

CHEMISTRY PAPER - III

Time Allowed : 2 1/2 Hours

Maximum Marks : 200

- Note : 1) Attempt question **one** and **fourteen** other questions.
 2) Log table is enclosed.

1. Solve any three of the following

A) Assign structure to the molecule having given data : 6

Mol. formula $C_8H_8O_2$ IR : 3000-2900, 1745, 1600, 1500, 750, 690 cm^{-1} .NMR : 7.3 δ (m, 5H) 3.9 δ (s, 3H).B) Deduce the structure of the molecules having mol. formula C_4H_8O . 6IR : 1710 cm^{-1} NMR : 0.9 δ (t, J=6 Hz, 3H) 2.2 δ (s, 3H), 2.6 δ (q, J=6 Hz, 2H).C) The IR spectrum of a hypothetical gas AB shows an absorption band at 3000 cm^{-1} . Calculate the force constant of the A-B bond.(Take reduced mass = 1×10^{-27} Kg.) 6D) From the hydrogen atom ($l = \frac{1}{2}$), draw the energy level diagram [in terms of the applied magnetic field, H and hyperfine field, A]. Indicate the ESR transitions. State the selection rules used. 6E) Replacement of the fluoride ion in $[FeF_6]^{2-}$ with the heavier halogens leads first to yellow solution (Cl⁻) then brown (Br⁻) and finally to spontaneous reduction of Fe(III) by ⁻. Explain. 6F) The IR spectrum of H₂O shows three bands with maxima at 3756 cm^{-1} , 3652 cm^{-1} and 1595 cm^{-1} . Explain whether the molecule will be linear or bent. 6

2. Make qualitative sketches of the following : 13

A) The hydrogenic 3 s wave function and its square.

B) The wavefunction for n=2 state of one-dimensional harmonic oscillator as well as the square of the wavefunction. How many nodes do these wavefunctions have ?

3. A) Normalize $\sin(x)$, $0 \leq x \leq 2\pi$. 5B) Explain with the help of a qualitative MO energy diagram, why the dissociation energy of O_2^+ is greater than that of O_2 . Is it true for N_2^+ and N_2 ? 8

4. A) Write down the symmetry elements and identify point symmetry groups for ethylene and cyclopropane molecules. 10

B) State the variation principle for the ground state. 3

5. A) Sketch the electron density contours for the bonding MO for the H_2 molecule. 5

B) Write down the Huckel secular determinant for the benzene molecule. Show, without fully solving the secular equation, that $\alpha + 2\beta$ is an eigen value. 8

6. A) The rotational spectra of CO and HF show series of equidistant lines spaced 3.8 and 42 cm^{-1} respectively. What is the ratio of the moments of inertia I_{CO} / I_{HF} ? 5

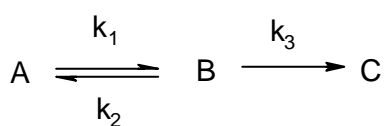
B) Iron compounds A, B and C exhibit the following Mossbauer data. 8

	Isomer shift (Fe) mm sec ⁻¹	Quadrupole splitting mm sec ⁻¹
A	0.2	0.4
B	1.2	2.5
C	1.4	0

Comment on the valency spin state and distortion from cubic structure for the three cases.

7. A) Write down the expression for the entropy of mixing, ΔS_{mixg} of ideal gases. From the expression, how do you conclude that $\Delta S_{mix} \geq 0$. 6

B) Write rate expressions for disappearance of A and formation of B and C for the following reaction 7



$$\frac{-d[A]}{dt} =$$

$$\frac{d[B]}{dt} =$$

$$\frac{d[C]}{dt} =$$

8. A) Calculate the pressure required to compress isothermally an ideal gas of volume 105 litres to 35 litres from an initial pressure of 1 atmosphere. 4

B) Calculate the ionic strength of a solution 0.2 molar in K_2SO_4 and 0.1 molar in KCl. 5

C) Write down the limiting law equation relating γ_{\pm} , the mean activity coefficient Z_+ and Z_- the valencies of cations and anions respectively and the ionic strength of the electrolyte. 4

