PARLIAMENT OF INDIA
(Joint Recruitment Cell)

MAIN EXAMINATION FOR POSTS of EXECUTIVE/LEGISLATIVE/COMMITTEE/PROTOCOL
OFFICER AND RESEARCH/REFERENCE OFFICER in LOK SABHA SECRETARIAT

4th SEPTEMBER, 2010

CHEMISTRY – PAPER – I

INSTRUCTIONS: Answers must be written in English only. Candidates should attempt at least 2 questions from each section and total of 5 questions. Assume suitable data if considered necessary and indicate the same clearly. The number of marks carried by each question is indicated against the same.

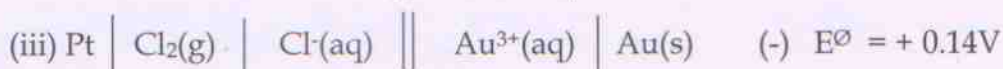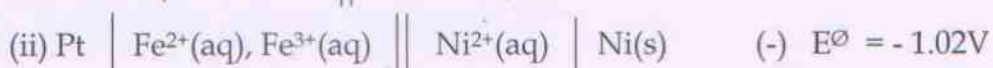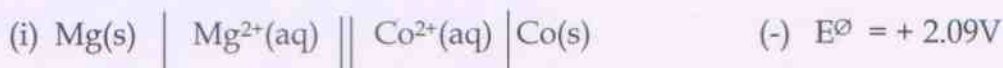Time: 3 hours   Marks: 300

Section 'A'

			Marks
Q. 1.	(a)	Explaining the meaning of the term "coordination number", state its relationship with radius ratio.	10
	(b)	Enumerating their main features and differences, explain different types of structures of 1:1 ionic compounds.	15
	(c)	Find out the coordination numbers of X^{n+} and Y^{n-} ions if the compound XY is isomorphus with (i) KCl, (ii) CsF and (iii) NiS.	15
	(d)	Draw the structures of cis and trans isomers of:	10

(i)   The octahedral complex, $[Cr(H_2O)_4(NO_2)_2]^+$.
(ii)   The square planar structure $[Pt(Py)_2Cl_2]$, where Py represents the monodentate ligand pyridine.

			Marks
	(e)	Do the rates of majority of chemical reactions increase with rise in temperature? Explain your statement.	10
Q. 2.	(a)	Consider the reaction and data given below.	15

$C_6H_6 (1) + 15/2\ O_2(g) \rightarrow 6CO_2 (g) + 3H_2O(1)\ \Delta H^0 = -3303\ kJ$
$\Delta H^0{}_f (CO_2\ g) = -393.5\ kJ$ and $\Delta H^0{}_f (H_2O.1) = -285.8\ kJ$

Find out the enthalpy of formation of benzene.

			Marks
	(b)	What is the basic principle of polarography? State Ilkovic equation with the help of all the terms and show that diffusion current is directly proportional to concentration.	10

(c) Giving explanations, state the differences between the terms in each of the three cases given below:
   (i)   isolated and closed systems
   (ii)   internal energy and enthalpy
   (iii) isothermal and adiabatic changes

(d) Consider the following cells and correct the cell notations in cases where it has been wrongly written.   **12**

(i) $Mg(s) \mid Mg^{2+}(aq) \parallel Co^{2+}(aq) \mid Co(s)$ (-) $E^{\varnothing} = +2.09V$

(ii) $Pt \mid Fe^{2+}(aq), Fe^{3+}(aq) \parallel Ni^{2+}(aq) \mid Ni(s)$ (-) $E^{\varnothing} = -1.02V$

(iii) $Pt \mid Cl_2(g) \mid Cl^-(aq) \parallel Au^{3+}(aq) \mid Au(s)$ (-) $E^{\varnothing} = +0.14V$

(iv) $Pb(s) \mid Pb^{2+}(aq) \parallel Zn^{2+}(aq) \mid Zn(s)$ (-) $E^{\varnothing} = -0.63V$

In each cell above, write down the half-reactions and overall reactions.

