

PARLIAMENT OF INDIA  
(Joint Recruitment Cell)

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

4<sup>th</sup> JUNE, 2009

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) What do you understand by the term "liquefaction of gases"? Explain critical temperature and critical pressure.	15
	(b) What do you understand by "imperfection in crystals"? Explain various types of defects and resulting changes in properties.	12
	(c) What distinguishes the transition elements, and the lanthanides & actinides?	12
	(d) What is meant by "coordination number"? State its relationship with radius ratio.	10
	(e) In fluorite, each unit cell contains four Ca <sup>2+</sup> ions and eight F <sup>-</sup> ions. The edge of a CaF <sub>2</sub> cubic cell has a length of 5.4 x 10 <sup>-8</sup> cm. What is the density of CaF <sub>2</sub> in g cm <sup>-3</sup> ?	11
Q. 2.	(a) Calculate the de Broglie wave length of an electron in a hydrogen atom. It has a mass of 9.1 x 10 <sup>-31</sup> kg and moves with a velocity of 2.188 x 10 <sup>6</sup> m s <sup>-1</sup> .	15
	(b) Explain the basic principle of polarography. Write Ilkovic equation explaining all the terms and show that diffusion current is directly proportional to concentration.	10

- (c) Differentiate between 15
  - (i) isothermal and adiabatic changes
  - (ii) internal energy and enthalpy
  - (iii) isolated and closed systems

(d) The electronic spectra of coordination compounds cannot be explained by valence bond theory and it is essential to consider splitting in d-orbitals. Justify. 10

(e) Briefly explain the nature of intermolecular forces acting between molecules of gases. 10

Q. 3. (a) What will be the coordination numbers of  $A^{n+}$  and  $B^{n-}$  ions if the compound AB is isomorphous with (a) NaCl, (b) CsCl and (c) ZnS. 15

(b) What are the main difficulties in the study of "fast reactions"? Which techniques are used to study them? 12

(c) What is the relation between free energy change and equilibrium constant? 8

(d) Consider the reaction below in the gaseous state. 15



Calculate the enthalpy of reaction for the oxidation of ammonia. Standard enthalpies of formation ( $\Delta H_f^\circ$ ) at 298 K for  $NH_3(g)$ ,  $H_2O(g)$  and  $NO(g)$  are:  $-47.65$ ,  $-241.6$  and  $+90.3$   $\text{kJ mole}^{-1}$ , respectively.

- (e) Draw the structures of *cis* and *trans* isomers of 10
  - (i)  $[Pt(Py)_2Cl_2]$ , a square planar structure where Py represents the monodentate ligand pyridine.
  - (ii)  $[Cr(H_2O)_4(NO_2)_2]^+$ , an octahedral complex.

Q. 4. (a) Explain ionization, coordination, linkage and optical isomerism in coordination compounds with a suitable example for each. 10

(b) How are metal carbonyls synthesized? What are the characteristic features of metal-carbon bonding in carbonyls? Draw the structures of  $Ni(CO)_4$ ,  $Fe(CO)_5$  and  $Cr(CO)_6$ . 15

(c) Briefly explain the different methods used for determining the order of a reaction. 12

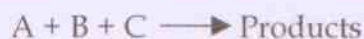
- (d) A current of 2 ampere was passed through a solution of copper sulphate for 16 minutes and 5 seconds. Calculate the amount of copper deposited. (At. Mass of Cu = 63.6 and 1 Faraday = 96,500 Coulombs). 14
- (e) What is a Voltaic Cell? Explain its construction and functioning with a suitable example and draw its sketch. 9
- Q. 5. (a) What are different types of structures of 1:1 ionic compounds? Give their main features and differences. 10
- (b) Explain the formation of  $\sigma$ - and  $\pi$ - bonds on the basis of MO theory. 12
- (c) Calculate the standard emf of the cells (i), (ii), (iii) and (iv) below which can be set up using the two couples given in each case. Depict the cell and write down the overall cell reaction in each case. 16
- (i)  $\text{Fe}^{2+}/\text{Fe}$ ;  $E^\circ = -0.44 \text{ V}$  and  $\text{Zn}^{2+}/\text{Zn}$ ;  $E^\circ = -0.76 \text{ V}$
- (ii)  $\text{Mg}^{2+}/\text{Mg}$ ;  $E^\circ = -2.37 \text{ V}$  and  $\text{Fe}^{2+}/\text{Fe}$ ;  $E^\circ = -0.44 \text{ V}$
- (iii)  $\text{Cl}_2/\text{Cl}^-$ ;  $E^\circ = +1.36 \text{ V}$  and  $\text{MnO}_4^-/\text{Mn}^{2+}$ ;  $E^\circ = +1.51 \text{ V}$
- (iv)  $\text{O}_2/\text{H}_2\text{O}$ ;  $E^\circ = +1.23 \text{ V}$  and  $\text{Pb}^{2+}/\text{Pb}$ ;  $E^\circ = -0.13 \text{ V}$
- (d) Discuss (i) Schottky and (ii) Frenkel defects. 12
- (e) Explain why rates of most reactions increase with rise in temperature? 10

