

CHEMISTRY PAPER - III

Time Allowed : 2 1/2 Hours

Maximum Marks : 200

N.B. :- (1) Question No. *One is compulsory*. Attempt any *Fourteen* other questions from the remaining.

1. Attempt any three of the following : 6
- a) Sketch the diagram of allowed transitions between the energy levels and the rotational spectrum of a non-rigid diatomic molecule. Compare the spacings between the allowed rotational energy levels of rigid and non-rigid molecules. 6
- b) Isomer shift (δ) for $K_4 [Fe (CN)_6] \cdot 3H_2O$ relative to stainless steel is $0.083 \text{ mm sec}^{-1}$ while that for $K_3 [Fe (CN)_6] \cdot 3H_2O$ is $0.084 \text{ mm sec}^{-1}$. Explain the above observation. 6
- c) Explain why XPS spectrum of 3-nitropyridine exhibits two distinct peaks in the region associated with N (1s) orbitals, near 400 eV binding energy. How would you expect the binding energies to be affected if the pyridine ring was attached to a metal ion as a ligand ? 6
- d) Predict the structures of the two compounds whose NMR data is given. Assign the signals. 6
- (i) $C_3H_3Cl_5$ δ 4.52 (t, 1H); 6.07 (d, 2H)
- (ii) $C_3H_5Cl_3$ δ 2.2 (s, 3H); 4.02 (s, 2H)
- e) Predict the structures of the compounds whose IR data is given below. 6
- Assign the IR bands.
- (i) C_3H_6O 1620 cm^{-1}
- (ii) C_4H_6 3300 and 2250 cm^{-1} .
2. The standard heat of hydrogenation of propene in the reaction.
- $$CH_2 = CHCH_3 (g) + H_2 (g) = C_3H_8 (g) \text{ is } -124 \text{ kJ/mol.}$$
- The standard heat of combustion of propane in the reaction
- $$C_3H_8 (g) + 5O_2 (g) = 3CO_2 (g) + 4H_2O (l) \text{ is } -2220 \text{ kJ/mol.}$$
- Calculate the standard heat of combustion of propene.
- Given : $\{H_2 (g) + \frac{1}{2}O_2 (g) = H_2O(l), \Delta H^\circ = -285.8 \text{ kJ / mol}\}$ 13
3. a) Write expressions for the activities of $NaCl$, $CaCl_2$ and $LaCl_3$ in terms of their molalities and mean ionic activity coefficients. 6
- b) The normal boiling point of carbon tetrachloride is $76.7^\circ C$. If CCl_4 obeys Trouton's rule, calculate the heat of vaporisation. 7
4. The respective vapour pressures of liquid and solid arsenic are given by
- $$\log_{10} P_{\text{torr}} = -\frac{2460}{T} + 6.7 \text{ and } \log_{10} P_{\text{torr}} = -\frac{6900}{T} + 10.8$$
- a) Determine the temperature at which the two forms of arsenic have the same vapour pressure. 7
- b) Calculate the normal boiling point of liquid arsenic. 6

5. Calculate $\langle P_x \rangle$ and $\langle x \rangle$ values for the ground state of the harmonic oscillator,

$$\psi_0(x) = \left(\frac{\alpha}{\pi} \right)^{1/4} \exp(-\alpha x^2 / 2)$$

Sketch $\psi_0(x)$ qualitatively. 13

6. Set up Huckel determinant for butadiene molecules and obtain the respective MO energies. 13

7. Using the definition

$$Q_{\text{rot}} = \sum g_J \exp(-\epsilon_J / kT)$$

Show explicitly, for a rigid rotor that

$$Q_{\text{rot}} = \frac{8\pi^2 I kT}{h^2}$$

Given that CO bond length = 1.13 \AA , calculate Q_{rot} at 10K and 1000K. 13

8. a) Given that

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

Obtain an expression for T in terms of the other quantities. 7

- b) How does a double sphere model explain the mechanism of a reaction between two ions in solution? 6

9. a) The order of enzyme-catalysed reaction changes with substrate concentration. Explain this observation on the basis of Michaelis Menten equation. 6

- b) State any three salient features of free radical polymerisation. 7

10. a) A crystal of KCl contains some Ca^{2+} ions. Will the density of this crystal be equal to less than or more than that of pure KCl? Explain. 5