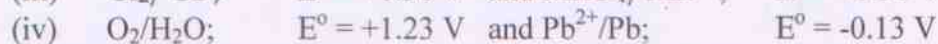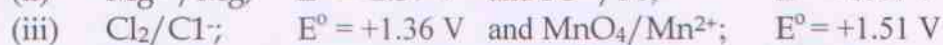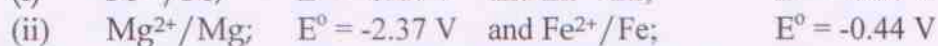(e) R, the gas constant has the dimensions of energy per mole per Kelvin. How can you show this?   **8**
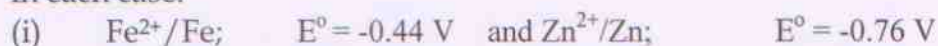
Q. 3.   (a) On the basis of MO theory, explain the formation of σ- and л- bonds.   **10**

      (b) The paramagnetic character of oxygen can be explained on the basis of MO theory, elaborate this statement.   **10**

      (c) Predict the bond order and nature of different bonds in the N_2 molecule on the basis of MO theory.   **10**

      (d) Consider the following cells and write down the overall cell reaction in each case.   **15**
      (i) Fe^{2+}/Fe; $E^{\circ} = -0.44$ V   and Zn^{2+}/Zn; $E^{\circ} = -0.76$ V
      (ii) Mg^{2+}/Mg; $E^{\circ} = -2.37$ V   and Fe^{2+}/Fe; $E^{\circ} = -0.44$ V
      (iii) Cl_2/Cl^-; $E^{\circ} = +1.36$ V and MnO_4/Mn^{2+}; $E^{\circ} = +1.51$ V
      (iv) O_2/H_2O; $E^{\circ} = +1.23$ V and Pb^{2+}/Pb; $E^{\circ} = -0.13$ V
      Find out their standard emf which can be set up using the two couples given in each case.

      (e) What are intermolecular and intramolecular forces? Explain the nature of intermolecular forces acting between molecules of gases, taking the example of water vapours.   **15**

Q.4. (a) What is an ideal gas? Write the equation of state for an ideal gas. The samples of gases G_1 and G_2 are at the same temperature and the molecules of gas G_1 can travel three times the speed of the molecules of the gas G_2. Calculate the ratio of masses of G_1 and G_2.

(b) Describe the main difficulties in the study of "fast reactions". Name a few techniques used to study them.　　　　　12

(c) State the relationship between equilibrium constant and free energy change.　　　　　10

(d) State the characteristic features of metal-carbon bonding in metal carbonyls. Draw the structures of:
$Cr(CO)_6$, $Fe(CO)_5$ and $Ni(CO)_4$　　　　　12

(e) Explain the terms "liquefaction of gases", critical temperature, critical volume and critical pressure.　　　　　12

Q.5. (a) Explain the construction and functioning of a Voltaic Cell with a suitable example and draw its sketch.　　　　　8

(b) Calculate the enthalpy of reaction for the oxidation of ammonia in the gaseous state from the reaction given below:　　　　　15
$$4NH_3 \ (g) + 5O_2 \ (g) \longrightarrow 4NO \ (g) + 6H_2O \ (g)$$

Standard enthalpies of formation (ΔH_f^o) at 298 K for NH_3 (g), H_2O (g) and NO (g) are: –47.65, -241.6 and + 90.3 kJ mole^{-1}, respectively.

(c) Solutions of copper sulphate and silver nitrate in separate electrolytic cells were connected in series and 0.106g copper was deposited from the former when an electric current was passed through the solutions. Find out the amount of silver deposited in the latter? (Atomic masses of Cu=63.55, Ag=107.9).　　　　　10

(d) What will be the amount of copper deposited if a current of 2 ampere is passed through a solution of copper sulphate for 965 seconds. (At. Mass of Cu = 63.6 and 1 Faraday = 96,500 Coulombs).　　　　　15

(e) Describe different methods applied for determining the order of a chemical reaction.　　　　　12

Section 'B'

Q.6. (a) Describe outer and inner orbital complexes?   10

(b) The different samples of the compound $CoCl_3.4NH_3$ exhibits two colours: violet and green. Using structural diagrams, explain how this could be possible?   8

(c) Distinguish between physical and chemical adsorption.   8

(d) What is the shape of d-orbitals and how do these split up in the presence of octahedral and tetrahedral fields? Calculate the magnetic moments of $[Ni(NH_3)_6]SO_4$ and $FeSO_4.6H_2O$.   16