### Section 'B'

- Q. 6. (a) Draw the shape of d-orbitals. How do these split up in the presence of octahedral and tetrahedral fields? Calculate the magnetic moments of  $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$  and  $[\text{Ni}(\text{NH}_3)_6]\text{SO}_4$  and predict their geometries. 12
- (b) Compare the solvent behaviour of liquid ammonia with that of water especially with regard to solvolysis, redox and complexometric reactions. 8
- (c) What is the physical significance of entropy? State and explain the third law of thermodynamics on this basis. 10



- (d) From the following data, determine the order of the reaction below with respect to each reactant and write down the rate equation for it. 20



S. No.	Initial concentrations			Initial rate ( $\text{mol dm}^{-3} \text{s}^{-1}$ )
	[A]	[B]	[C]	
1.	0.06	0.28	0.12	$1.5 \times 10^{-6}$
2.	0.06	0.56	0.12	$3.0 \times 10^{-6}$
3.	0.12	0.56	0.12	$1.2 \times 10^{-5}$
4.	0.06	0.28	0.24	$3.0 \times 10^{-6}$

- (e) Calculate the activation energy of a reaction whose rate becomes three times when the temperature is increased from 27 °C to 37 °C. 10
- Q. 7.
- (a) Predict the bond order and nature of different bonds in  $\text{N}_2$  molecule on the basis of MO theory. 10
  - (b) What are outer and inner orbital complexes? 8
  - (c) Distinguish between physical and chemical adsorption. 8
  - (d) Using valence bond theory, discuss the paramagnetic nature of  $[\text{NiCl}_4]^{2-}$  complex ion (due to two unpaired electrons) and diamagnetic nature of  $[\text{Ni}(\text{CN})_4]^{2-}$  complex ion. 16
  - (e) Calculate the uncertainty in the position for the following objects if the uncertainty in their velocities is  $1 \times 10^{-4} \text{ m s}^{-1}$  in each case: 18
    - (i) A cricket ball with mass of 200 g.
    - (ii) A moped with a mass of 50 kg.
    - (iii) An electron with a mass of  $9.1 \times 10^{-31} \text{ kg}$ .
- Q. 8.
- (a) Write notes on: 12
    - (i) magnetic behaviour of the first row transition metal ions
    - (ii) lanthanide contraction
  - (b) What is the most common oxidation state for the lanthanides? Why are cerium (IV) and terbium (V) oxidation states extra stable? 12
  - (c) What is an adsorption isotherm? Briefly discuss Freundlich's isotherm. Is it applicable to adsorption from solutions as well? 16

