

**CHEMISTRY SCIENCE PAPER - III****Time Allowed : 2 1/2 Hours****Maximum Marks : 200**

N.B. :- (i) Attempt Question No. 1 and Fourteen other questions.

(ii) Log table is enclosed.

Q.1. Attempt any three of the following:

(A) Deduce the structure of a compound based on the following data:

Molecular formula :  $C_7H_{12}O_3$ I.R. ( $cm^{-1}$ ): 1740, 1715, 1160 1030.M.S.(m/z): 144( $M^+$ ), 129,99,74,55,43(base peak).P.M.R.( $\delta$ ): 1.22(3H, t J = 7Hz), 2.10 (3H, s), 2.6(2H,t J= 6.5Hz),

2.72 (2H, t, J=6.5 Hz), 4.1 (2H, q, J = 7Hz).

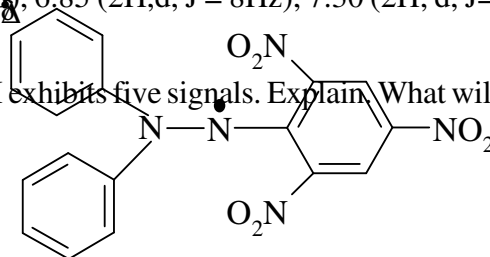
(B) Assign structure to the compound based on the following data:

Molecular formula:  $C_{11}H_{13}NO$ I.R. ( $cm^{-1}$ ): 2225, 1600, 1510, 840M.S. (m/z): 175 ( $m^+$ ), 149, 107.P.M.R. (  $\delta$  ): 1.46 (6H,S), 3.95 (3H, S), 6.85 (2H,d, J = 8Hz), 7.30 (2H, d, J= 8Hz).

(C) The solution ESR spectrum of DPPH exhibits five signals. Explain. What will be their intensity ratio?

Given:

i) Structure of DPPH:

ii)  $^{14}N$  ( $I = 1$ ).

(D) Explain following Mossbauer spectral observations:

Sr.No.	Compound	$\delta$ , mm/s	$E_Q$ , mm/s
i)	$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	1.19	1.75
ii)	$K_4 Fe (CN)_6 \cdot 3H_2O$	-0.13	-

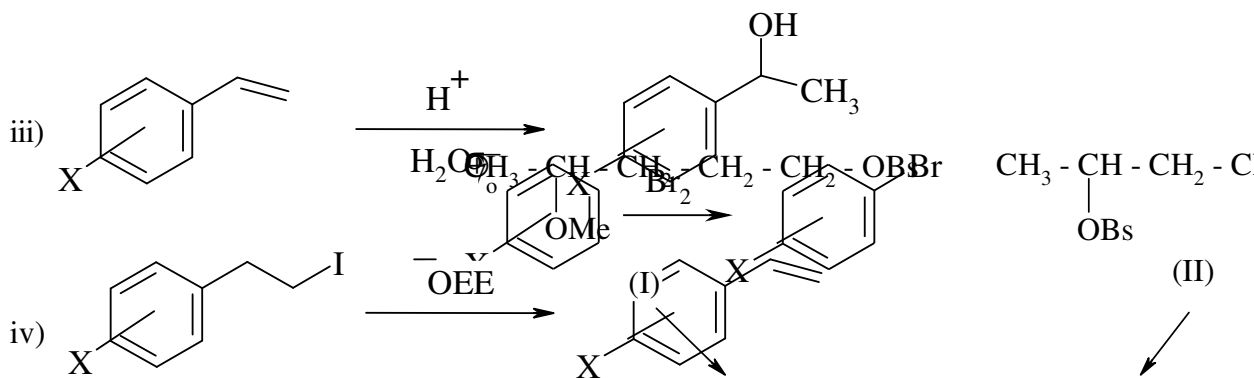
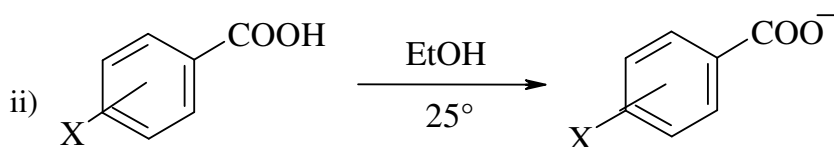
Given: At.no. of Fe = 26

- (E) The infrared absorption spectrum of HCl shows an intense band at  $2886\text{ cm}^{-1}$  and a weak band at  $5668\text{ cm}^{-1}$ . Calculate  $\nu_e$ , the fundamental absorption wave number and  $X_e$  the anharmonicity constant.
- (F) A particular NMR operates at  $300\text{ MHz}$ . What magnetic field is required to bring a  $\text{C}^{13}$  nucleus to resonance at this frequency?  $\mu_N$  (nuclear magneton) =  $3.53 \times 10^{-24}\text{ erg/gauss}$ .

