

**CHEMISTRY****Paper – III****Time Allowed : Three Hours****Maximum Marks : 200****Question Paper Specific Instructions**

***Please read each of the following instructions carefully before attempting questions :***

***There are TEN questions divided under TWO sections.***

***Candidate has to attempt SIX questions in all.***

***Question No. 1 in Section A and Question No. 6 in Section B are compulsory. Of the remaining questions, candidates have to answer FOUR questions, choosing TWO from each section.***

***The number of marks carried by a question / part is indicated against it.***

***Neat sketches are to be drawn to illustrate answers, wherever required. These shall be drawn in the space provided for answering the question itself.***

***Unless otherwise mentioned, symbols and notations have their usual standard meanings.***

***Assume suitable data, if necessary, and indicate the same clearly.***

***Attempts of questions shall be counted in sequential order. Unless struck off, attempt of a question shall be counted even if attempted partly.***

***Any page or portion of the page left blank in the Question-cum-Answer (QCA) Booklet must be clearly struck off.***

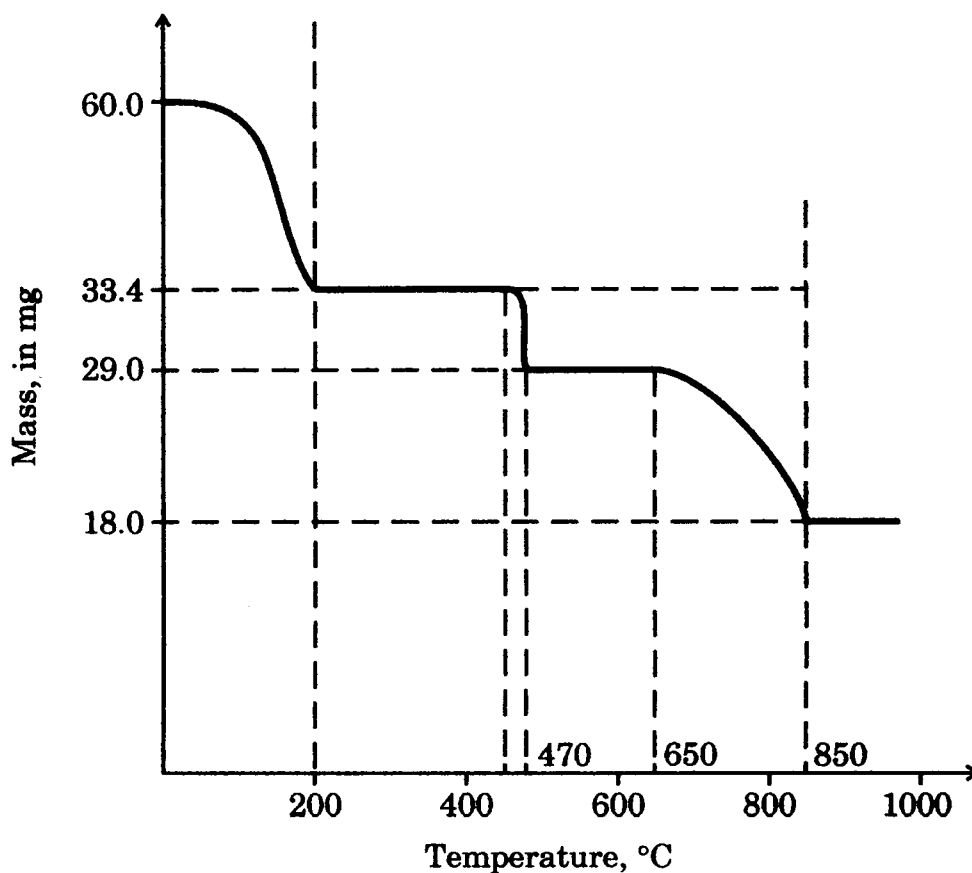
***Answers must be written in ENGLISH only.***

