

## 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. Attempt any three of the following 6
- A) Assign structure to the molecule having given data :  
Mol-form :  $C_9H_{10}O_2$   
IR : 1730, 1600, 1250, 750, 700  $cm^{-1}$ .  
PMR :  $\delta$  1.3(3H, t, J = 7Hz), 4.4 (2H, q, J = 7 Hz), 7.4 (3H, m), 8.1 (2H, m).  
8.1 (2H, m).
- B) Deduce the structure of the molecule having mol-formula.  $C_5H_{10}O$  6  
UV : no  $\lambda$  max above 200 nm.  
IR (neat) : No bands above 3000  $cm^{-1}$  and 2000 – 1600 region.  
PMR :  $\delta$  1.22 (3H, d, J = 6.5 Hz), 2.0 (4H, m), 3.65 (2H, t, J = 6.0 Hz), 3.8 (1H, m).
- C) The compound  $FeSO_4 \cdot 7H_2O$  shows quadrupole split Mossbauer spectrum while  $FeCl_3$  shows a single line. Explain the above behaviour. 6
- D) Draw the energy level diagram for the molecule or ion with S= 1 in  
(i) absence and (ii) presence of zero field splitting. 6
- E) State the rule of mutual exclusion in connection with the I.R. and Raman spectra of molecules. Illustrate the use of this in understanding the molecular structure by giving one example. 6
- F) Sketch schematically the Potential Energy curves of a diatomic molecule for ground and excited states. Represent the transition corresponding to  $\nu'$ -progression originating from the lowest state. 6
2. A) In the so-called potential energy curve for a diatomic molecule, it is the total electronic energy plotted versus internuclear separation. Explain. 5
- B) Normalize the Heitler–London ( $\Psi_{HL}$ ) wavefunction for the  $H_2$  molecule (usual notations used)  
$$\Psi_{HL} = [1s_a(1)1s_b(2) + 1s_b(1)1s_a(2)]$$
  
S is the overlap integral  $\int 1s_a(1)1s_b(1)d^3r_1$  and  $1s_a, 1s_b$  denote normalized hydrogenic orbitals. 8

3. A) What are the energies in eV and degeneracies of the following orbitals for H-atom? 13  
 (i) 1s            (ii) 3p            (iii) 4s            (iv) 3d

4. Prepare a table of microstates for a  $d^2$  configuration. What are the possible term symbols generated? Identify the term symbol of the ground state. 13

5. Show that the following three hybrid orbitals form an orthonormal set. 13

$$\Psi_1 = \frac{1}{\sqrt{3}}s + \sqrt{\frac{2}{3}}pz$$

$$\Psi_2 = \frac{1}{\sqrt{3}}s - \sqrt{\frac{1}{6}}pz + \sqrt{\frac{1}{2}}py$$

$$\Psi_3 = \frac{1}{\sqrt{3}}s - \frac{1}{\sqrt{6}}pz + \sqrt{\frac{1}{2}}py$$

Choose an appropriate label ( $sp$  /  $sp^2$  /  $sp^3$ ) for these orbitals and provide your reasoning.

6. A) One mole of an ideal gas at temperature  $T_1$  and having volume  $V_1$  is heated to temperature  $T_2$  when its volume becomes  $V_2$ . Show that the change in its entropy will be given by 6

$$\Delta S = C_v \ln(T_2/T_1) + R \ln(V_2/V_1)$$

- B) Estimate the molar enthalpy of atomization of gaseous ammonia at 25°C and 1 atm. from the following data. 7

(i) Bond strength :

$$\Delta N_2(g) : 945 \text{ kJ/mole}, H_2(g) : 436 \text{ kJ/mole}.$$

(ii)  $\Delta H^\circ_{\text{formation}}$  of  $NH_3(g)$  :  $-46.10 \text{ kJ/mole}$ .