- (d) What are the differences in the characteristics of homogeneous and heterogeneous catalysts? 10
- (e) Show that  $R$ , the gas constant has dimensions of energy per mole per Kelvin. 10
- Q. 9. (a) Write the general outer shell electronic configuration for atoms of  $f$ -block transition elements. Which electrons are primarily involved in chemical bonding? 10
- (b) Name the following complexes: 16
- |                                      |                                  |
|--------------------------------------|----------------------------------|
| (i) $K_2[Fe(C_2O_4)_2] \cdot 2H_2O$  | (ii) $K_3[Mn(CN)_6]$             |
| (iii) $[Ni(NH_3)_4(H_2O)_2](NO_3)_2$ | (iv) $[Pd(NH_3)_4(OH)_2]$        |
| (v) $Na[AgI_2]$                      | (vi) $K[Cr(NH_3)_2(H_2O)_2Cl_2]$ |
| (vii) $[Co(H_2O)_6]^{3+}$            | (viii) $Na[Al(H_2O)_2(OH)_4]$    |
- (c) Giving suitable examples, explain Aufbau principle, Hund's rule of maximum multiplicity and Pauli's exclusion principle. What are their significance in writing electronic configurations of atoms? 14
- (d) A student prepared one sample of  $CoCl_3 \cdot 4NH_3$  which was violet coloured and another sample of  $CoCl_3 \cdot 4NH_3$  which was green. Explain, using structural diagrams, how this could be possible? 12
- (e) How liquid crystals are different from solid crystals? Compare their characteristic features. 8
- Q. 10. (a) How do the solid catalysts function? 10
- (b) Give five examples of important industrial processes in which heterogeneous catalysts are used. 15
- (c) How does MO theory explain the paramagnetic character of oxygen? 12
- (d) Conductivity of any electrolyte decreases on dilution of its solution, whereas its equivalent conductivity increases. Explain. 11
- (e) Calculate the number of atoms in: 12
- |  |
|--|
| (i) 1 mole of nitrogen molecule ( $N_2$ )    |
| (ii) 1 mole of phosphorus molecule ( $P_4$ ) |

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CHEMISTRY - Paper - II

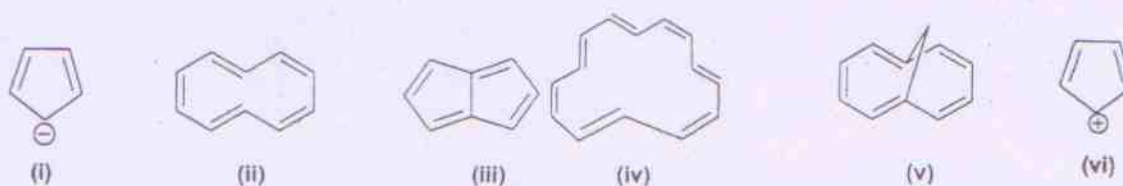
INSTRUCTIONS: Answers must be written in English only. Candidates should attempt at least 2 questions from each section and total of 5 questions. The number of marks carried by each question is indicated against the same.

Time: 3 hours

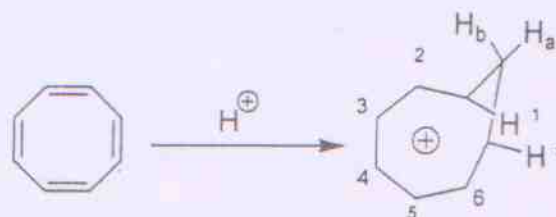
Marks: 300

Section - A

Q1 (a) Categorize the species (i) - (vi) based on aromatic, anti - aromatic, and non - aromatic. How will you use NMR chemical shift to differentiate annulenes belonging to the aforementioned structures. [5 × 6 = 30]



(b) What do you mean by homo - aromatic compounds? How will you justify that the product in the following reaction is homo - aromatic compound based on NMR study. [20]



(c) Draw the energy profile diagram for a two - step reaction of type  $A \rightarrow [B] \rightarrow C$ , with the first step as the rate - determining step. Indicate the substrate, product, transition state, intermediate, and activation energy with suitable examples. [10]

Q2 (a) Account for the formation of a single intermediate undergoing further reaction to give identical product, when  $\text{PhCH}_2\text{COCH}_2\text{Cl}$  or  $\text{PhCHClCOCH}_3$  reacts with  $\text{NaOCH}_3/\text{CH}_3\text{OH}$ . [20]

(b) Which of the following carbo-cation has the longest half - life and why. [5 × 4 = 20]