Q2) (A) Match the  $p$  values given below with the appropriate reaction, giving reasons.

$p$ :  $-3.57$ ;  $-12$ ;  $1.75$ ;  $2.07$

i)

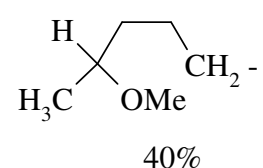


(B) Match the  $\sigma$  values given below with appropriate substituents.

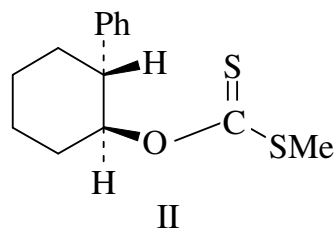
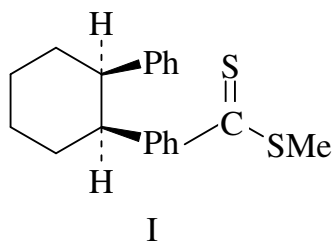
$\sigma$ :  $0.54$ ;  $0.35$ ;  $0.82$ ;  $-0.20$

Substituent: P- (CH<sub>3</sub>)<sub>3</sub>; P- CF<sub>3</sub>; P-OCF<sub>3</sub>; P-N Me<sub>3</sub> 60%

(C) Acetolysis of 4-methoxy-1-pentyl brosylate (I) and 5-methoxy-2-pentyl brosylate (II) gave the same mixture of products. Explain



Q3) (A) a) What is the relation between I and II? s Select your answers from the alternatives given below: [1]



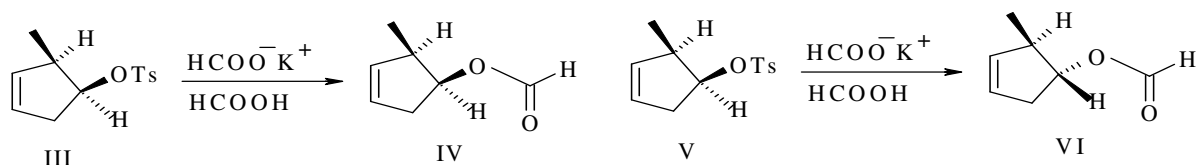
- i) identical  
 ii) enantiomers  
 iii) diastereomers  
 iv) conformational isomers  
 v) constitutional isomers

b) Draw their conformational structures in the most stable form. [2]

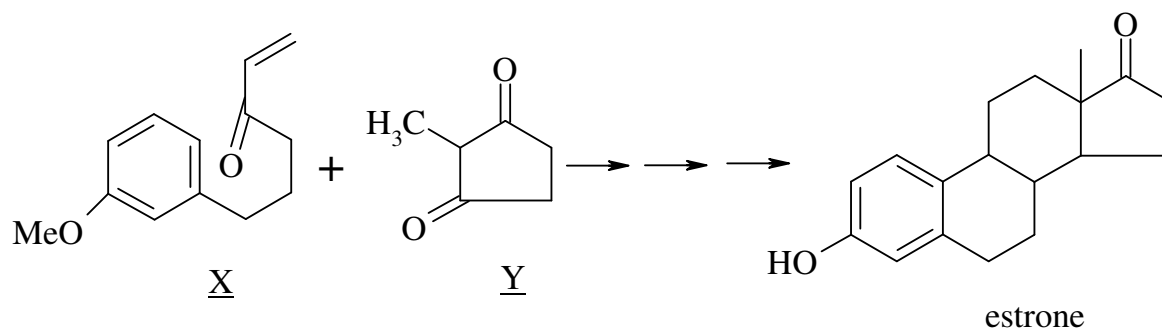
c) Both I and II undergo Pyrolytic syn elimination. Write the stereostructures of the products formed in each case indicating major and minor products formed. [2]

d) Which I or II gives 3-Phenylcyclohexene as the major product and why?