(e) From the following data, determine the order of the reaction below with respect to each reactant and write down the rate equation for it.   18

$$X + Y + Z \longrightarrow \text{Products}$$
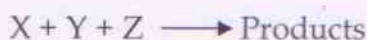
S. No.	Initial concentrations			Initial rate
	[X]	[Y]	[Z]	$(/\,mol\ dm^{-3}\ s^{-1})$
1.	0.06	0.28	0.12	1.5×10^{-6}
2.	0.06	0.56	0.12	3.0×10^{-6}
3.	0.12	0.56	0.12	1.2×10^{-5}
4.	0.06	0.28	0.24	3.0×10^{-6}

Q.7. (a) Write notes on: 10
     (i) magnetic behaviour of the first row transition metal ions
     (ii) lanthanide contraction

(b) Give the most common oxidation state for the lanthanides. The cerium (IV) and terbium (V) oxidation states are extra stable, explain.   10

(c) With the help of valence bond theory, discuss the paramagnetic nature of $[NiCl_4]^{2-}$ complex ion (due to two unpaired electrons) and diamagnetic nature of $[Ni(CN)_4]^{2-}$ complex ion.   16

(d) Conductivity of any electrolyte decreases on dilution of its solution, whereas its equivalent conductivity increases. Explain.   12

(e) Calculate the number of atoms in: 12
     (i) 1 mole of ozone molecule (O_3)
     (ii) 1 mole of phosphorus molecule (P_4)

Q.8.　(a)　The reaction between mercuric chloride and potassium oxalate can be represented as:

$$2HgCl_2(aq) + K_2C_2O_4 \longrightarrow Hg_2Cl_2(s) \downarrow + 2KCl + 2CO_2$$

The reaction was started with different initial concentrations of the reactants and amount of Hg_2Cl_2 precipitated in short intervals of time was measured. The results of the experiments are:

S.No.	Initial Concentrations (mol dm^{-3})		Time (/s)	Amount of Hg_2Cl_2 Precipitated (/mol)
	$HgCl_2$	$K_2C_2O_4$		
1.	0.16	0.8	135	0.0136
2.	0.08	0.8	132	0.0064
3.	0.16	0.4	250	0.0062

Find out the rate law for the reaction and the order of the reaction.

(b)　Calculate the activation energy of a reaction, if its rate constant is 3.46 10-s^{-1} at 25 °C and 1.35 10^{-4}s^{-1} at 35 °C.　　12

(c)　State and explain the physical significance of entropy, how is it useful in understanding the third law of thermodynamics?　　10

(d)　With respect of terms: solvolysis, redox and complexometric reactions, compare the solvent nature of liquid ammonia and water.　　8

(e)　What will be the activation energy of a reaction whose rate becomes three times when the temperature is increased from 27 °C to 37 °C.　　10

Q.9.　(a)　Giving suitable examples, explain Aufbau principle, Hund's rule of maximum multiplicity and Pauli's exclusion principle. How are these useful in writing electronic configurations of atoms?　　10

(b)　Are liquid crystals different from solid crystals? Compare their characteristic features.　　15

(c)　What do you understand by the term "imperfection in crystals"? Explain various types of defects and resulting changes in properties.　　12

(d)　Explain ionization, coordination, linkage and optical isomerism in coordination compounds with a suitable example for each.　　12

(e)　Write the general outer shell electronic configuration for atoms of f-block transition elements. Which electrons are primarily involved in　　11

chemical bonding?

Q. 10. (a) Explain the terms "adsorption isotherm" and "Freundlich's isotherm". Is "Freundlich's isotherm" applicable to adsorption from solutions as well?

(b) What are the differences between physical and chemical adsorption? 8

(c) What are solid catalysts? Explain their functions. 8

(d) How do the homogeneous and heterogeneous catalysts function? 8

(e) Give two examples of important industrial processes in which homogeneous catalysts are used and three processes in which heterogeneous catalysts are used. 20

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4ᵗʰ SEPTEMBER, 2010

CHEMISTRY – PAPER- II

INSTRUCTIONS : Answers must be written in English only. Candidates should attempt at least 2
questions from each section and a total of 5 questions. The number of marks carried by each question
is indicated against the same.