7. Show that the translational partition function for a gas is given by 13

$$Q_t = \frac{(2\pi mkt)^{3/2}}{h^3} V$$

$$\int_0^\infty e^{-ax^2} dx = \frac{1}{2} \sqrt{\pi/a}$$

8. A) Consider a molecular sample containing an unpaired electron interacting with a nucleus with spin 1/2 placed in a strong magnetic field. Sketch a schematic energy level diagram for the electron. Show the allowed e.s.r. transitions and the resulting e.s.r. spectrum. Indicate the hyperfine splitting in the diagram. 8

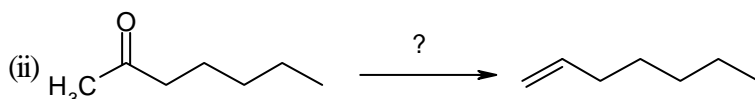
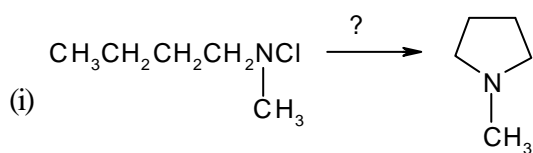
- B) With brief explanation, schematically draw the high resolution  $^1H$  n.m.r. spectrum of acetaldehyde. 5

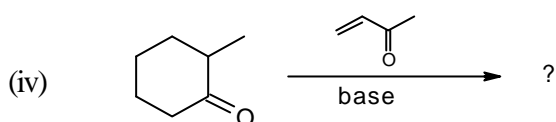
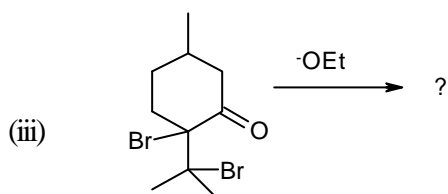
9. A) State Le Chatelier's principle and sum up in a few sentences the effects of concentration, temperature, pressure and catalyst on the course of chemical reactions. 9
- B) For which of the following equilibria does decrease in pressure NOT favour the forward reaction ?
- (i)  $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$  4
- (ii)  $\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g})$
- (iii)  $\text{NH}_4\text{Cl}(\text{g}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$
- (iv)  $2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$
10. A) What are concentration cells ? Give an example each of the electrode and electrolyte concentration cell with proper and correct representation. Give equation for the E.M.F. of the above type of cells. 8
- B) Calculate  $K_{\text{sp}}$  of AgCl by forming a suitable cell, given that : 5  
 $E^\circ(\text{AgCl}, \text{Ag}, \text{Cl}^-) = 0.2224 \text{ V}$   
 $E^\circ(\text{Ag}^+, \text{Ag}) = 0.7990 \text{ V}$
11. A) Write down the Langmuir's adsorption isotherm. Explain the meaning of the various terms in the equation. Show graphically the variation of  $\theta$  with  $p$ . How does one calculate the fraction of the solid surface covered ? 10
- B) What are micelles ? 3
12. A) The rate equation for the first order reaction is given by : 7  

$$K_R = \frac{1}{t} \ln \frac{C_0}{C}$$
 Where,  $C_0 =$  initial concentration  
 $C =$  concentration at time 't'  
 Obtain the equation for the half-life for such a reaction.
- B) Show the shapes of curves for reaction rate vs. temperature for : 6  
 (i) general chemical reactions.  
 (ii) reactions that reach an explosive state  
 (iii) reactions that are enzyme-catalyzed
13. A) In photochemical combination of chlorine and hydrogen 20 moles of chlorine have been converted into HCl by irradiating light of  $\lambda = 4000$ . Calculate the quantum yield for this reaction if the radiation energy absorbed by this system is  $3 \times 10^{-11} \text{ J}$ . 8

- B) What are the different types of catalysis. Give suitable examples of each type. 5
14. A) Explain the terms 7  
 (i) Edge dislocations  
 (ii) Screw dislocations  
 State the properties of solids that are influenced by the presence of dislocations.
- B)  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$  are heated together to form  $\text{MgAl}_2\text{O}_4$ . Explain the mechanism of this solid state reaction. 6
15. Draw schematic curves of the electrical conductivity of metals and intrinsic semiconductors as a function of temperature. Comment on the trends shown. 13
16. A) Draw a block diagram of a double beam fluorospectrometer and label various components of the instrument. 7
- B) Define the following terms (any three) 6  
 (i) resonance fluorescence  
 (ii) internal conversion  
 (iii) quantum yield of fluorescence  
 (iv) Stokes shift  
 (v) radiation buffer
17. A) List the advantages and disadvantages of the dropping mercury electrode compared with platinum or carbon micro electrodes. 7
- B) What are ion-selective electrodes ? Explain with one typical example the working of any one of these electrodes. 6
18. A) Explain the terms 6  
 (i) distribution coefficient  
 (ii) stripping  
 (iii) backwashing
- B) Copper sulphate pentahydrate was heated from room temperature to  $900^\circ\text{C}$ . Draw schematic TG and DTA curves, label various steps involved in them 7
19. A) On the basis of valence bond theory explain geometry and magnetic behaviour of  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $[\text{NiCl}_4]^{2-}$ . 6
- B) Give one method of preparation and structure of iron pentacarbonyl. 7