- b) The electrical conductivity of pure silicon is increased considerably when either pentavalent or trivalent ion impurities are incorporated into its structure. Draw suitable diagrams and explain why this is so. 8

11. a) Discuss the electrical conductivity of metals in terms of the free electron theory. 8

- b) What are edge and screw dislocations? 5

12. a) Give in brief the synthesis of (i) tetrasulphur tetranitride from ammonia and sulphur dichlorides and (ii) iodine trichloride from iodine pentoxide and HCl. 6

- b) The magnetic moment of $[\text{Mn}(\text{CN})_6]^{3-}$ is 2.8 BM. The magnetic moment of $[\text{MnBr}_4]^{2-}$ is 5.9 BM. What are the geometries of these complex ions? (Magnetic moments are measured at RT). 7

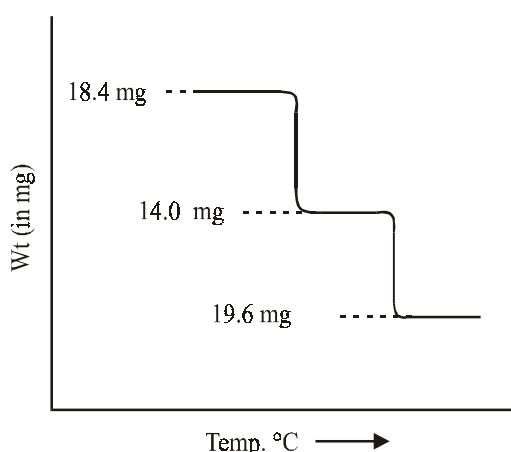
13. a) $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ absorbs light of wavelength 5000 \AA . Name one ligand which would form a titanium (III) complex absorbing light of lower wavelength than 5000 \AA and one ligand which would form a complex absorbing light of wavelength higher than 5000 \AA . 7
- b) Account for the fact that cerium shows 3+ and 4+ oxidation states while europium exhibits 2+ and 4+ oxidation states in their compounds. 6
14. a) Predict whether the following reactions will proceed via inner sphere or outer sphere mechanism. Give the products also.
- i) $[\text{Fe}(\text{CN})_6]^{4-} + [\text{IrCl}_6]^{2-} \rightarrow$
- ii) $[\text{Co}(\text{NH}_3)_5\text{NCS}]^{2+} + [\text{Cr}(\text{H}_2\text{O})_6]^{2+} \rightarrow$ 6
- b) Name the factors that determine the magnitude of crystal field splitting. 7
15. a) Explain why threshold energy for (n, p) reaction is greater than that of (n, r) reaction. 8
- b) Uranium minerals, which are old enough for radioactive equilibrium to have been established, contain 1 atom of radium to 2.8×10^6 atoms of uranium. The half life of radium has been found by direct measurement to be 1620 years. Estimate the half life of uranium. 5
16. a) Derive EMF expression for the following cell reaction. 5
- $$\text{Cr}^{6+} + 3\text{Fe}^{2+} \rightarrow \text{Cr}^{3+} + 3\text{Fe}^{3+}$$
- b) Draw the shapes of the following molecules / ions indicating the position(s) of lone pair (s) of electrons (if any). 8
- i) $\text{Si}_2\text{O}_7^{6-}$ ii) SF_6 iii) ICl_5 iv) XeF_2
17. a) Ferredoxins are iron clusters involved in electron transfer in biological processes. Draw core structure of these units. 5
- b) Write down the isomers you can get in the following substitution reactions : 8
- $$\left[\begin{array}{c} \text{Cl} \quad \text{Pt} \quad \text{Cl} \\ \diagdown \quad \diagup \\ \text{Cl} \quad \text{Cl} \end{array} \right]^{2-} \xrightarrow{\text{NH}_3} ? \xrightarrow{\text{NH}_3} ?$$
- $$\left[\begin{array}{c} \text{H}_3\text{N} \quad \text{Pt} \quad \text{NH}_3 \\ \diagdown \quad \diagup \\ \text{H}_3\text{N} \quad \text{NH}_3 \end{array} \right]^{2+} \xrightarrow{\text{Cl}^-} ? \xrightarrow{\text{Cl}^-} ?$$
18. a) Mention the principles on which the separation of lanthanides using ion exchanger is based. 4
- b) Draw the structure of B_2H_6 and label the different types of bonds present in the molecule. 9

19. a) Give IUPAC nomenclature for the following complexes :
- i) $[\text{Co}(\text{en})\text{Cl}_3(\text{H}_2\text{O})]$
- ii) $\text{K}_4[\text{Co}(\text{CN})_6]$ 4
- b) The raman spectra in the region of the $\text{C}\equiv\text{O}$ and $\text{M}-\text{C}$ stretching vibrations of the isostructural series $\text{Ni}(\text{CO})_4$, $\text{Co}(\text{CO})_4^-$ and $\text{Fe}(\text{CO})_4^{2-}$ exhibit the following bands.