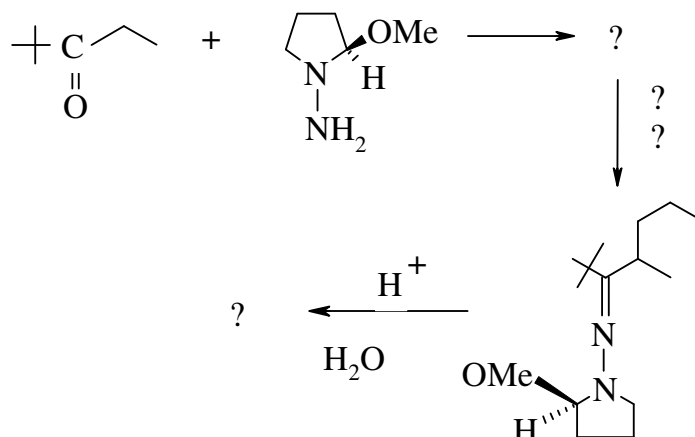
(B) Solvolysis of III with  $\text{AcO}^- \text{K}^+$  in AcOH gives IV with retention of configuration. But V gives VI with complete inversion of configuration under similar reaction conditions. Explain with mechanism and stereochemistry. [2]



Q4) A) Give the synthetic scheme for the synthesis of a steroid hormone, estrone, from the starting materials X and Y using Robinson annulation, cyclization, catalytic reduction and demethylation. [6]

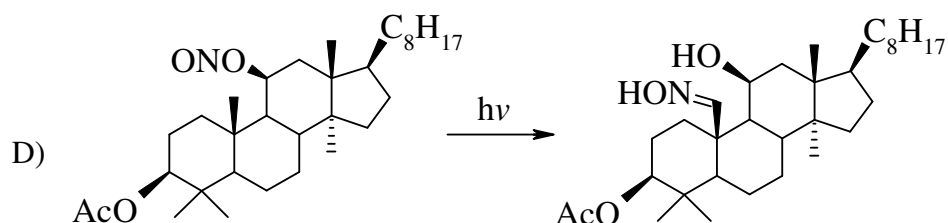
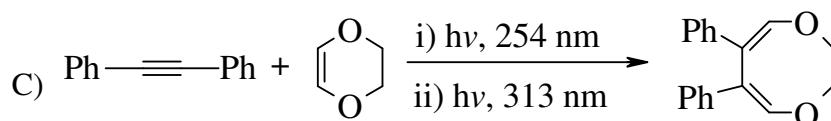
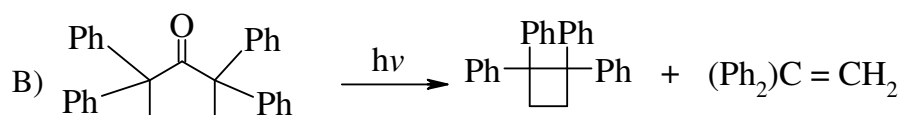
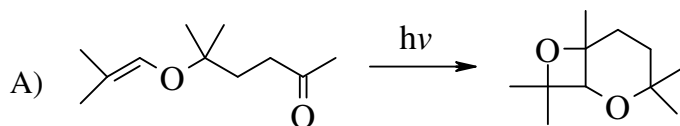


- B) Complete the following reaction sequence by filling the gaps and answer the questions given below.

