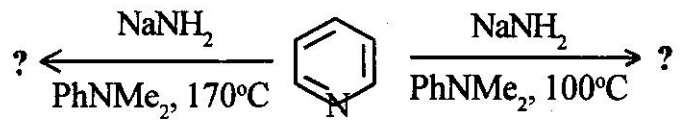
(*c*) What is the difference between a nucleoside and a nucleotide ? 2

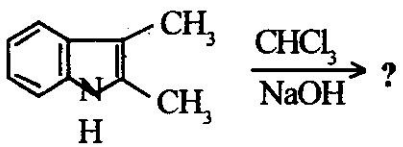
(*d*) Give an example of conjugated protein. 1

4. (*a*) Treatment with sodium borohydride converts aldose **A** into an optically inactive alditol. Ruff degradation of **A** forms **B**, whose alditol is optically active. Ruff degradation of **B** forms D-glyceraldehyde. Identify **A** and **B**. 2 + 1

(*b*) What is peptide linkage ? Describe the geometry of peptide linkage. 1 + 2

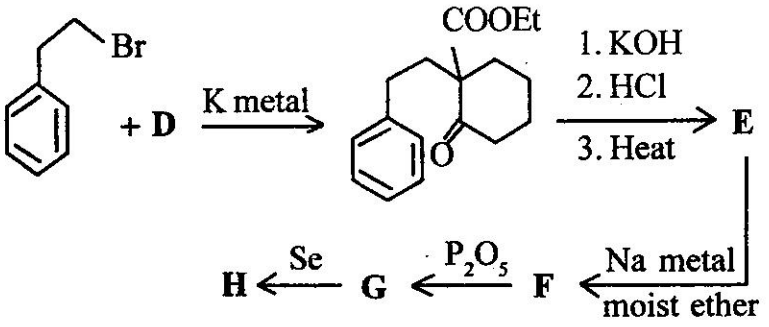
(*c*) Predict the product(s) of the following reaction : 2 + 2

(*i*) 

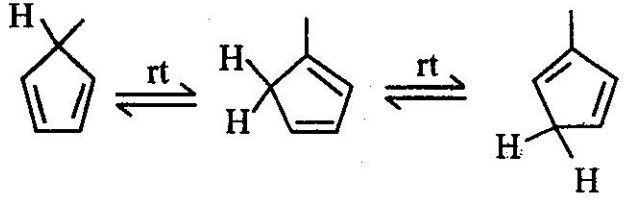
(*ii*) 

(*Continued*)

5. (*a*) Identify D → H from the following reaction scheme : 5

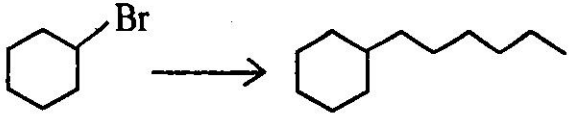


(*b*) Explain the formation of the following products : 2



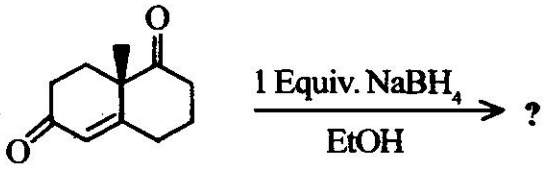
(*c*) What are the pyrimidine bases which occur in DNA ? 1

(*d*) Apply Corey-House synthesis to carry out the following transformation : 2

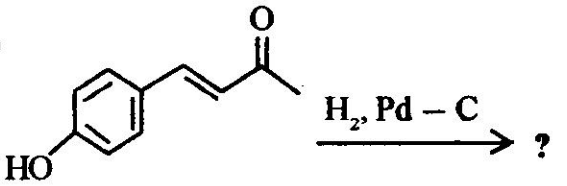


6. (*a*) Predict the product(s) and account for the chemoselectivity. 2 × 2

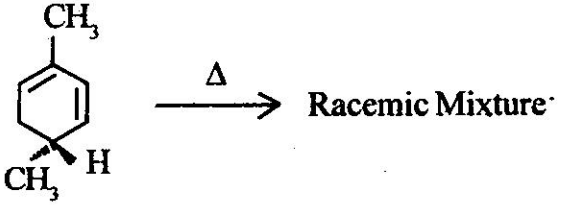
(*i*)



(*ii*)



(*b*) Explain the racemisation of the following compound on heating : 2



(*Continued*)