20. A) Draw molecular orbital energy level diagram of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ . 6
- B) Give one method of preparation and draw the structure of ferrocene. 7
21. A) Explain the role of haemoglobin and Vitamin  $\text{B}_{12}$  in biological systems. 6
- B) From the following data calculate the binding energy of a helium  ${}^4_2\text{He}$  nucleus. 7  
(1 amu = 931 MeV. Mass of proton = 1.00728 amu, mass of neutron = 1.00867 amu, actual mass of  ${}^4_2\text{He}$  = 4.0015 amu).
22. A) Give IUPAC nomenclature for the following 8
- (i)  $[\text{Cd}(\text{SCN})_4]^{2-}$
- (ii)  $\text{Li}[\text{AlH}_4]$
- (iii)  $\text{K}_2[\text{OsCl}_3\text{N}]$
- (iv)  $[\text{Cr}(\text{C}_6\text{H}_6)_2]$
- B) What are phosphazenes? Explain three main structural types of these compounds. 5
23. A) Write down the expression for two principal sets of equilibrium constants ( $K_i$ 's and  $\beta_i$ 's) for expressing the formation of a series of complexes  $\text{ML}$ ,  $\text{ML}_2$ ,  $\text{ML}_3$  etc. How are they related? 7
- B) Why alkali metals are soft, low melting and of low density? 6
24. A) Explain the use of diborane in hydroboration. 8
- B) Give the preparation, structure and uses of sodium borohydride. 5
25. A) Give the structure of ozone and mention its main uses. There is a layer of ozone in the upper atmosphere. Why it is this important to man? 9
- B) Explain the changes which occur on heating sulphur. 4
26. Complete the following. Name the reaction involved. 13





27. A) Match the given Hammett sigma value with appropriate group 4

Groups :  $p\text{-N}_2^+$ ,  $m\text{-O}^-$ ,  $p\text{-NO}_2$ ,  $p\text{-NMe}_2$

$\sigma$  values : 0.78, -0.70, -0.83, 1.91

B) Match the  $\rho$  (rho) value with appropriate reaction given reasons. 5

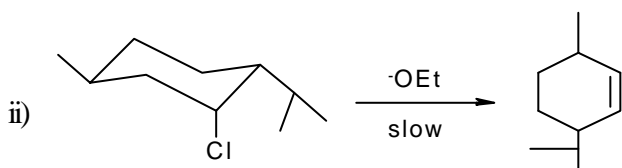
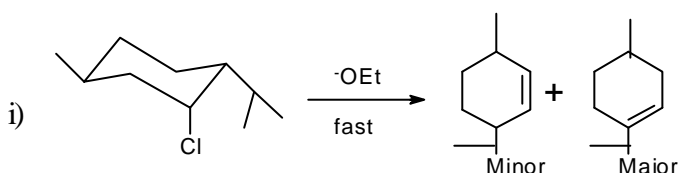
i) Basic hydrolysis of ethyl benzoates

ii) Ionization of anilinium ions.

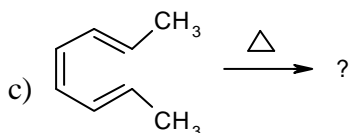
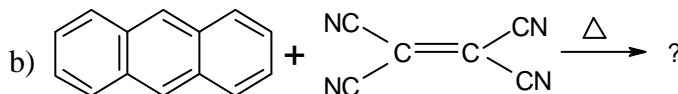
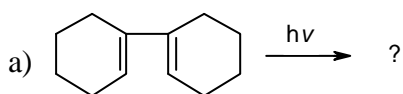
iii) Reaction of methyl iodide with N, N-dimethylaniline

iv) Reaction of methyl iodide with N, N-dimethyl benzylamine.