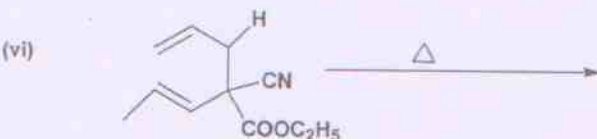
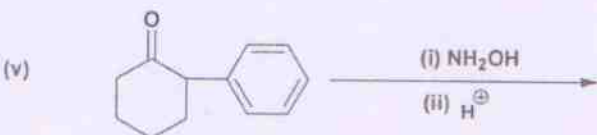
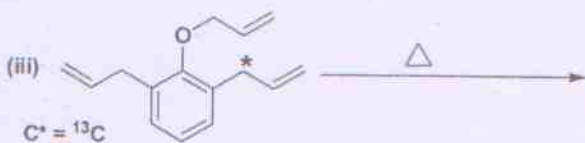
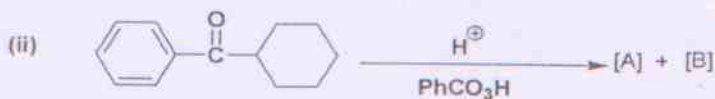
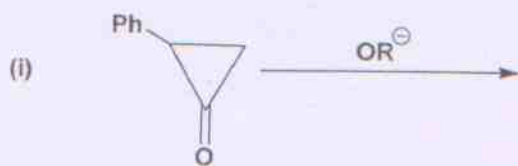
(c) Offer suitable mechanism for the reaction indicating stereo - chemical aspects, if any. [20]



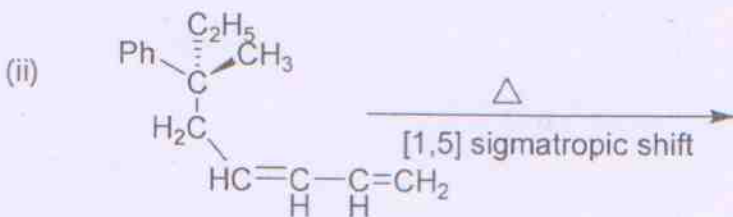
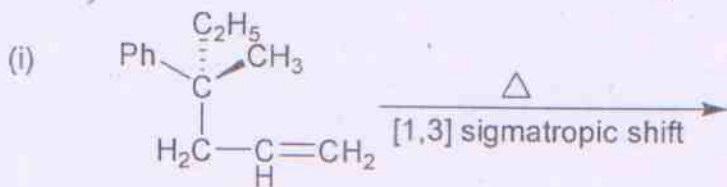


Q3 (a) Complete the given reactions and predict the reaction mechanism.

[ 6 × 5 = 30 ]



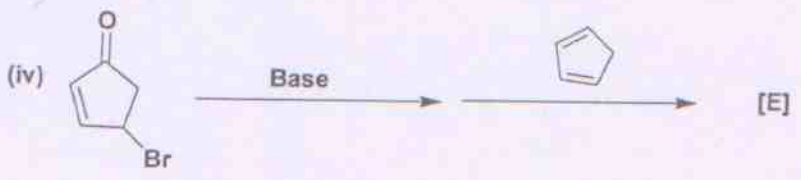
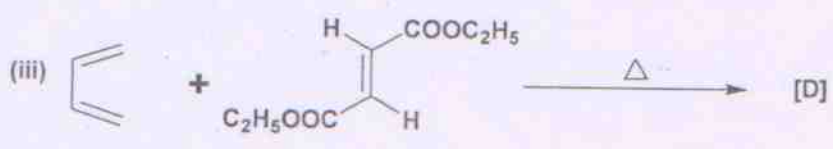
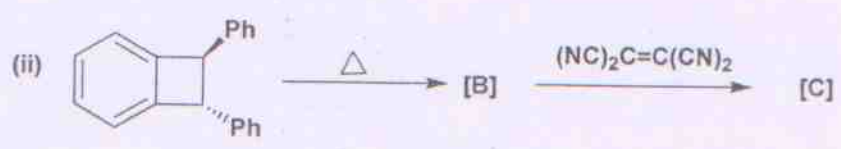
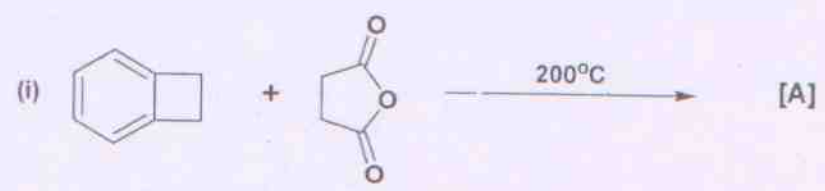
(b) Give stereochemistry at the chiral center in the given sigmatropic rearrangements. [ 5 × 2 = 10 ]