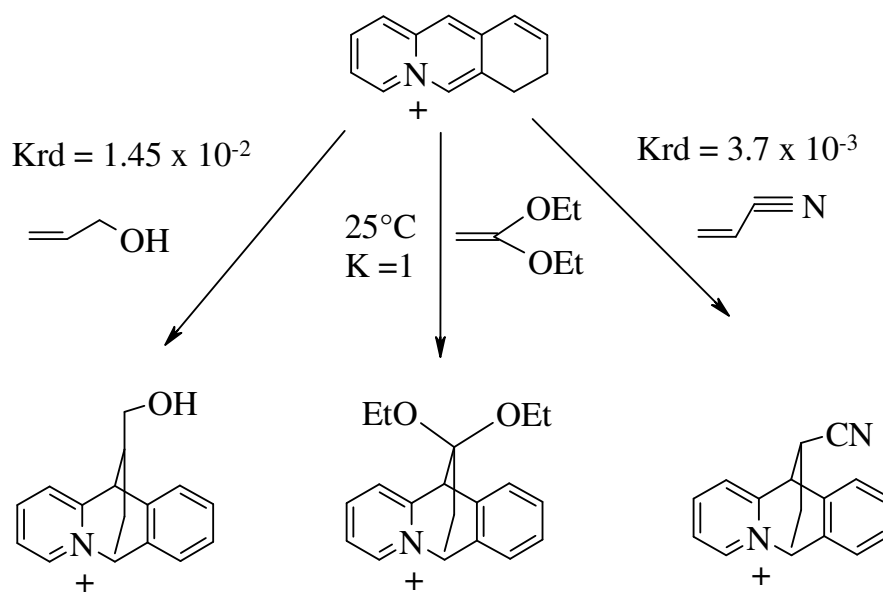


- The above sequence of reactions is, an example of what type of synthesis?
- Identify the chiral auxiliary. What is its role in the synthesis?
- What is the configuration of the product?
- Name the reactions involved in all steps.

- Q5) Indicate the type of the reaction and mechanism involved in each step of the following transformations. [13]



Q6) A)



a) Name the above reactions.

b) Explain the differences observed in their relative rates on the basis of electron demands.

[5]

B) i) Which starting materials (diene and dienophile) will be required to prepare the following compounds.

[4]



ii) From which compounds are the following 1,3-dienes generated in situ.

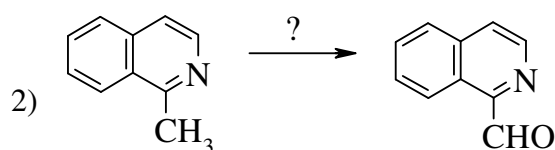
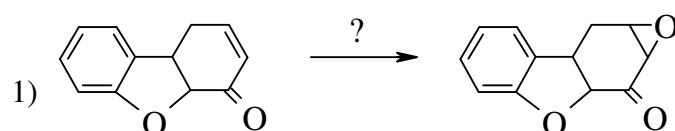
a) 1,3-butadiene

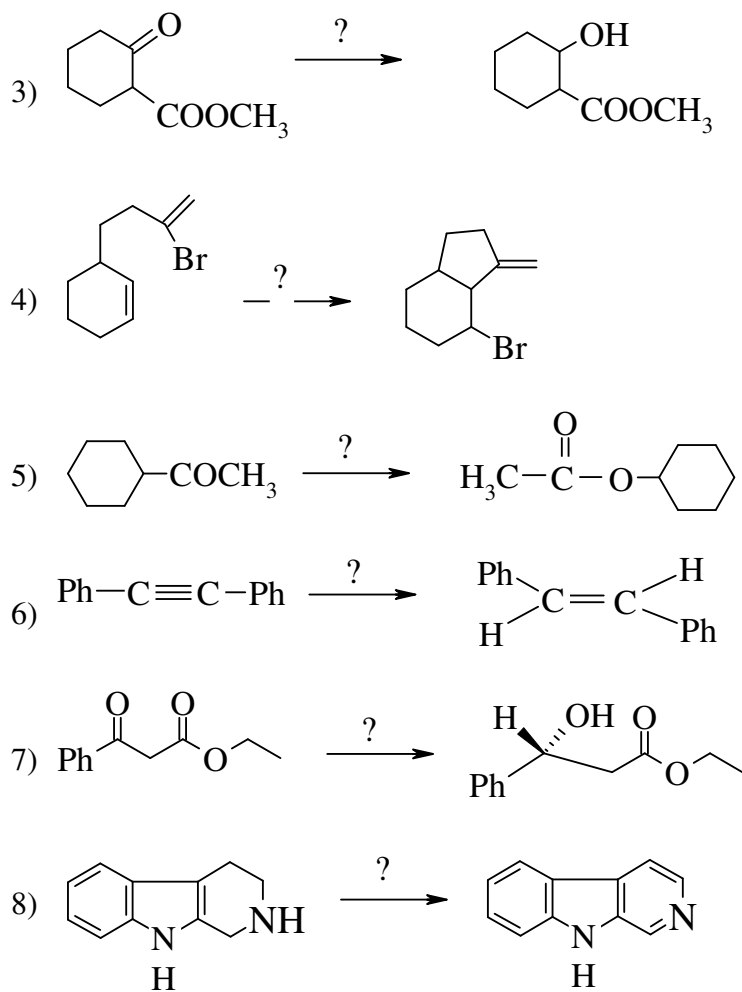
b) 1,3-cyclopentadiene

[4]

Q7) A) Indicate appropriate reagents for the following reactions.