	$\text{C}\equiv\text{O}$ region	$\text{M}-\text{C}$ region
$\text{Fe}(\text{CO})_4^{2-}$	1788 cm^{-1}	$550, 464\text{ cm}^{-1}$
$\text{Co}(\text{CO})_4^-$	$1988, 1883\text{ cm}^{-1}$	$532, 439\text{ cm}^{-1}$
$\text{Ni}(\text{CO})_4$	$2121, 2039\text{ cm}^{-1}$	$422, 381\text{ cm}^{-1}$

Give brief explanation of the above data. 9

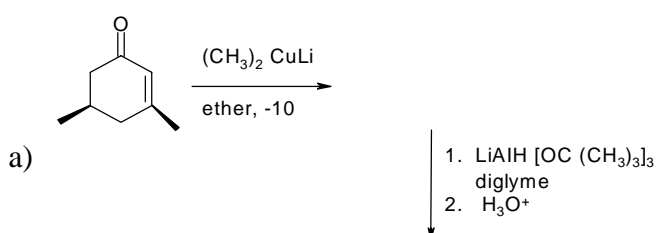
20. a) The thermogram of a mixture of CaCO_3 and MgCO_3 show mass loss at 500°C and 900°C as shown below. If the decomposition temperatures of MgCO_3 and CaCO_3 are 500°C and 900°C respectively, find the amount of calcium and magnesium in the mixture. 7

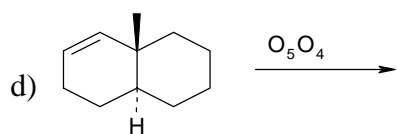
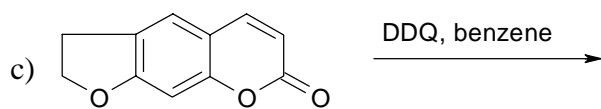
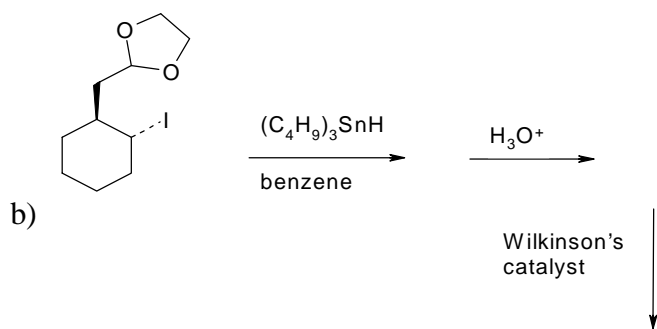


- b) Exactly 25.0 ml of an unknown solution of cadmium ion give a diffusion current of $39.5\ \mu\text{A}$. To this solution exactly 5.0 ml solution of 0.01 M cadmium ion was added which gave diffusion current of $88\ \mu\text{A}$. Calculate the concentration of unknown solution. 6

21. a) Derive an expression for Beer's law and mention the reasons for deviations from it. 6
- b) Calculate the amount of iron left unextracted from 100 ml solution in 6 M HCl containing 200 mg of Fe^{3+} after two extractions with 25 ml of diethyl ether. [Given : the distribution ratio is 150]. 7

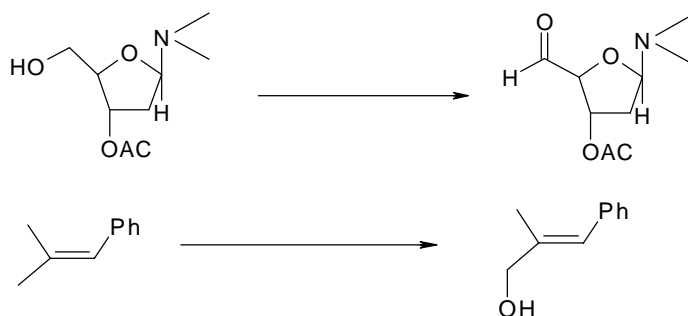
22. Complete the following by inserting structures at the appropriate places. 13