(c) Explain the FMO method of analysis of thermal [1,3] carbon - shift, [1,5] carbon - shift, and [3,3] sigmatropic rearrangement. [ 15 ]

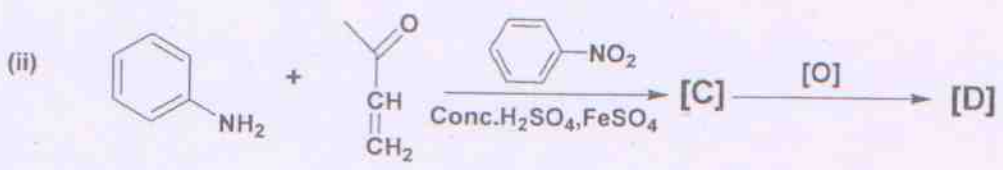
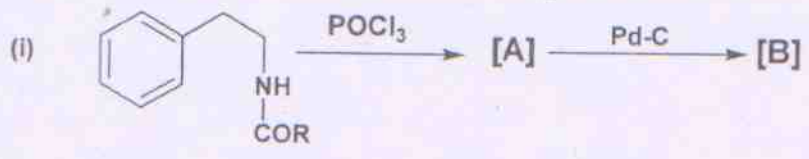
(d) Explain why cycloaddition of two molecules of ethylene is thermally not allowed. [5]

Q4 (a) Complete the following reactions and provide the mechanism: [5 x 4 = 20]



(b) Show how kinetics is used to determine the mechanism of benzoin condensation. [10]

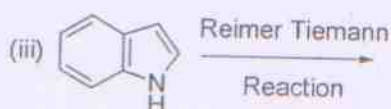
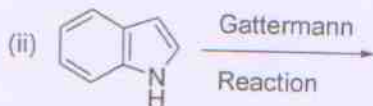
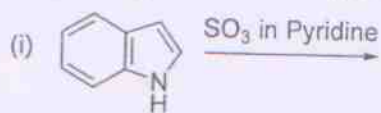
(c) Complete the following reactions and provide the mechanism: [10 x 3 = 30]





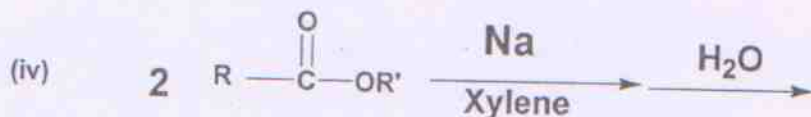
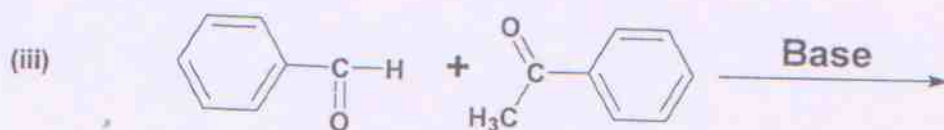
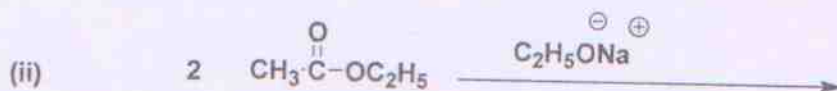
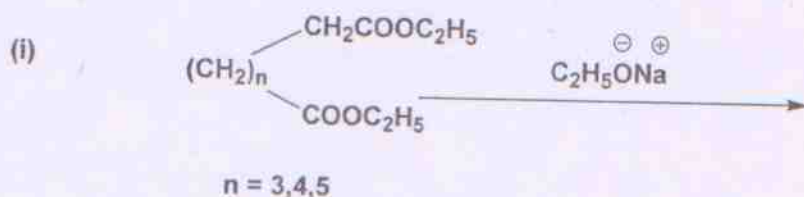
Q5 (a) Complete the following reactions and provide the necessary structures.