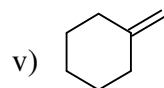
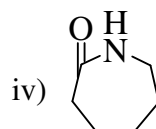
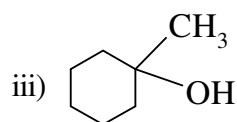
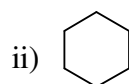
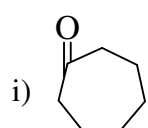
[8]





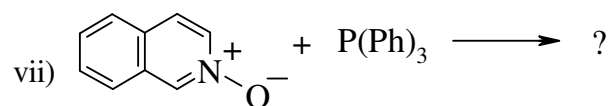
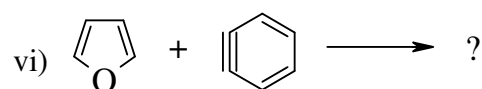
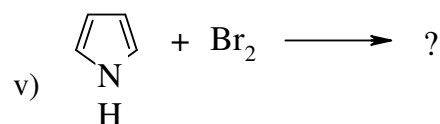
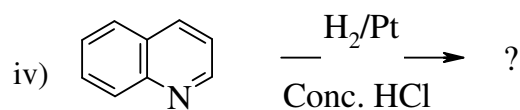
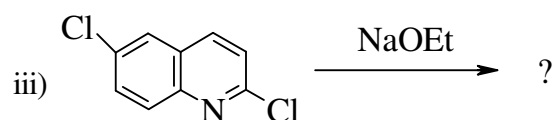
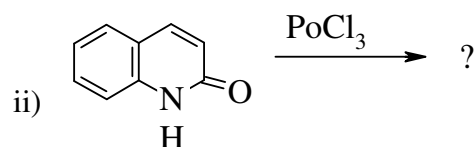
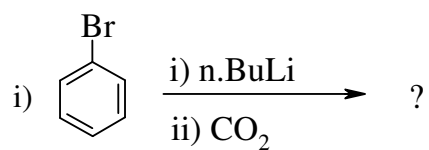
B) Give reagents to transform cyclohexanone into each of the following compounds separately.

[5]



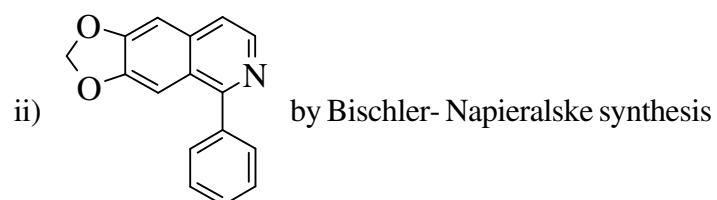
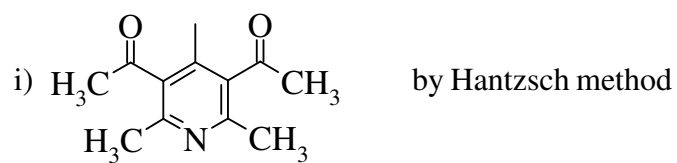
Q8 A) Write the products of the following reactions.

[7]

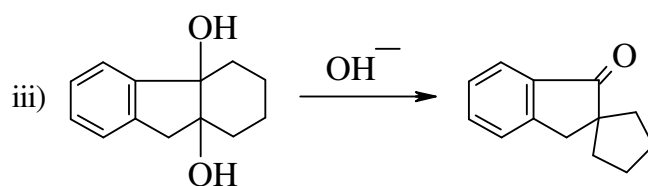
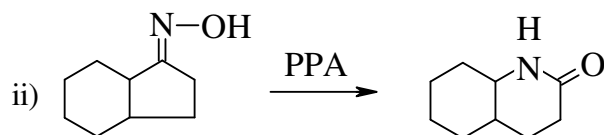
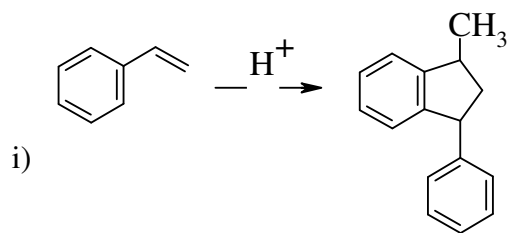


B) Write the steps involved in the synthesis of the following:

[6]



Q9) A) Propose the mechanisms for the following conversions and name the reaction involved.[6]