9. A) State and explain the Phase Rule.

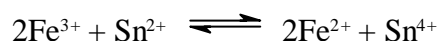
B) What is the maximum number of phases that can exist in equilibrium for a one component system? Explain briefly. 5

C) Draw the vapour pressure diagrams for binary mixture showing ideal, behaviour and positive and negative deviations from Raoult's law. 6

10. A) Give a brief account of 3 kinds of electrodes with one example each that are used for work in electrochemistry. 6

B) Calculate the equilibrium constant 7

K of the reaction :



given $E^0, \text{Fe}^{3+}/\text{Fe}^{2+} = 0.77$ volt

and $E^0, \text{Sn}^{4+}/\text{Sn}^{2+} = 0.15$ volt

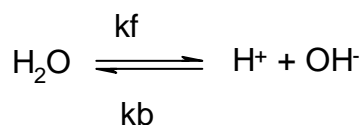
Comment on the practical utility of the result of K value in analytical chemistry.

11. A) Define partition function. Write down an expression for the rotational partition function for a diatomic molecule. 7

B) The internuclear distance of $^{127}\text{I}_2$ is 2.66×10^{-10} m. Calculate the rotational partition function at 300 K and 1000 K. 6

12. A) For a first order chemical reaction, the time required for half the reactant to be used up is independent of the initial concentration of the reactants. Prove this statement. 5

B) The relaxation time for the reaction 8

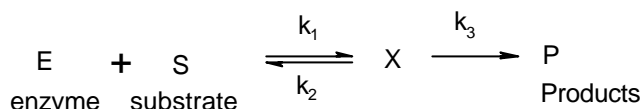


is found to be $36 \mu\text{s}$ at 25°C . The ionic product of water at 25°C is 1×10^{-14} . Calculate the rate constants for the forward (kf) and the reverse reaction (kb).

13. A) Explain briefly the following terms with one example each. Colloids, Macromolecules, Micelles. 6

B) For the enzyme catalysed reaction

2



Define Michaelis constant K_m in terms of k_1 , k_2 and k_3 .

C) Write down the rate of the above reaction in terms of maximum rate (v_{\max}), k_m and substrate concentration $[S]$. 5

14. A) What are Schottky defects ? Draw a suitable diagram and explain. 4

B) Draw schematic band diagram of an intrinsic (pure) semiconductor. Label valence and conduction bands. Where will be the position of the Fermi level ? Will it be near the bottom of the conduction bands, top of the valence band or centre of the forbidden energy gap ? 5

C) Explain the Wagner mechanism for sulphidizing of silver metal $\alpha\text{-Ag}_2\text{S}$. 5

15. A) Give IUPAC nomenclature for the following : 8

- i) $\text{K}_3[\text{Fe}(\text{CN})_5\text{CO}]$
- ii) $[\text{Co}(\text{en})\text{Cl}_3(\text{H}_2\text{O})]$
- iii) $[\text{Co}(\text{en})_3]\text{Cl}_3$
- iv) $[\text{Pt}(\text{py})_4] [\text{PtCl}_4]$

B) With the help of a diagram, explain the splitting up d orbitals in tetrahedral and square-planar symmetries during complex formation. 5

16. A) Account for the fact that $[\text{CoF}_6]^{3-}$ is formed by sp^3d^2 hybridisation, while $[\text{Co}(\text{NH}_3)_6]^{3+}$ is formed by d^2sp^3 hybridisation. 6

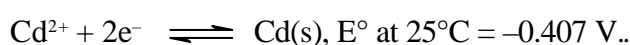
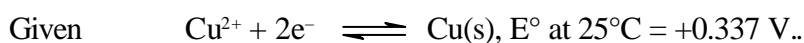
B) The magnetic moment of $[\text{Mn}(\text{CN})_6]^{3-}$ is 2.81 BM, while that of $[\text{MnBr}_4]^{2-}$ is 5.91 BM. Discuss the geometries of these complex ions in terms of the hybridisations involved. 7