[5 × 3 = 15]



(b) Name the reactions and explain the mechanism for the following condensation reactions:

[5 × 4 = 20]



(c) Describe the directed Aldol condensation reaction.

[10]

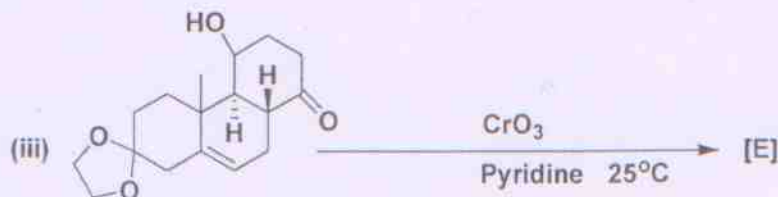
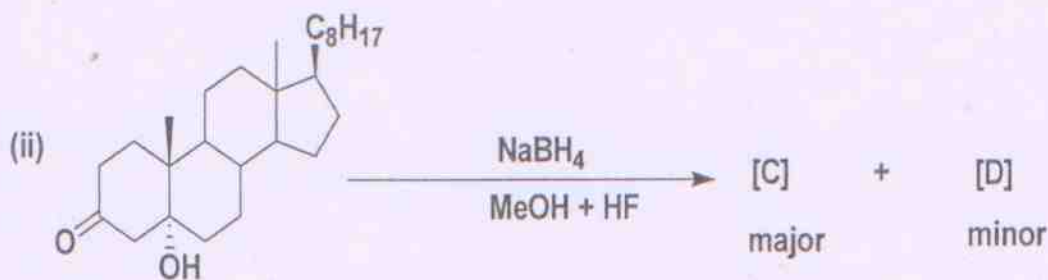
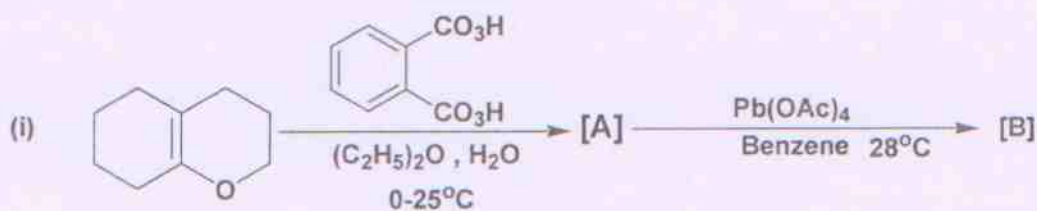
(d) Explain how peptides are synthesized using Merrifield resin.

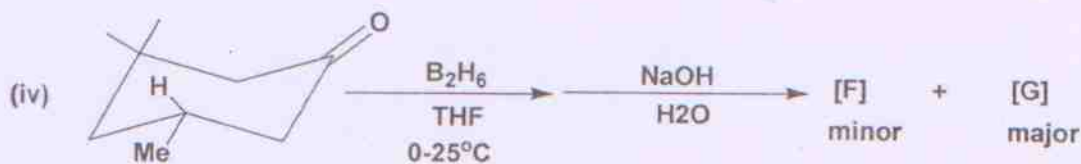
[15]

Section – B

- Q6 (a) How is the structure of nucleic acid related to their function in hereditary? [10]
- (b) What is the structure of Nylon – 6 made by alkaline polymerization of caprolactum? [15]  
Suggest a mechanism for this process. Is the mentioned polymerization a chain reaction or a step reaction?
- (c) Predict the mass spectral pattern expected for the molecular ion of  $\text{PFCl}_2$ . [10]
- (d) Explain the principle and method of estimating the molecular weight of a polymer by the sedimentation method. [15]
- (e) How is polystyrene is manufactured. What are its unique characteristic features in relation to its application? [10]

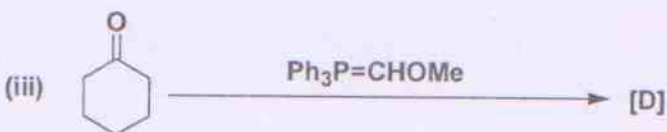
Q7 (a) Explain the formation of products, stereochemical aspects and mechanism for the following reactions: [10 × 4 = 40]





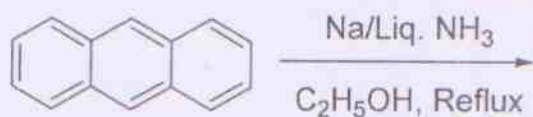
(b) Identify the products in the following sequence of reaction and indicate how these could be formed including stereochemical aspects.