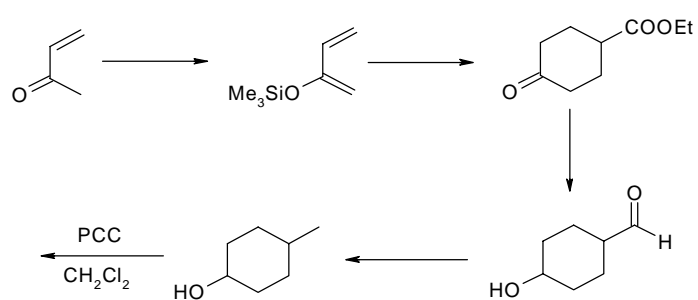
23. a) Indicate the reagents for the following transformations

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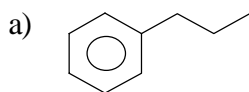
b) Complete the following

9

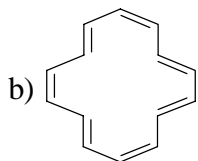


24. Match the following

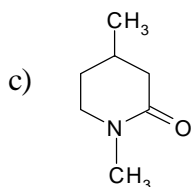
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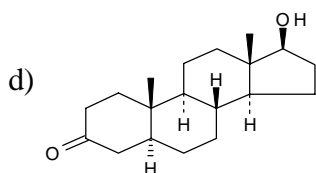
(i) u.v. band at 241 nm



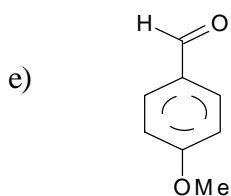
(ii) Peak at m/z 91



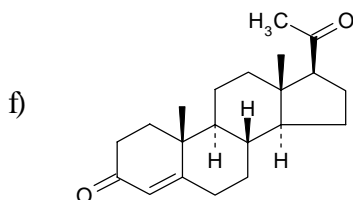
(iii) Positive cotton effect



(iv) Sustains ring current



(v) IR at 1670 cm⁻¹

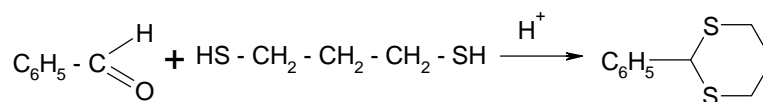


(vi) A signal at δ 10 ppm

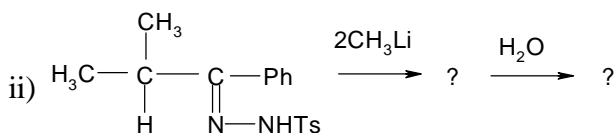
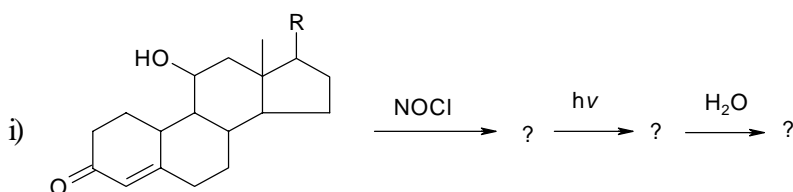
Ans. (a) (b) (c)
(d) (e) (f)