## SECTION A

- Q1.** (a) The following results were obtained in the replicate determinations of Fe content in a mineral ore (in mg) :
- 10.5, 10.6, 10.3, 10.6, 10.2 and 10.4.
- Calculate the relative standard deviation (RSD) of this data. 5
- (b) (i) What types of analyte can be separated by HPLC but not by GLC ? 2
- (ii) What is the range of particle size used as stationary phase packing material in most packed GLC columns ? 3
- (c) What are the common sources suitable for infrared spectrometric analysis of an organic compound ? 5
- (d) What is the advantage and disadvantage of GF-AAS as compared to Flame-AAS ? 5
- (e) How is temperature axis in thermogravimetry method calibrated ? 5
- (f) How do K & L X-ray peaks of an element originate in XRF method ? Give a typical labelled wavelength dispersive XRF spectrum showing  $K_{\alpha}$  &  $K_{\beta}$  peaks of an element, e.g. Zn. 5
- (g) How does high concentration of calcium interfere with ICP-MS analysis of iron ? 5
- (h) What are the major constituents of type metal ? Suggest a method for non-destructive analysis of the constituents in type metal. 5  
(Description of the method is not required)
- Q2.** (a) An analyte was estimated in the ppb to ppm range in a 1  $\mu$ L sample. Comment on the type of analysis as per sampling protocol. 5
- (b) A chromatographic column is tested and found to produce a peak having a Gaussian shape and a width of 25 sec at a retention time of 35 min. How many theoretical plates does the column have under the conditions of the test ? If the column described above is 3 m long, what is the height equivalent to a theoretical plate (HETP) in this case ? 7+3

- (c) A dolomite sample is analyzed by thermogravimetry. Using the given data, determine the concentration of  $\text{CaCO}_3$  &  $\text{MgCO}_3$  (in wt%) in the dolomite sample. (Y-axis not in scale)

10



Given : atomic mass of Ca, Mg, C and O are 40, 24, 12 and 16, respectively.

- (d) In XRF instrument, when tube voltage is set at 24 kV, KX-ray lines of Ag are not observed. Explain the observation.

5

Given : K absorption edge of Ag =  $0.485 \text{ \AA}$

K emission line of Ag =  $0.497 \text{ \AA}$

- Q3.** (a) The spectral data for a series of solutions of a complex formed by a metal (M) and a ligand (L) is presented below. Use this spectral data for predicting the stoichiometry of this complex ( $ML_n$ ).

15

S.No.	Volume of metal ion solution ( $V_M$ ) (mL)	Volume of ligand solution ( $V_L$ ) (mL)	Total Volume (mL)	Absorbance (at $\lambda_{max}$ )
1	10	90	100	0.18
2	20	80	100	0.69
3	30	70	100	0.65
4	40	60	100	0.51
5	50	50	100	0.42
6	60	40	100	0.36
7	70	30	100	0.28
8	80	20	100	0.22
9	90	10	100	0.15

- (b) Calculate the percentage distribution of an analyte in a Craig apparatus after 3 transfers in each tube (limited to 4 tubes) for which  $V_S = 3$  mL and  $V_M = 6$  mL. [Distribution coefficient ( $K_D$ ) is 3]

10

- (c) 1 g of bituminous coal is burnt in a bomb calorimeter. Due to combustion of the coal, temperature of water in bomb calorimeter increased by  $2.6^\circ\text{C}$ . Calculate the gross calorific value of the coal sample.

5

Given : Mass of water = 2.0 kg

Water equivalent of the calorimeter = 0.6 kg

Specific heat of water =  $4.2 \text{ kJ/kg}^\circ\text{C}$

- Q4.** (a) (i) Powder XRD of a crystalline material exhibited diffractions at  $2\theta$  values corresponding to the following planes :

(110), (200), (211) and (220)

The material belongs to which crystal structure ? Give reasons.

(ii) Determine the density of the material.

Given :  $\sin 30^\circ = 0.5$ ,  $\sin 60^\circ = \frac{\sqrt{3}}{2}$  5+10=15

Molecular mass of the material = 60 g/mol

(211) plane is observed at  $2\theta = 60$  degree

$\lambda = 1.54 \text{ \AA}$

(b) Briefly outline the complexometric method for determining alumina content in a bauxite ore. 10

(c) Sensitivity of Sr measurement by AAS is improved in  $N_2O$ -acetylene flame by adding K in the sample. Explain why. 5

**Q5.** (a) What are the effects of polychromatic radiation on absorbance of an analyte following Lambert-Beer's law ? 5

(b) Briefly describe the sequence of steps involved in analyzing a solid sample by ICP-MS. 10

(c) Certain coal samples were analyzed for their 'C' content by two different analytical methods. Following results were obtained :

Sample	Method A (in percentage)	Method B (in percentage)
1	62.1	62.8
2	60.8	60.9
3	61.9	62.2
4	60.9	60.5
5	59.7	59.9
6	61.4	61.2