17. A) What is meant by effective atomic number (EAN) ? Calculate EAN of the following : 6

- i) $[\text{Fe}(\text{CN})_6]^{4-}$
- ii) $[\text{Cr}(\text{NH}_3)_6]^{3+}$
- iii) $[\text{Pt}(\text{NH}_3)_4]^{2+}$

B) With the help of suitable examples, explain the nephelauxetic effect. 7

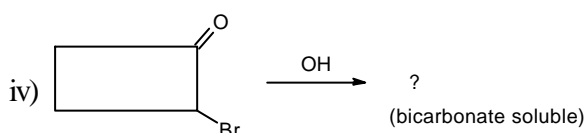
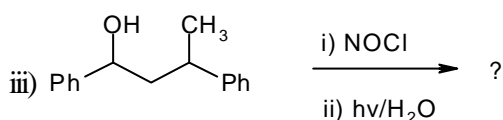
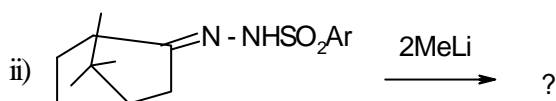
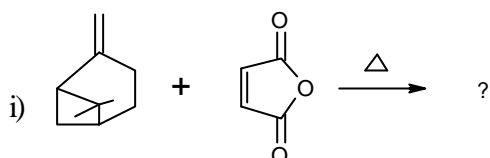
18. A) Explain briefly the spectrochemical series. Arrange the following ligands in decreasing order of their ability to cause splitting : 8
 Br^- , H_2O , en, OH^- , CN^- , I^-
- B) With the help of suitable examples explain Jahn-Teller effect. 5
19. A) Give briefly biochemical functions of the following essential trace elements in biological systems. (i) iodine, (ii) copper, (iii) manganese and (iv) molybdenum. 8
- B) Give one method of synthesis of dibenzene chromium from CrCl_3 . Write its structure giving important physical properties. 5
20. A) The Mossbauer spectrum of $\text{Na}_4[\text{Fe}(\text{CN})_6]$ consists of a single line, while that of $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ shows a quadrupole doublet. Explain the above observation. 6
- B) Give balanced equations for the extraction of copper from chalcopyrites. 7
21. A) What is a crown ether ? Give its applications. 7
- B) Draw the structures for (i) a cyclic silicate anion, (ii) a pyroxene and (iii) an asbestos. 6
22. A) What are molecular sieves ? Discuss briefly their applications. 8
- B) What are phosphazenes ? Explain three main structural types of these compounds. 5
23. A) Draw a typical cell arrangement for amperometric titrations with a rotating platinum electrode and label various components of the cell. 7
- B) Explain advantages and disadvantages of dropping mercury electrode as compared with platinum and carbon microelectrodes. 6
24. A) Distinguish between (i) voltametry and polarography, (ii) a limiting current and a residual current. 6
- B) Consider a cell consisting of copper electrode in contact with 1.0 M Cu^{2+} , 7
a cadmium electrode in contact with 1.0 M Cd^{2+} and a connecting salt bridge.
The cell has a resistance of 4 ohms. Calculate the potential needed to develop a current of 0.0200 A in the electrolytic cell.



25. A) Draw a schematic diagram of a photoelectric colourimeter and label various components of it. 7

B) Explain with the help of a diagram the working of hollow cathode lamp as a source of radiation for AAS. 6

26. Complete the following giving the name of the reaction involved? 13



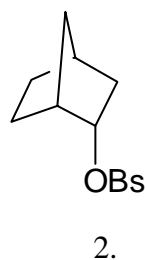
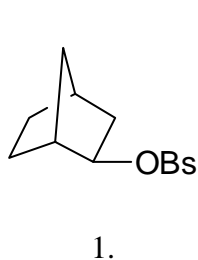
27. A) pK_a values of *p*-nitrobenzoic acid, *p*-methoxy benzoic acid, *m*-chlorobenzoic acid and benzoic acid are 3.44, 4.47, 3.83 and 4.2 respectively, calculate σ_{p-NO_2} , σ_{p-OMe} , σ_{m-Cl} . 3