[5 × 4 = 20]



Q8 (a) Explain the application of Na/liq. NH<sub>3</sub> as a reducing agent. Also explain the applicability of the said reagent in the reduction of the following substrate:

[10]

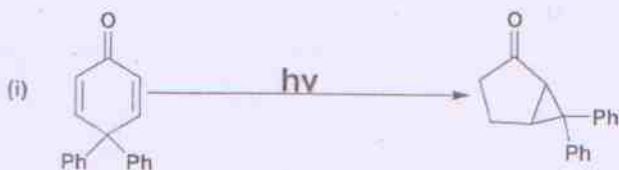


(b) Absorption of photons by organic molecule leads two possible effects: primary and secondary. Mention with example the primary and secondary effect given by the molecule.

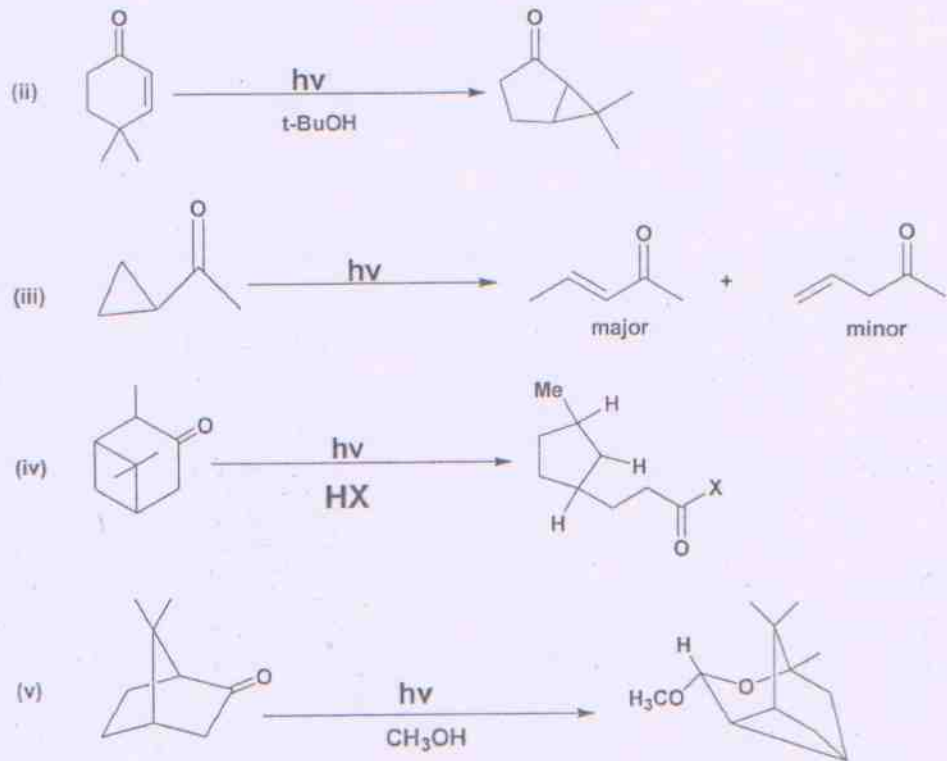
[15]

(c) Suggest mechanism for the following photo - reactions:

[7 × 5 = 35]