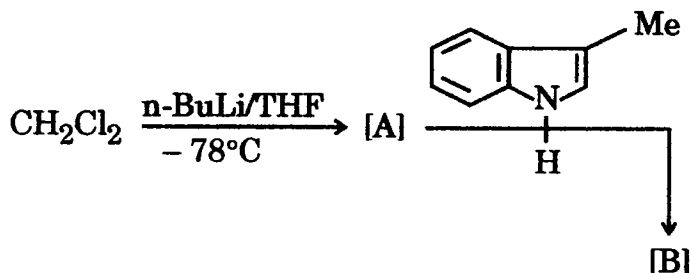
Decide by use of an appropriate 't'-test whether the different results of the two methods are significant at a confidence level of 90%. 10

Sample Size	t'			
	CONFIDENCE LEVEL			
	90%	95%	99.9%	99.5%
6	1.943	2.447	3.707	4.317

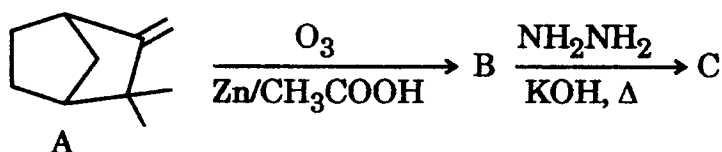
(d) What information is obtained in the analysis of petroleum product by Aniline point and Doctor test, respectively ? 3+2=5

## SECTION B

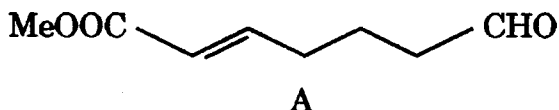
- Q6.** (a) Predict the product(s) A and B in the following reaction and explain the mechanism involved.



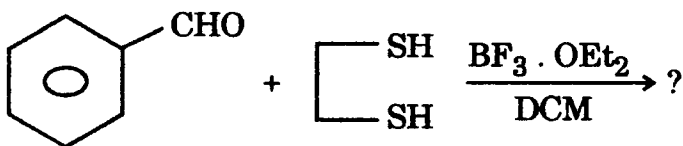
- (b) Complete the following reaction and sketch a suitable mechanism for conversion of B → C.



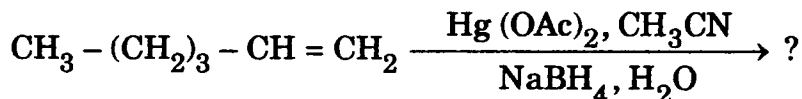
- (c) In the following reaction sequence, reaction of aldehyde A with benzylamine followed by sodium borohydride ( $\text{NaBH}_4$ ) reduction results in formation of compound B which upon heating gives compound C (tertiary amine). Identify A, B and C. Which name reaction is involved in conversion of B to C?



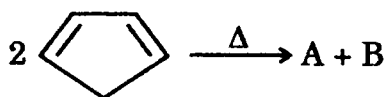
- (d) Predict the product of the following reaction and give the plausible mechanism.



- (e) Write the product and propose a suitable mechanism for the following reaction:



- (f) Identify the reaction and predict the products A and B based on FMO approach. Give suitable justification for which product is major. 4



- (g)  $^1\text{H}$  NMR spectrum of two isomeric esters P & Q with molecular formula  $\text{C}_7\text{H}_{14}\text{O}_2$  are given below. Identify the structures of P & Q. 4

Compound P

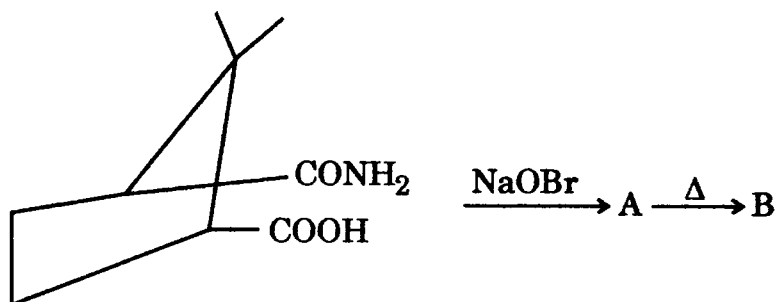
$^1\text{H}$  NMR ( $\text{CDCl}_3$   $\delta$ ): 3.78 – 3.8 (d, 1H), 2.52 – 2.7 (q, 2H),  
1.7 – 1.9 (sept, 1H), 2.2 – 2.4 (t, 3H), 0.72 – 0.9 (d, 2H)