Time : 3 hours   Marks : 300

SECTION – A

1. (a) Give a brief structural description of secondary structure of protein   (20 marks)

(b) Explain McLafferty rearrangement taking the following compound as an example.
(10 marks)
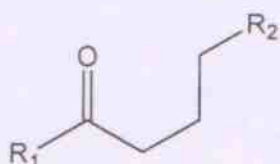
(c) Draw the structure of A. B. C and D   (20 marks)

Diethylmalonate + A —(Sodium ethoxide)→ B —(SN₂)→ C —(NaOH. H₂O and then HCl. H₂O)→

D —(Heat)→ MeO～～COOH
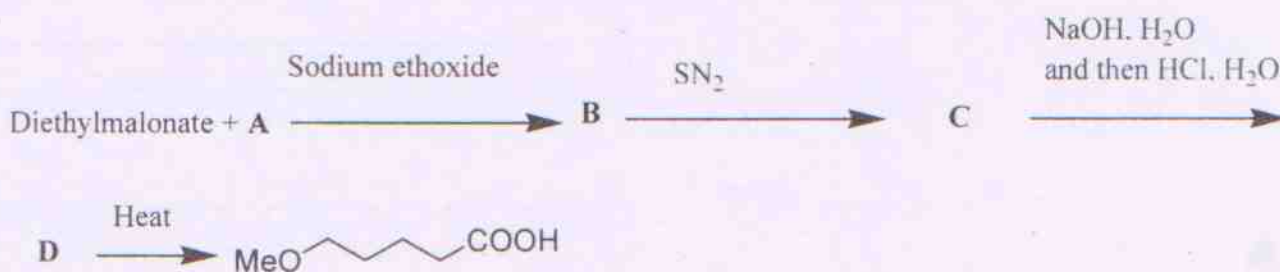
(d) Draw the energy diagrams for an SN₁ and SN₂ reactions.   (10 marks)

2. (a) Write the mechanism of the following conversion.   (20 marks)
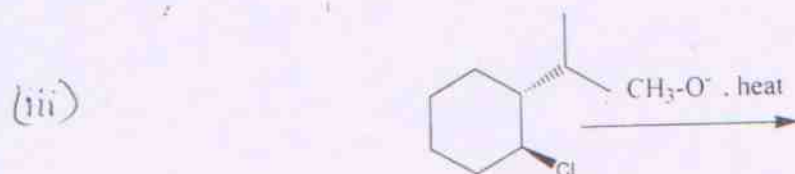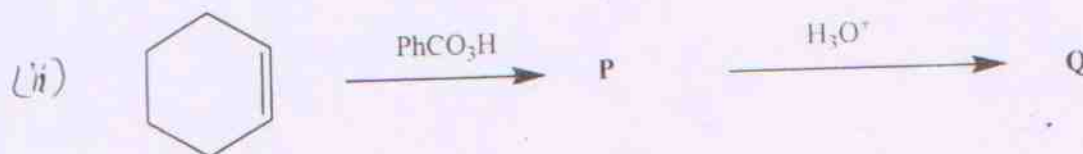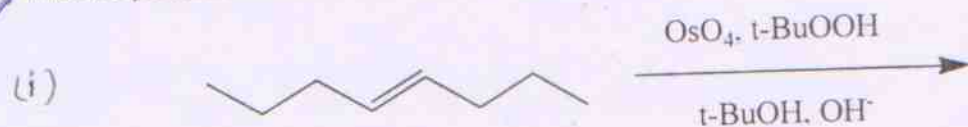

—(NaOH)→
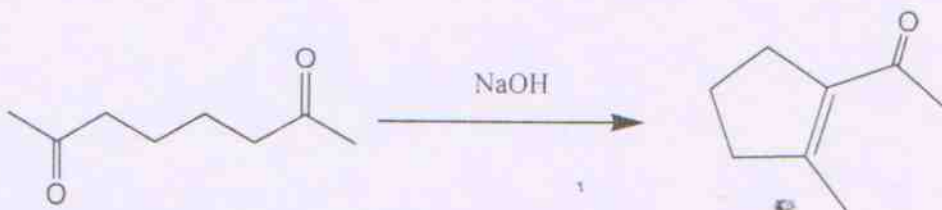
(b) Addition of HBr to 1.3-butadiene at 0°C and at 40°C gave different ratios of the same products. Draw
the structure of products and explain the reason for this behavior.   (20 marks)

$$Cl\diagup\diagup\diagup_{S}\diagdown\diagup\diagdown Cl \quad + \quad 2H_2O \longrightarrow HO\diagup\diagdown\diagup_{S}\diagdown\diagup\diagdown OH$$
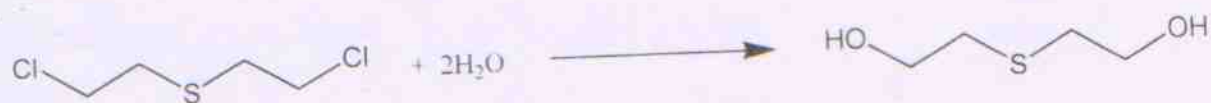
3 (a) Write the products formed in the following reactions: (5 x 6 = 30 Marks)