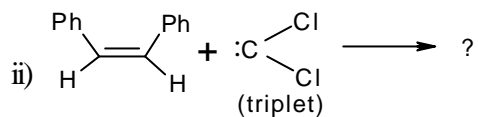
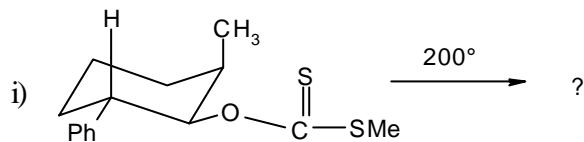
C) Account for the difference in the behaviour of a and b towards base catalysed elimination of HCl. 4



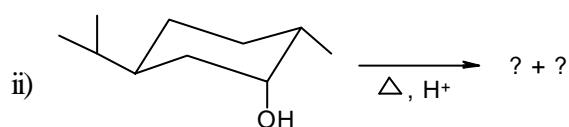
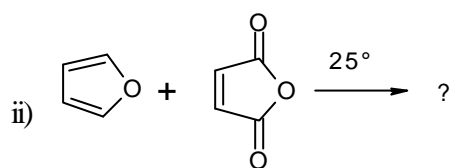
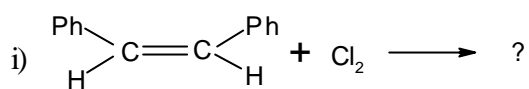
28. Predict the product and its stereochemistry (if any) for the following reactions. Indicate for each reaction (i) type of pericyclic reaction (ii) necessary selection rule. 13



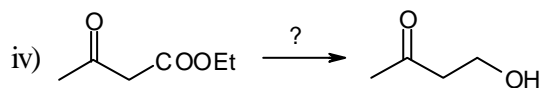
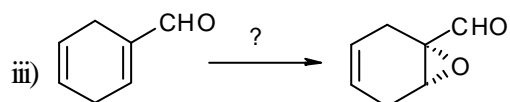
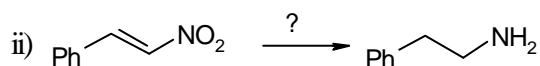
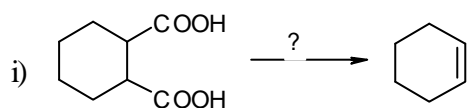
29. A) Predict the product and its stereochemistry in the following reactions. Justify your answer. 7



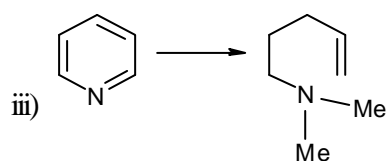
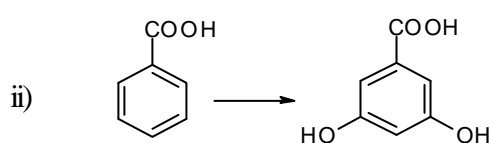
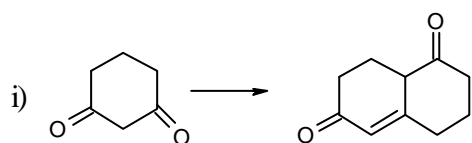
B) Predict the product and its stereochemistry in the following reactions. Justify your answer. 6



30. Indicate reagents for following conversions and justify your choice. 13

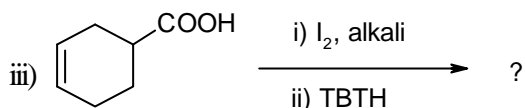
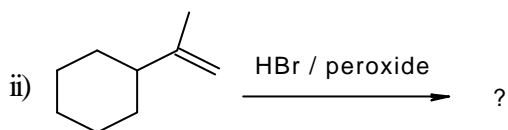
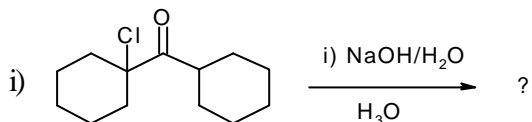