Compound Q

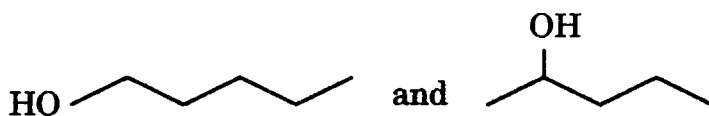
$^1\text{H}$  NMR ( $\text{CDCl}_3$   $\delta$ ): 2.3 – 2.6 (q, 2H), 1.45 (s, 9H), 1.1 – 1.3 (t, 3H)

- (h) The mass spectrum of 3-butyn-2-ol shows a large peak at  $m/z$  55. Draw the structure of fragment and explain why it is particularly stable. 4
- (i) Acetone absorbs at 279 nm in hexane whereas the value of  $\lambda_{\text{max}}$  in water is 264.5 nm. Provide a suitable justification to your answer. 4
- (j) Mass spectrum of Butyrophenone shows two peaks  $m/z$  106 and 120 due to McLafferty rearrangement. Justify your answer. 4

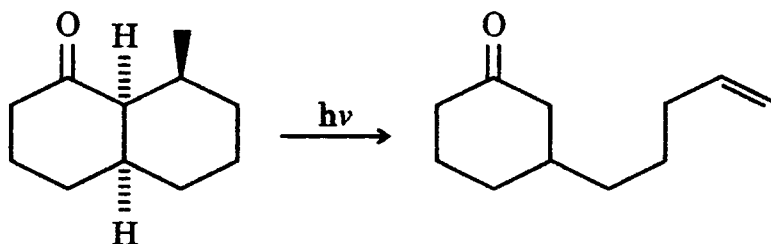
- Q7. (a) Complete and outline the mechanism of the following reaction. How will you establish that Hofmann rearrangement is intermolecular in nature? 10



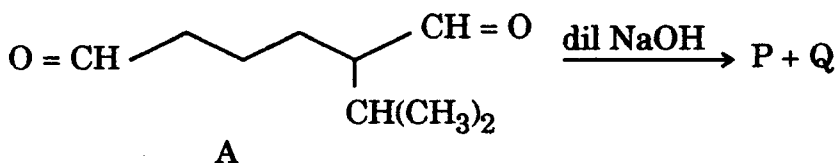
- (b) How would you differentiate between the following pairs of alcohols with the help of mass spectrometry? 5



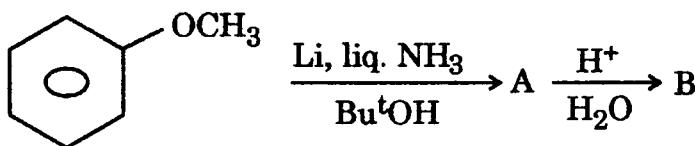
- (c) Predict the mechanism of the following photochemical conversion. Name the reaction and give justification. 5



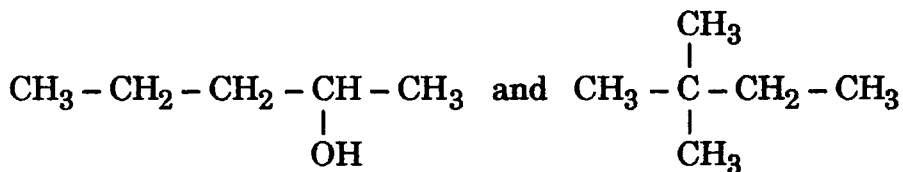
- (d) Base catalyzed condensation of dialdehyde A can result in the formation of two products (P, Q). Identify the two products. Which one is actually obtained and why? Also give the mechanism of its formation. 10



- Q8. (a) Write the structure of the product(s) in the following conversion and explain the mechanism. 10

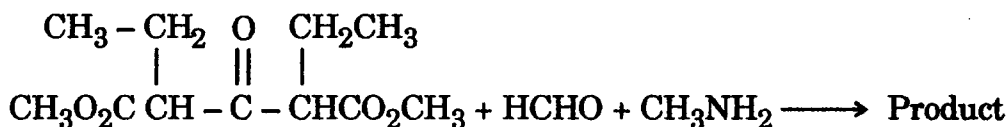


- (b) How could the following pairs of isomeric compounds be differentiated by mass spectrometry? 5



- (c) Explain the mechanism of free radical polymerization of ethylene. How will you explain the formation of branchings in the resulting polymer? 5