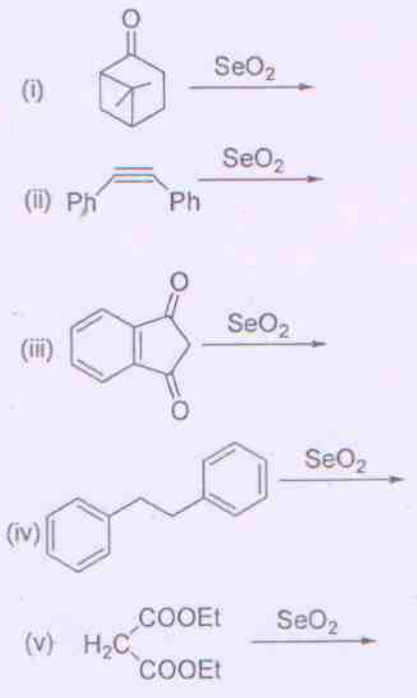






Q9 (a) Describe the applications of  $\text{SeO}_2$  as an oxidizing, dehydrogenating, catalytic, and allylic hydroxylation in the given reactions:

[5 x 6 = 30]



(b) Assign a structure to an organic compound C<sub>3</sub>H<sub>6</sub>O which shows the following structural data:

[15]

IR bands: 3300 cm<sup>-1</sup>; 3050 cm<sup>-1</sup>, 1650 (medium) cm<sup>-1</sup>, 1050 (strong) cm<sup>-1</sup>; 995 cm<sup>-1</sup> and 990 (strong) cm<sup>-1</sup>

MS (m/z): 57 (Base peak)

<sup>13</sup>C NMR data: δ 115, 140, 65 ppm

(c) Propiophenone on treatment with *m*-chloroperbenzoic acid in CH<sub>2</sub>Cl<sub>2</sub> gives a single product, which in its IR spectrum shows a strong band at 1745 cm<sup>-1</sup>. Predict the structure of the compound and give the mechanism of its formation. How <sup>1</sup>H NMR spectroscopy may be used to contain the structure of the mentioned compound.

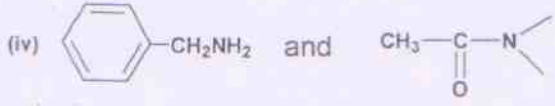
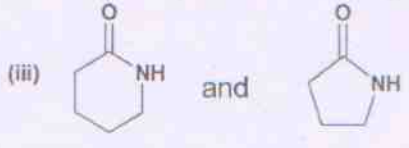
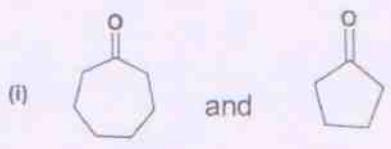
[15]

Q10 (a) How could the data from a resolution mass spectrum be used to distinguish between C<sub>6</sub>H<sub>13</sub>Cl and C<sub>3</sub>H<sub>5</sub>Br.

[5]

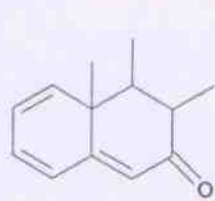
(b) How will you distinguish between the following pairs of the compounds using IR spectra:

[5 × 4 = 20]

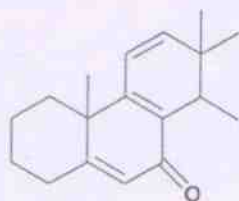


(c) On the basis of the Woodward rule, calculate the expected position of the absorption maxima in the following compounds:

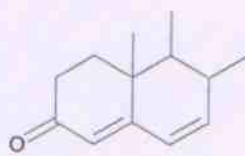
[6 × 5 = 30]



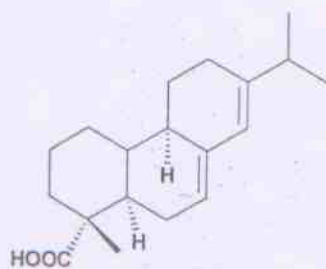
(i)



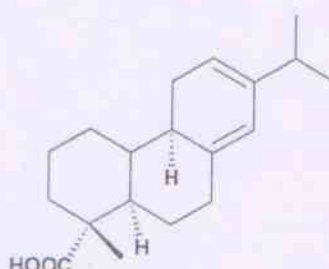
(ii)



(iii)



(iv)



(v)

(d) Predict the proton NMR spectrum for  $^{14}\text{NH}_4\text{Cl}$  ( $I = 1$  for  $^{14}\text{N}$  and  $I = \frac{1}{2}$  for  $^1\text{H}$ ).

[ 5 ]