(*c*) Predict the product/s with plausible mechanism;

$$CH_3CH_2NH_2 + HCOOH(\text{excess}) \xrightarrow[100^\circ C]{\text{Formalin}} ?$$

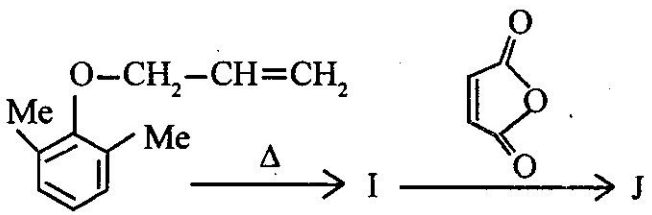
what is the name of this reaction and the function of formic acid ? $2\frac{1}{2}+1\frac{1}{2}$

GROUP – A (c)

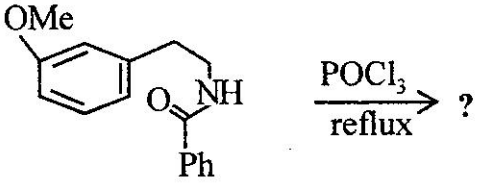
7. Answer any *five* questions : 2×5

(*a*) What is mutarotation ? Why sucrose does not exhibit mutarotation ?

(*b*) Predict the product of the following reaction



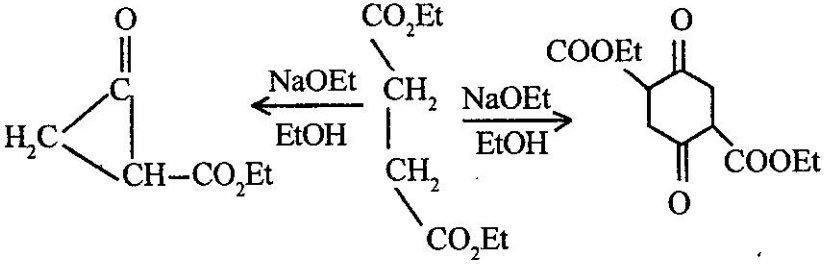
(*c*) Explain the formation of the product(s) in the following reaction :



(*d*) What are the principal force factors that maintain secondary and tertiary structures of protein.

(*e*) What is coenzyme ? Give an example.

(*f*) Account for the following observations :



(*g*) In aqueous solution, D-glucose gives β-D-glucopyranose as major species whereas it produces Methyl α-D-glucopyranoside as major product on treatment with CH_3OH and HCl. Explain.

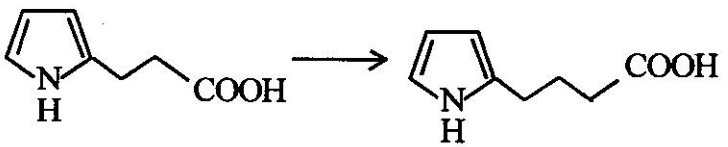
(*Continued*)

(*h*) Outline a Strecker synthesis for (D, L)-phenyl alanine.

(*i*) What would be the configuration of the product ? Use FMO approach;

Trans-3, 4-Dimethyl cyclobutene $\xrightarrow{\Delta}$?

(*j*) Give a plausible synthetic route for the following transformation :



(*Inorganic*)

[*Marks* : 45]

Time : 2 hours

GROUP – B (a)

Answer any **one** question :

8. (*a*) How are electronic spectra of d^1(oct), d^9(tet) and d^9(oct) are related for *d-d* transitions ?

(*b*) How do Na^+ ions transport across biological membranes ? What are the effects of Na^+ in mamalian system ?

(*c*) Copper(II) acetate monohydrate shows subnormal magnetic moment at room temperature– Explain.

(*d*) In the two complex ions, $[Co(NH_3)_5NCS]^{2+}$ and $[Co(CN)_5SCN]^{3-}$ the site of attachments of NCS^- and SCN^- with Co(III) ions are via Sulphur and Nitrogen respectively. Explain.

(*e*) Compare the oxygen binding affinity of haemoglobin and Myoglobin.

(*f*) Give a flow diagram for extraction of 'Au' from its ore. Write the related chemical reactions. 2 + 2 + 2 + 3 + 3 + 3

9. (*a*) "Zinc is the constituent of more than 250 metalloenzymes in biology"- Account on the statement mentioning at least one biochemical process.