(i)

$$\diagdown\diagup\diagdown\diagup\diagdown\diagup \quad \xrightarrow[\text{t-BuOH, OH}^-]{\text{OsO}_4, \text{t-BuOOH}}$$

(ii)

$\xrightarrow{\text{PhCO}_3\text{H}}$ P $\xrightarrow{\text{H}_3\text{O}^+}$ Q

(iii)

$\xrightarrow{\text{CH}_3\text{-O}^-, \text{ heat}}$

(iv)

$$\diagdown\diagup\diagdown\diagup\diagdown\diagup \quad \xrightarrow{\begin{array}{l}1.\ \text{Hg(OAc)}_2, \text{H}_2\text{O} \\ 2.\ \text{NaBH}_4\end{array}}$$

(v)

$\xrightarrow{\begin{array}{l}1.\ \text{OsO}_4, \text{ether} \\ 2.\ \text{NaIO}_4, \text{H}_2\text{O}\end{array}}$

(b) One of the following compounds undergoes acetolysis in a faster rate than the other. Which is faster and why?. Explain the stereochemistry of the products you expect   (30 marks)

M

N
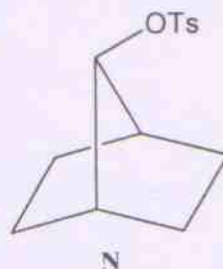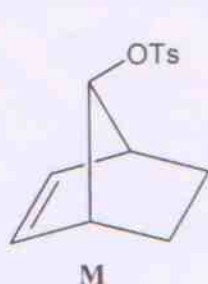
4 (a) Explain the observed yield in the following reaction.   (20 marks)
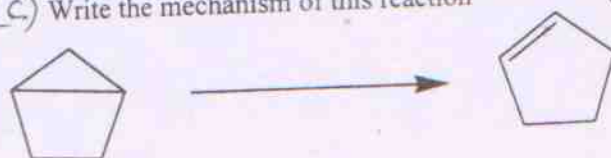

90%   10%
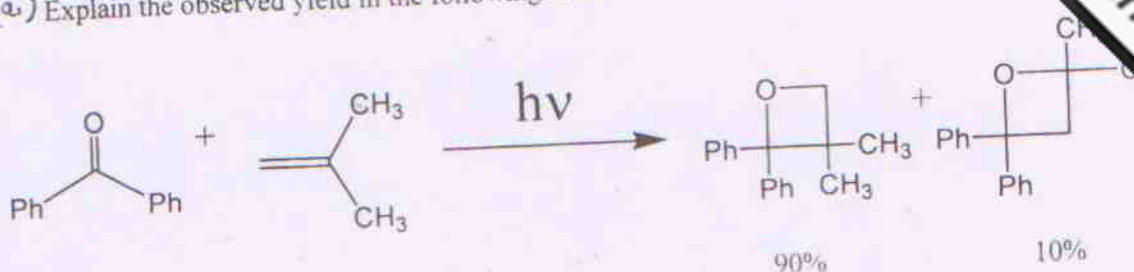
(b) Predict the product in the following thermal reaction   (20 Marks)
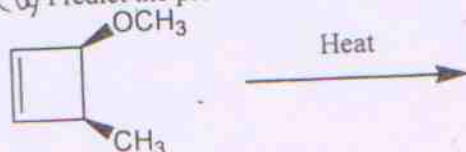
(c) Write the mechanism of this reaction   (20 marks)

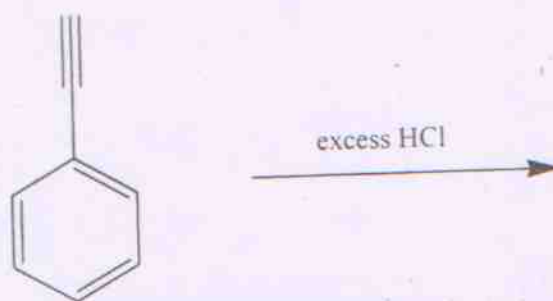5. (a) Which one of the following show higher frequency of vibration in the IR spectrum and explain why? (20 marks)