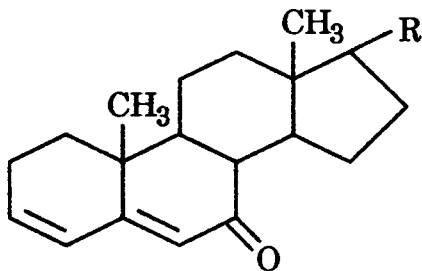
- (d) Write the product of the following reaction and explain the mechanism of its formation. 10



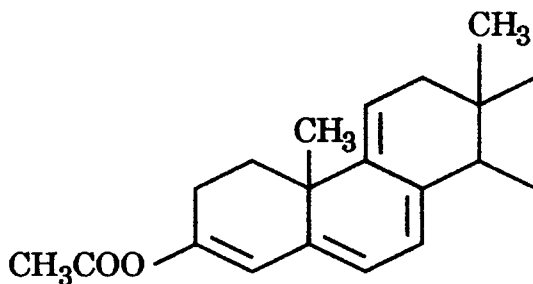


- Q9. (a) Using Woodward's rules, calculate the  $\lambda_{\max}$  value for the following compounds :

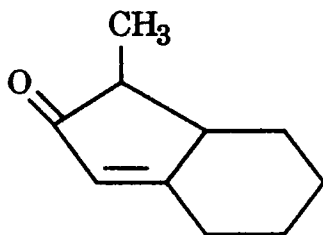
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I



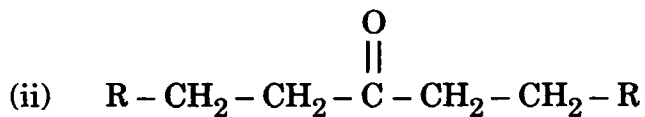
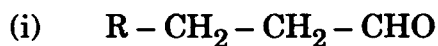
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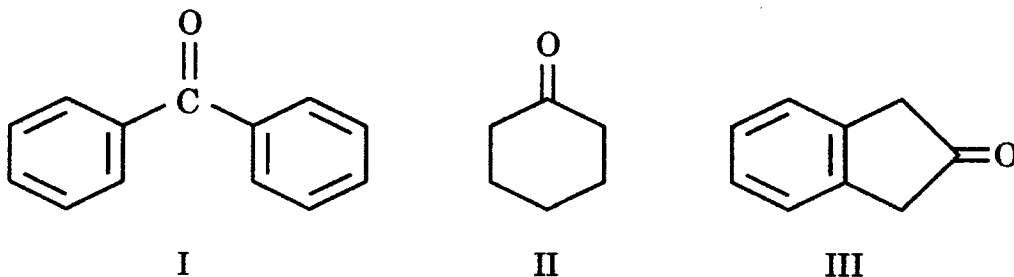
III

- (b) How will you convert organoborane intermediate i.e.  $(R - CH_2 - CH_2)_3 B$  derived from  $R - CH = CH_2$  into the following compounds ?