25. a) Give a mechanism for the following reaction

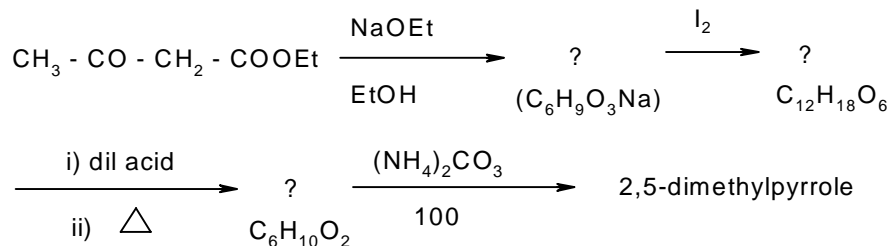
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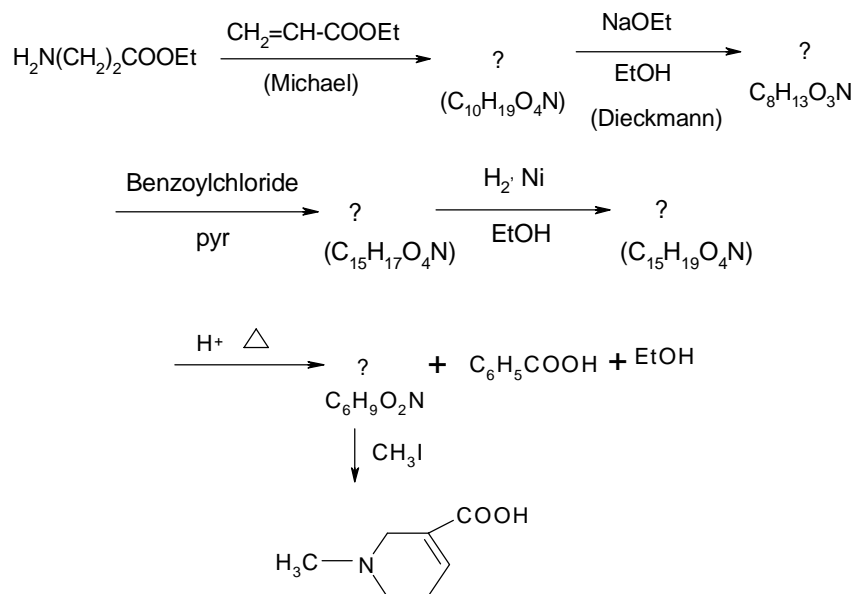
b) Complete the following



26. a) Complete the steps in the synthesis of 2,5-dimethylpyrrole shown below



b) Complete the steps in the synthesis shown below :

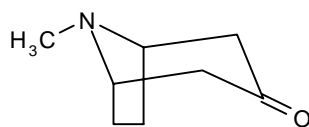
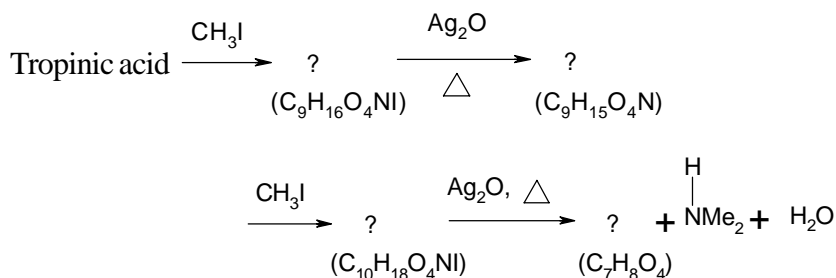


27. a) Tropinic acid, C₈H₁₃O₄N shows the following behaviour. Draw structural information from each observation. 3

i) Neutralization equivalent 94 ± 1,

ii) Dissolves in aq. HCl but does not react with benzene sulfonyl chloride, cold dil KMnO₄ or Br₂/CCl₄.

b) Tropinic acid is formed by oxidation of tropinone. From this suggest the structure of tropinic acid and complete the sequence shown below. Tropinic acid 10



Tropinone

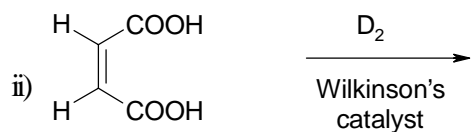
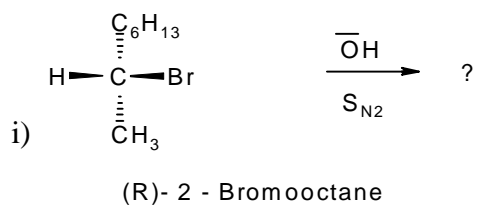
28. Match the following

- | | |
|--------------------------|-------------|
| a) m – Me | i) + 0.78 |
| b) p – Me | ii) – 0.27 |
| c) p – NO ₂ | iii) + 0.12 |
| d) p – COCH ₃ | iv) – 0.07 |
| e) m – OMe | v) + 0.50 |
| f) p – OMe | vi) – 0.17 |

Ans. a) b) c)
 d) e) f)

13

29. a) Predict the product formed in the following reactions and state whether the reactions are enantioselective or diastereoselective. Give reasons. 4



b) Draw two chair conformations of each of the following. Indicate the expected energy difference in the conformers. Given ΔF for CH₃, Et, OH and Cl are 1.8, 1.9, 0.7 and 0.4 kcal/mole respectively.

- i) cis-4-methylcyclohexanol
- ii) trans-3-ethylcyclohexylchloride.