(i) $C=O$ versus $C=S$; (ii) $C\equiv C$ versus $C=C$
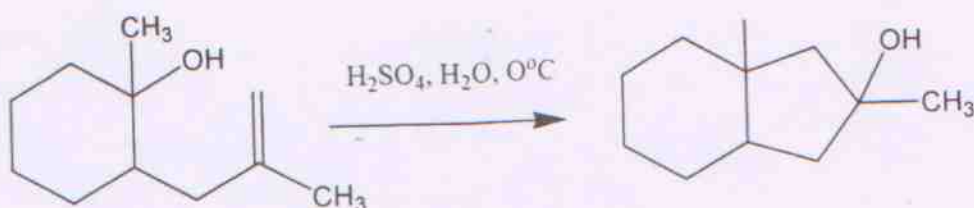
(b) Explain the following (i) spin-spin splitting (ii) Coupling Constant   (20 marks)

(c) What is the major product in the following reaction? Explain   (20 marks)
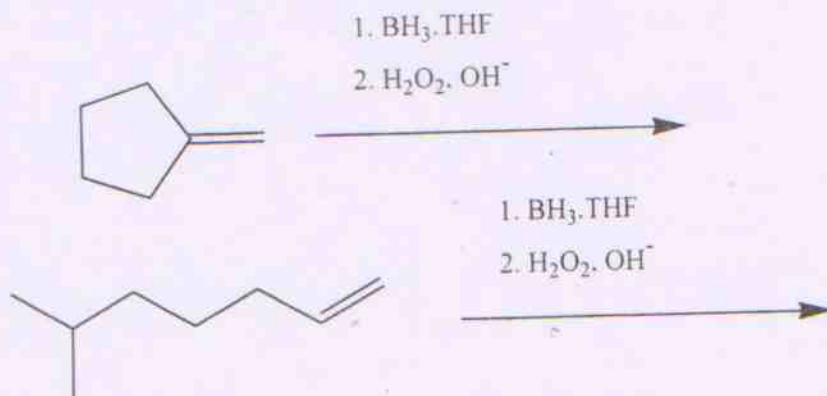

excess HCl

SECTION –B

6 (a) Propose a mechanism of the following conversion. First step in the reaction is the protonation of tertiary alcohol   (30 marks)

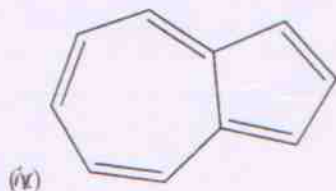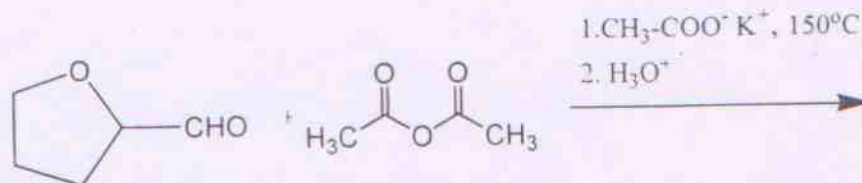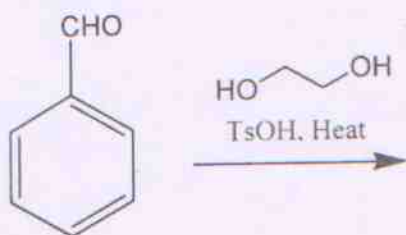(b) Draw the structure of major product expected from each of the reactions: (20 marks)

1. BH_3.THF
2. H_2O_2, OH^-

1. BH_3.THF
2. H_2O_2, OH^-

(c) Which of the following are aromatic ?. Explain.   (10 marks)
(i) Cyclobutadienyl dianion (ii) Cyclooctatetrenyl dianion (iii) Cycloheptatrienyl anion

(iv)

7. (a). Write the mechanism of the following reaction. Show all the steps involved.   (30 marks)

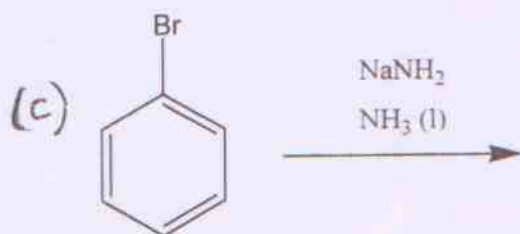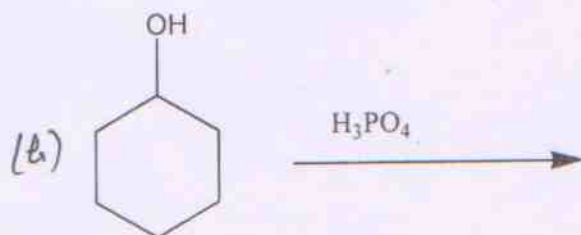HO OH
TsOH. Heat