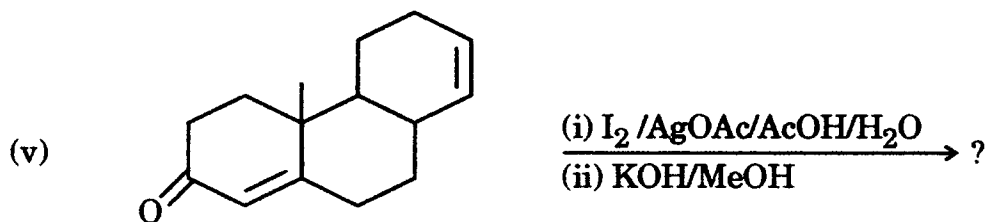
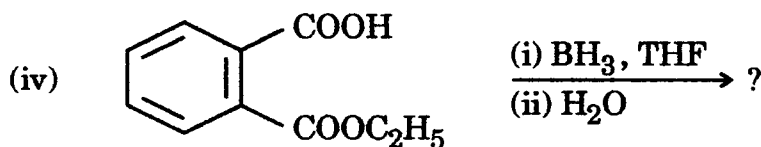
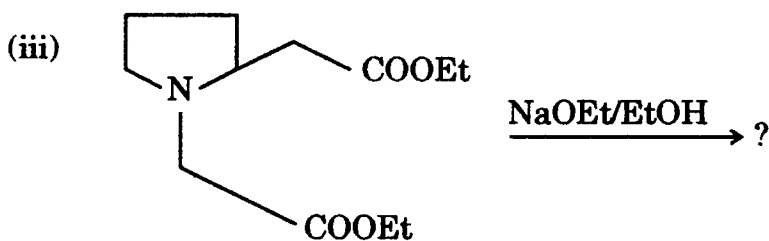
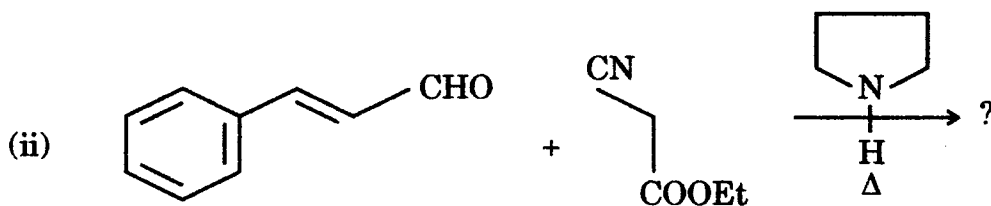
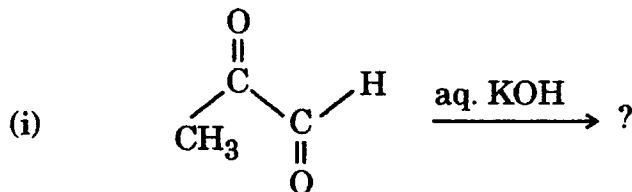
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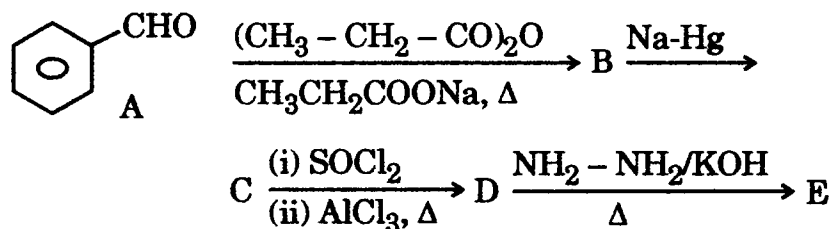
- (c) Arrange the following carbonyl compounds in order of their increasing carbonyl stretching frequency. Justify your answer. 5



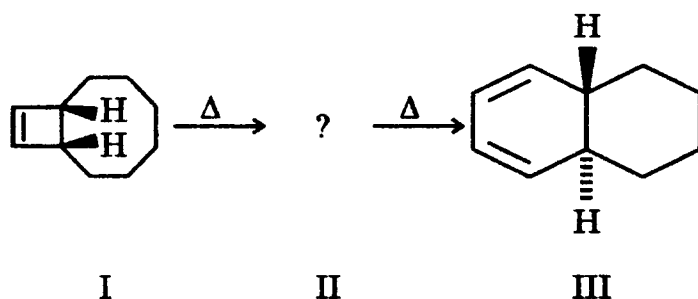
- (d) Identify the structure of the product(s) in the following reactions : 5



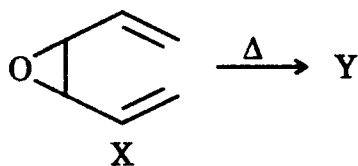
- Q10.** (a) Complete the following reaction and identify the products B, C, D and E. Sketch a plausible mechanism for conversion of A → B. 10



- (b) Predict the intermediate II in the following electrocyclic reaction which involves  $4\pi$  and  $6\pi$  electron system. Propose mechanism with suitable explanation. 5



- (c) Identify the product Y for the thermal sigmatropic reaction of X. Name the reaction and give suitable mechanism. 5



- (d) Identify the structure of organic compound which exhibits the following spectral data : 10

MS [m/z] (Relative Intensity) :

194, 196 ( $M^+$ ,  $M^+ + 2$ ), 177, 179 (30), 115 (40), 97 (50), 60 (100).

IR,  $\nu$   $\text{cm}^{-1}$  : 3500 – 2500, 2942, 1711, 1195

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  : 10.6 (1H,  $\text{D}_2\text{O}$  exchangeable), 3.4 (t, 2H),  
2.59 (t, 2H), 1.87 – 1.82 (m, 2H), 1.65 (pent., 2H),  
1.55 (pent., 2H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  : 179, 33.6, 33.4, 32.3, 27.5, 23.7