B) The reaction of 1- fluoronaphthalene with excess of PhLi followed by carbonation gives two isomeric acids A and B having formula  $C_{17}H_{12}O_2$ . However 2- fluoronaphthalene under identical conditions yields A, B and a third isomer C. What are A, B and C? Explain their formation. [7]

Q10) A) State the four points of Huckel's criteria for aromaticity. [2]

B) Draw the structures of a) cyclobutadiene b) cyclopentadiene c) cyclohexatriene and d) cyclooctatetraene. Explain which are aromatic and which are not aromatic giving reasons in support of your answer. [4]

C) Match the entries in column A and B

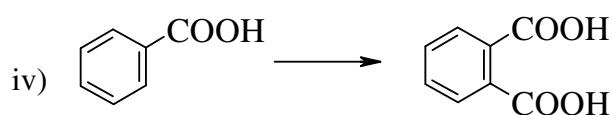
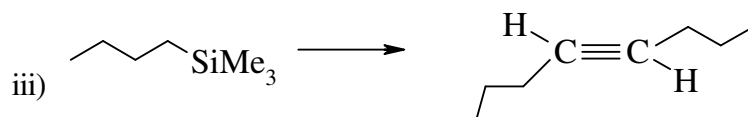
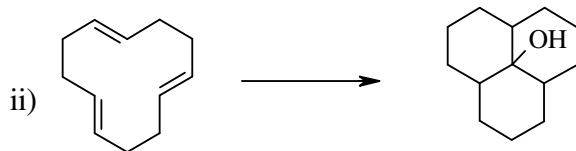
<u>A</u>	<u>B</u>
i) codon	a) N-terminal analysis
ii) A-T	b) multiple peptide
iii) ph-N=C=S	c) sequence of 3 bases
iv) G-C	d) energy currency
v) quaternary structure of protein	e) Three H-bonds
vi) $NAD^{\oplus}$	F) Two H-bonds
vii) ATP	g) biological oxidizing agent

i)..... ii)..... iii)..... iv)..... v) ..... vi) ..... vii) .....

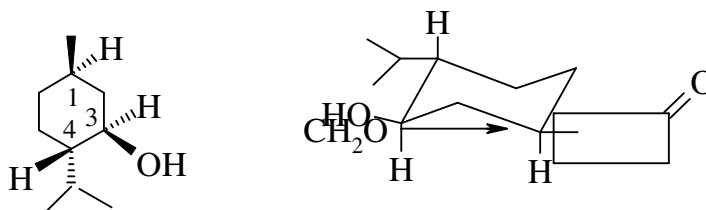


Q11) A) How will you achieve the following transformations? Identify various steps. [13]

i)



Q12) A) The stereostructures (planar and conformational) of the naturally occurring (-)-menthol are given below:

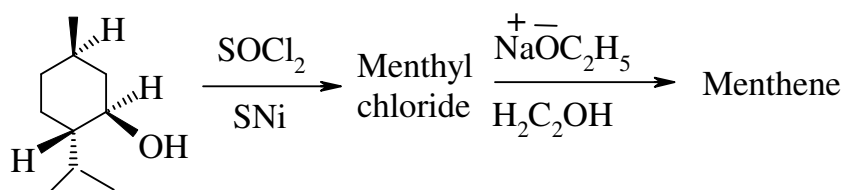


a) Write R/S configuration at the chiral centres in the planar structure. [1]

b) How many stereoisomers are theoretically possible for (-)-menthol?  
(Write only the number) [1]

c) Draw their stereostructures either in the planar or conformational form. [4]

B) (-)-Menthol on treatment with  $\text{SOCl}_2$  gives its chloride which on reaction with sodium ethoxide in ethanol give menthene. Write the stereostructures of the chloride and the menthene formed indicating the mechanism and stereochemistry involved. [4]

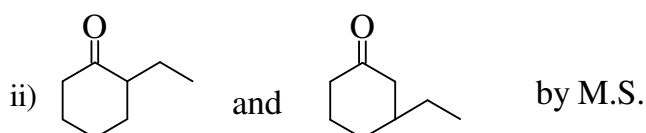


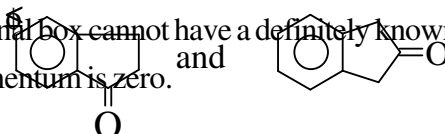
- C) Write the Biogenetic pathway for menthol starting with IPP (isopentenyl pyrophosphate) and DMAPP (dimethylallyl pyrophosphate). [3]

- 13) A) Deduce the structure of a compound on the following data: [7]  
 M.S. (M/Z) : 139 and 137 [Two molecular ion peaks in the ratio (1:3)], 102.  
 I.R. : 1565, 1375  $\text{cm}^{-1}$ .  
 P.M.R. ( $\delta$ ): 1.00 (3H, t, J= 7Hz), 1.50 (2H, sextet, J=7 Hz), 2.22 (2H, m),  
 5.82 (1 H, t, J= 7Hz).