1. CH_3-COO^- K^+, 150°C
2. H_3O^+

(b) Write the product formed in the reactions.   (20 marks)

$$\ce{CH2=CH-COOEt ->[HCN] P ->[H3O^-, Heat] Q}$$
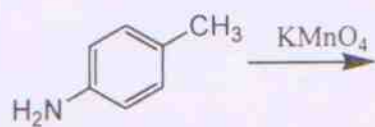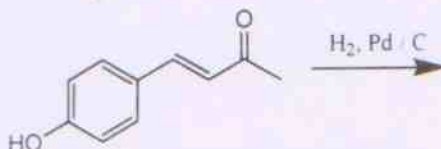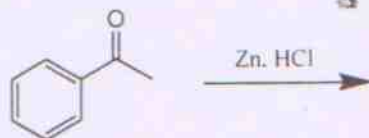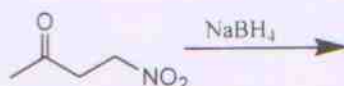
$$\ce{CH2=CH-CH3 ->[HCN] R ->[H2, Ni] S}$$

(c) Explain the following (a) Number average molecular weight Mn (b) Polydispersity index (10 marks)
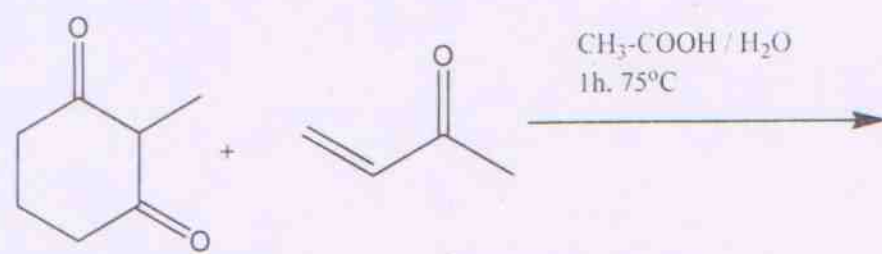
8.   Write the product formed and the mechanism of each of the following reactions (3 x 20 marks)

(a) $\ce{CH3CH2-OH ->[H2SO4, 140°C]}$

(b)   cyclohexanol $\ce{->[H3PO4]}$

(c)   bromobenzene $\ce{->[NaNH2][NH3 (l)]}$

9. (a) Write the product formed in the reactions (20 marks)

O=...—NO$_2$ $\xrightarrow{\text{NaBH}_4}$

(acetophenone) $\xrightarrow{\text{Zn. HCl}}$

(4-hydroxyphenyl but-3-en-2-one) $\xrightarrow{\text{H}_2,\ \text{Pd / C}}$

(4-amino toluene, CH$_3$ / H$_2$N) $\xrightarrow{\text{KMnO}_4}$

(b) Write product and mechanism of the following reaction. (20 marks)

(2-methyl-1,3-cyclohexanedione) + (but-3-en-2-one) $\xrightarrow[\text{1h. 75}^{\circ}\text{C}]{\text{CH}_3\text{-COOH / H}_2\text{O}}$

(c) Explain (a) Primary kinetic isotope effect (b) Secondary kinetic isotope effect   (20 marks)

10 (a) For each of the following compounds, show how they can be converted to benzoic acid.   (20 Marks)
     (i) Toluene (ii) Benzonitrile (iii) N-methylbenzamide (iv) Bromobenzene

(b) Between polypropylene and PVC, which has a higher melting temperature T_m ? Why?   (10 marks)

(c) Write the mechanism of the acid catalyzed hydrolysis of methyl acetate.   (10 marks)

(d) Draw the structures of the products formed from the following compounds upon treatment with alcoholic KOH.   (20 marks)

     (i) 1-Bromocyclohexane
     (ii) (S)-2-chlorobutane
     (iii) 1-Bromo-1-methylcyclohexane
     (iv) 4-Bromoheptane

In each case, indicate the major and minor products.