B) Match the ρ value with the appropriate reaction giving reasons. 6

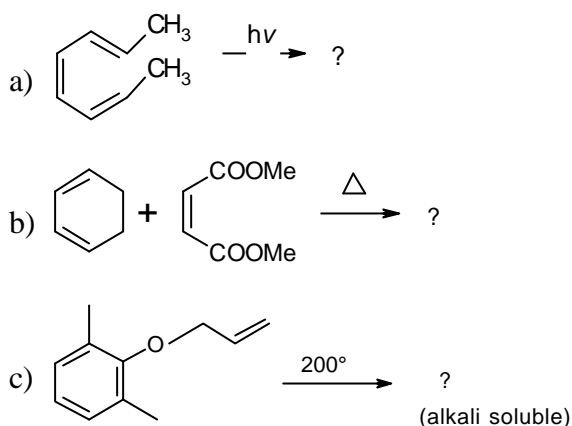
$$\rho = 2.45, 0.75, -2.40, -7.30$$

- Nitration of substituted benzenes.
- Ionization of substituted benzene thiols.
- Ionization of substituted benzenephosphonic acids.
- Reaction of substituted *N,N*-dimethyl aniline with CH_3I .

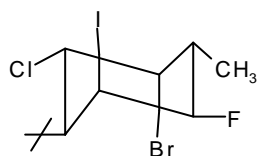
C) Explain why acetolysis of *exo*-brosylate 1 is faster than that of *endo*-brosylate 2. 4



28. Predict the product and its stereochemistry for the following reactions. Indicate for each reaction (i) type of pericyclic reaction (ii) necessary selection rule. 13

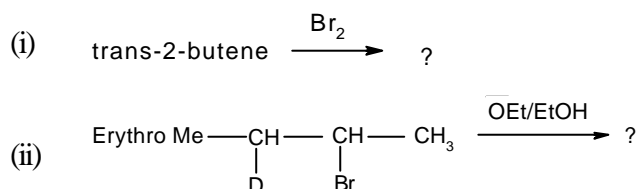


29. A) In the conformation shown below 6

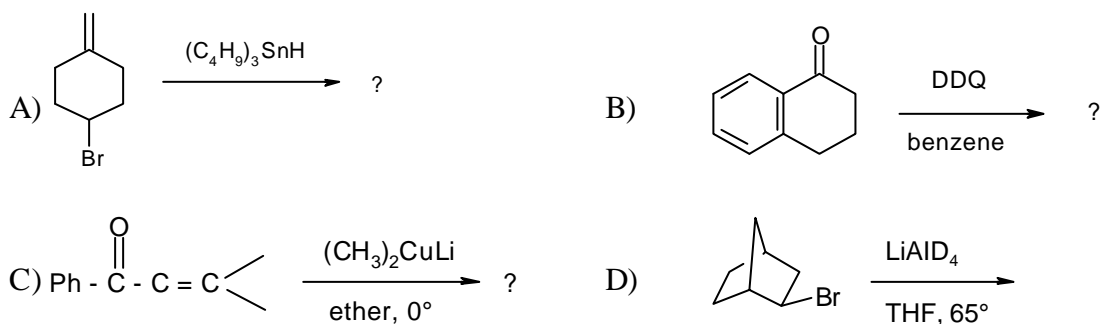


- i) Indicate the groups that are axial.
- ii) Indicate the groups that are equatorial.
- iii) Indicate with reasons the halide that would be lost most easily in a base catalysed reaction.

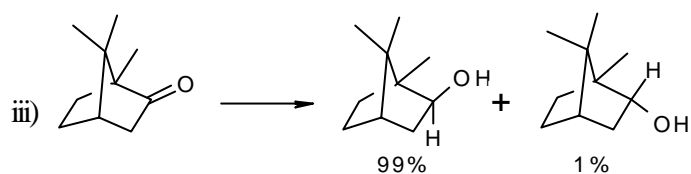
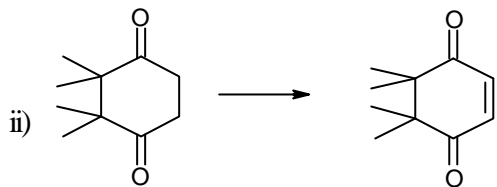
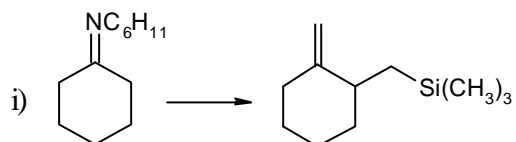
- B) Predict the product and its stereochemistry in the following reaction. Justify your prediction. 7