(*b*) $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic, explain using CFT.

(*c*) Electronic absorption spectrum of 4f-metal ions consist of sharp lines while those of the 3d-metal ions display broad bands- Explain.

(*d*) What is nitrogenase ? What is its biological function ?

(*e*) An octahedral d^8 complex showed *d*-absorption bands at 10739, 17489 and 28217 cm^{-1}. Assign the bands from orgel diagram and calculate 10 Dq.

(*f*) How the orbital moment is quenched in most of the first transition series complexes ? Why the quenching is not perfect in Ni(II), octahedral and Co(II) tetrahedral complexes ?

2 + 2 + 2 + 3 + 3 + 3

GROUP – B (b)

Answer any **two** questions :

10. (*a*) Explain stereochemical non-rigidity with a suitable example.

(*b*) In between $[Ni(CO)_4]^{2+}$ and $[Ni(CO)_4]$, which one is more stable and why ?

(*c*) Discuss the bonding in Zeise's salt.

(*d*) Of the redox couples $[Co(H_2O)_6]^{3+}/[Co(H_2O)_6]^{2+}$ and $[Co(NH_3)_6]^{3+}/[Co(NH_3)_6]^{2+}$ which one is more oxidizing and why ?

2 + 3 + 3 + 2

11. (*a*) Define heptacity of an organometallic ligand. Indicate the various modes of binding of cyclopentadiene.

(*b*) Which one is better ligand H_2O or OH^- ? Why ?

(*c*) Write down the names of redox enzymes in PS-I and PS-II of photosynthesis.

(*d*) Justify the trend in LMCT energies :

$$CrO_4^{2-} < MoO_4^{2-} < WO_4^{2-}$$

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

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

2 + 2 + 2 + 2 + 2

(*Continued*)

12. (*a*) Give two evidences of metal-ligand orbital overlap.

(*b*) What is Cis-platin ? State its use.

(*c*) How does Pt occur in nature ? Give a scheme for isolation of pure Pt from principal natural source.

(*d*) Arrange the following complexes in order of increasing lability

$[K(H_2O)_6]^+$, $[Al(H_2O)_6]^{3+}$, $[Fe(H_2O)_6]^{3+}$

$2 + 2 + (1 + 4) + 1$

13. (*a*) Except $[CoF_6]^{3-}$ all other octahedral complexes of Co(III) are low spin complexes.– Explain.

(*b*) Draw a polarogram and identify each part. Define diffusion current (i_d) and half-wave potential ($E_{1/2}$).

(*c*) BaDS can behave as a good redox indicator for the titration of Mohr's salt by $K_2Cr_2O_7$ in presence of H_3PO_4– Explain.

(*d*) State with equation what happens when an acidic solution of Ti^{4+} is treated with dilute solution of H_2O_2 followed by addition of few drops of NH_4HF_2 solution. 2 + 3 + 2 + 3

GROUP – B (c)

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

(*a*) Fe(III) can be determined colorimetrically as its thiocyanato complexes but not as its fluoro complex.

(*b*) Draw all the optical and geometrical isomers of $[Co(en)_2Cl_2]^+$

(*c*) What do you mean by the statement that temporary hardness of a water sample is 4·5 ppm ?

(*d*) Room temperature magnetic moment of the complex ion $[Fe(H_2O)_5NO]^{2+}$ is 3·9 BM. Comment on the oxidation state of 'Fe' in the complex ion.

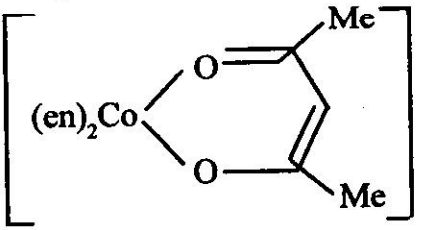
(*e*) What happens when an aqueous solution of K_2CrO_4 is acidified with H_2SO_4 and H_2O_2 is added in cold condition. The resulting

solution is finally shaken with diethyl ether. Give related equations of the above reaction scheme.

(*f*) In $[Cu(H_2O)_6]^{2+}$, two water molecules undergo exchange with bulk solvent molecules much more rapidly than the other four. Explain.

(*g*) What are spinel and inverse spinel ?

(*h*) Write the IUPAC name of the following compounds :



and

$[Cr(C_6H_6)(CO)_3]$