- B) Distinguish between the following pairs by the indicated spectral method. [6]

i)



- Q14) A) Show that a particle in a one dimensional box cannot have a definitely known momentum and that the average value of the momentum is zero.  by C-13 NMR [7]

- B) Sketch the wave functions and the probability densities of the quantum mechanical harmonic oscillator for the states  $\nu = 1$  and  $\nu = 2$ . 'What is' quantum tunnelling? [7]

- Q15) A) What is the most probable distance of 15 electron from the nucleus in the hydrogen atom.

$$\text{Given } \Psi = \frac{1}{\sqrt{\pi}} e^{-r}. \text{ (in a.u.)}$$

[Hint: you have to maximize the probability density.] [7]

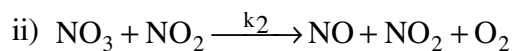
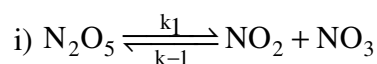
- B) Using  $\Psi = a(x - x^2)$  (upside down parabola) as a trial function for the particle in one dimensional box (0  $< x < a$ ), estimate the ground state energy. [6]

- Q16) A) Explain how the unimolecular reaction can follow the second order kinetics using Lindemann theory.

[8]

B) For the reaction, [5]

the proposed mechanism is



iii)

Show that rate law follows the equation

$$\frac{d[\text{O}_2]}{dt} = k[\text{N}_2\text{O}_5]$$

Identify k in terms of  $k_1$ ,  $k_{-1}$  and  $k_2$ .

Q17) A) What is molecular partition function? Explain how the knowledge of this enables one to obtain internal energy and specific heat at constant volume for a system. [8]

B) Calculate vibrational partition function for  $\text{Br}_2$  at 300 K, if the vibrational frequency is  $151.2\text{cm}^{-1}$ . [5]

Q18) A) Match the entries in column A from those given below:  $3\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$  [7]

Column A	Column B
i) Enzyme catalysis	i) Seebeck effect
ii) Interpretation of wave function	ii) Neel temperature
iii) Thermodynamics of polymer solution	iii) Onsager's reciprocal relations
iv) Spectral line width	iv) Doppler broadening
v) phenomenological laws	v) Transition state theory
vi) Eyring equation	vi) Max Bron
vii) Antiferromagnetism	vii) Joule Thomson experiment
	viii) Flory -Huggins theory
	ix) Michaelis - Menten mechanism
	x) Lindemann theory
	xi) Quantization of angular momentum
	xii) Rule of mutual exclusion

B) Write down the symmetry elements and derive the point group for  $\text{SO}_2$ . Construct the group multiplication table. Is the group abelian? Explain. [6]

Q19) A) Show that [6]

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$$

B) Deduce Saxens relations on the basis of Onsager's reciprocity theorem. [7]

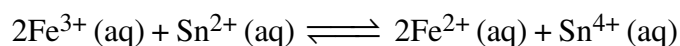
Q20) A) A quantity of a substance in a closed system is made to undergo a reversible process from an initial volume of  $2\text{m}^3$  and initial pressure  $10^5 \text{Nm}^{-2}$  to final volume of  $4\text{m}^3$ . Calculate the work done by the substance if  $PV = \text{constant}$ . [7]

B) If Trouton's law is followed by i) benzene and ii) n- octane, calculate the heat of vaporization of each molecule boiling points of benzene and n- octane are  $80.1^\circ\text{C}$  and  $125.7^\circ\text{C}$  respectively at 1 atm. [6]

Q21) A) Obtain the transformation matrix for a  $\text{Cu}^+$  operation using the  $P_x$  and  $P_y$  as the basis. [7]

B) Show that . Explain with suitable example. [6]