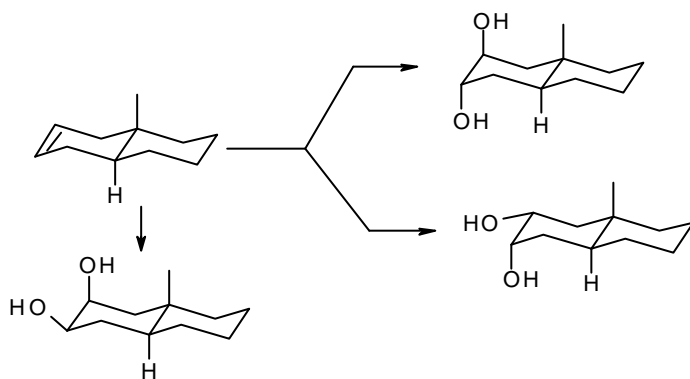
30. Give the products of the following reactions. 13



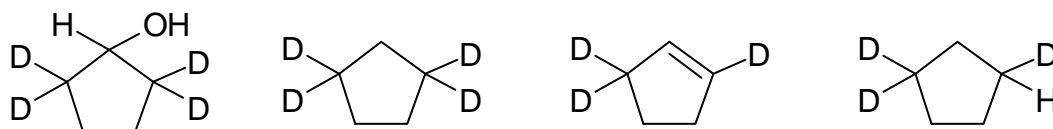
31. A) Indicate the reagents for the following conversions, which may involve more than one step. 7



B) Indicate the reagents for the following 6

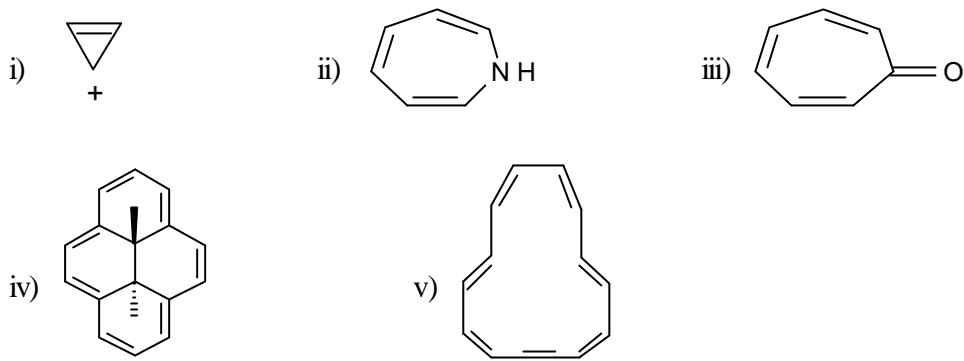


32. A) Show how each of the following compounds can be prepared from cyclopentanone, D_2O and necessary organic or inorganic reagents. 6



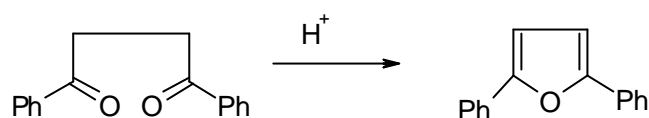
B) Indicate, giving reasons, which of the systems given below is aromatic.

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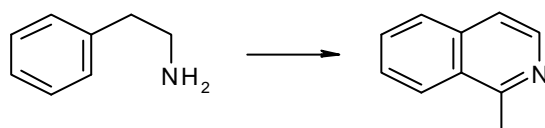
33. A) Suggest mechanism for the following :

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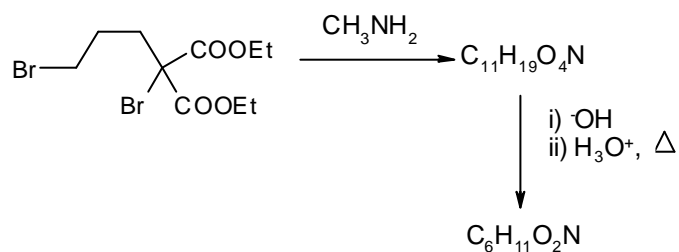
B) How is the following transformation carried out ?