31. A) Indicate the reagents for the following conversions, which may involve more than one step. 7



B) Predict the products for the following reactions :

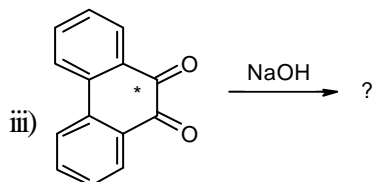
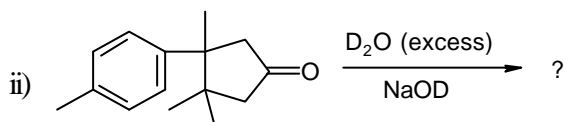
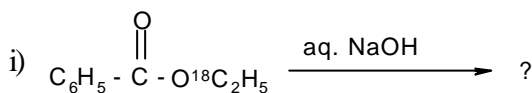
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TBTH = tributyltin hydride

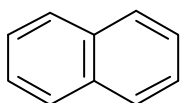
32. A) Trace the position of label in the product. Explain your answer.

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B) Classify the following hydrocarbons into alternant and non-alternant systems.

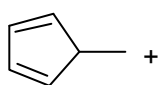
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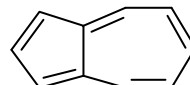
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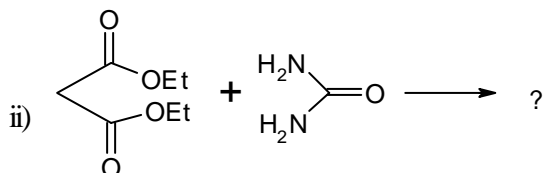
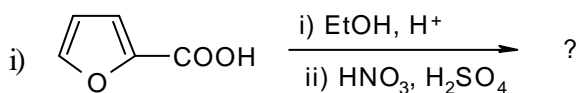
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33. A) Predict the products in the following :

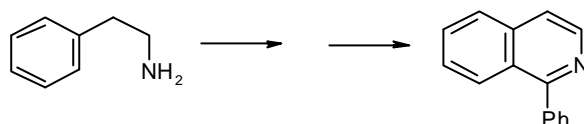
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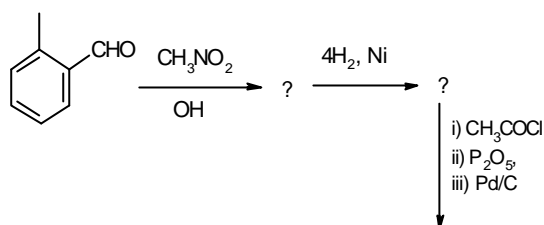
B) How will you carry out the following conversion ?

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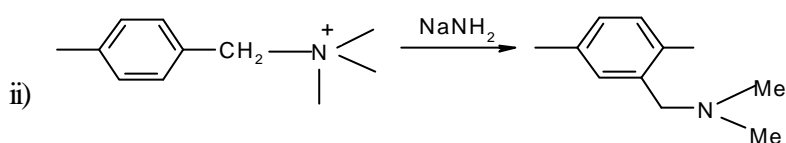
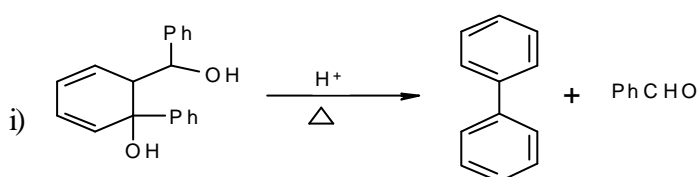
C) Complete the following sequence

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34. A) Propose mechanism for the following :

7



B) Match the following

6

- |   |                             |
|---|-----------------------------|
| i) nicotinamide adenine dinucleotide (NADH) | a) chromosome of cells      |
| ii) Edman method of peptide synthesis       | b) 2,4-Dinitrofluorobenzene |
| iii) DNA                                    | c) Phenyl isothiocyanate    |
| iv) Sanger method of peptide synthesis      | d) reduction                |

i)                      ii)                      iii)                      iv)

35. Predict the major product of the following photochemical reactions. Explain the process involved.

13