Q22) A) Set up the electrochemical cell for the reaction  $2\text{Fe}^{3+}(\text{aq}) + \text{Sn}^{2+}(\text{aq}) \rightleftharpoons 2\text{Fe}^{2+}(\text{aq}) + \text{Sn}^{4+}(\text{aq})$  [6]



Calculate the equilibrium constant for the reaction

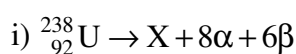
Given:  $E^0 = 0.77 \text{V}$  [6]



B) Distinguish physisorption and chemisorption. How physisorption changes to chemisorption? explain with suitable PE diagram. [7]

Q23) A) Calculate the mean binding energy of  $^4\text{He}$  atom.  
Given  $m_{\text{H}} = 1.0078$ ;  $m_{\text{N}} = 1.0087$ ;  $m^4\text{He} = 4.0026$ . [7]

B) Identify 'X' in the following nuclear reactions and justify your answer. [6]



ii)



- B) Give the molecular structures of  $\text{P}_4$ ,  $\text{S}_8$  and  $(\text{PNCl}_2)_3$ . [6]
- C) What is oleum? [2]
- Q29) A) Draw structure and mention the geometry and hybridisation involved for the following compounds–  
 i)  $\text{XeF}_4$  ii)  $\text{XeOF}_4$  [6]
- B) Draw structure, give nomenclature and mention the hybridisation involved for the following compounds–  
 i)  $\text{I}_2\text{O}_5$  ii)  $\text{IF}_7$  [6]
- C) In  $\text{H}_5\text{IO}_6$ , the oxidation state of I is \_\_\_\_\_. (Fill in the blank) [1]
- Q30) A) Name the species and draw the structures of  
 A)  $\text{Fe}(\text{CO})_5$  b)  $\text{Ni}(\text{CO})_4$   
 C)  $\text{Mo}(\text{CO})_6$  d)  $\text{V}(\text{CO})_6$  [8]
- B) Explain the role of  $[\text{HCo}(\text{CO})_4]$  as a catalyst in hydroformylation reaction. [5]
- Q31) A) For the compound  $\text{MX}_6$  ( octahedral ) and  $\text{MX}_4$  (square planar) draw the d-orbital energy level diagrams with tables of the central metal M in one place. Show the correlation between the two sets of d-orbitals. [8]
- B) Estimate the spin- only magnetic moment for a  $d^6$  ion in octahedral and tetrahedral fields generated by weak and strong ligands. [5]
- Q32) A) Arrange the following complex ions in order of increasing  
 $[\text{CoI}_6]^{3-}$ ,  $[\text{CoI}_6]^{4-}$ ,  $[\text{Rh}(\text{CN})_6]^{3-}$ ,  $[\text{Rh}(\text{H}_2\text{O})_6]^{3-}$ ,  $[\text{RhI}_6]^{3-}$ ,  $[\text{Ir}(\text{CN})_6]^{3-}$
- B)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  shows three absorption bands at 17400, 24600 and 37900  $\text{cm}^{-1}$ . Assign the three bands and calculate the crystal field and bonding parameters.  
 Given:  
 i)  $\nu_1 = 10 Dq$  ii)  $\nu_2 = 18 Dq - C$   
 ii)  $\nu_3 = 15 B + 12 Dq + C$  iii)  $B_0$  for Cr III is 918  $\text{cm}^{-1}$  [7]
- Q33) A) Distinguish between outer sphere and inner sphere electron transfer reactions with suitable examples. (7)



- B) How PLOT and WCOT columns differ from each other ? (4)
- C) Enlist four detectors used in Gas chromatograph instrument and explain merits and demerits of any one. (4)
- Q.37 A) Match the entries in column A with those given in column B.
- | (A)                                      | (B)                           |
|--|-------------------------------|
| i) Photosynthesis                        | a) $\text{Cu}^{+2}$           |
| ii) Nitrogen fixation                    | b) $\text{Ca}^{+2}$           |
| iii) Hemocyanin                          | c) Non-heme iron              |
| iv) Protein folding                      | d) Purple bacteria            |
| v) Ferredoxin                            | e) $\text{O}_2$ binding model |
| vi) $[\text{Co}(\text{salen})\text{py}]$ | f) Rizobium bacteria          |
- Answer : i) ..... ii) ..... iii) ..... iv) ..... v) ..... vi) ..... (6)
- B) Explain the magnetic properties of Hb and  $\text{HbO}_2$ . (3)
- C) Give names of any four therapeutic agents with respect to their use as medicine. (4)

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