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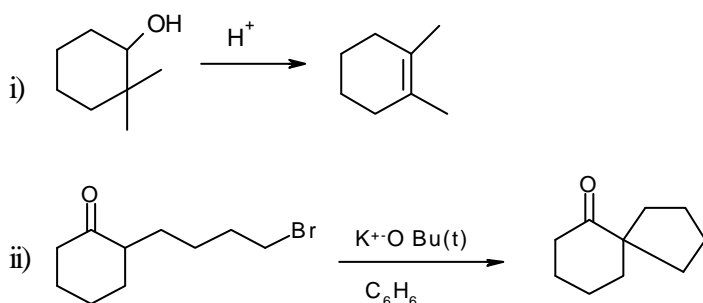
C) Write the structures for the intermediate and the final product.

5



34. A) Propose mechanisms for the following :

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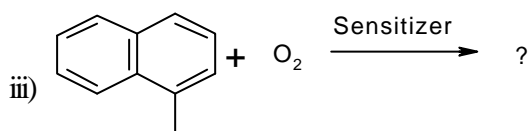
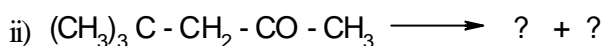
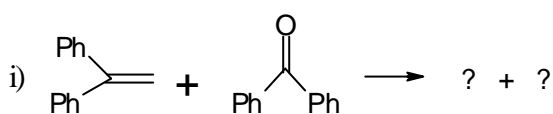
B) match the following

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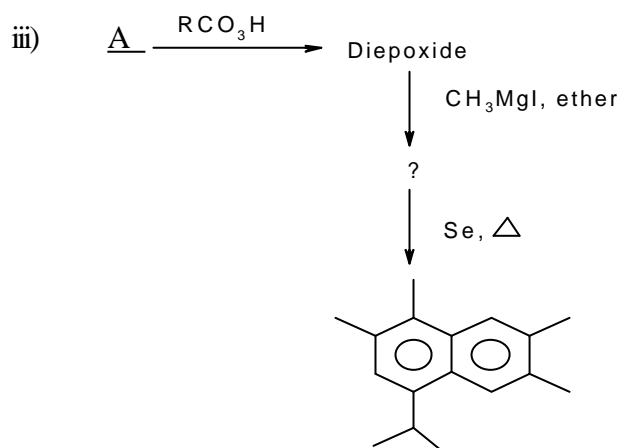
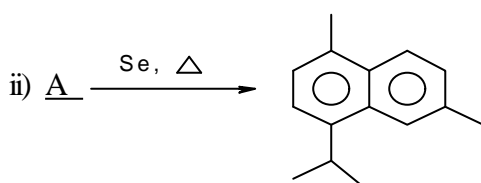
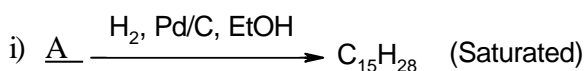
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|---------------------|--------------------------------|
| i) Prosthetic group | a) Ribose |
| ii) Coenzyme | b) Deoxyribose |
| iii) DNA | e) Non protein part of peptide |
| iv) RNA | d) Organic cofactor |
| v) Sanger | e) N-terminal analysis |
| vi) Edman | f) FDNB |

- i) ii) iii) iv) v) vi)

35. Predict the major products of the following photochemical reactions. Explain briefly the process involved. 13



36. A) A compound A ($\text{C}_{15}\text{H}_{24}$) undergoes following reactions. 8



Giving reasons, answer the following :

- How many double bonds and rings are present in A?
- What is the nature of the carbon skeleton?
- What is the position of the double bonds and the structure of A?
- Formulate the reactions involved in (iii).