SDFG-T-CHM

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_α & K_β peaks of an element, e.g. Zn. *5*

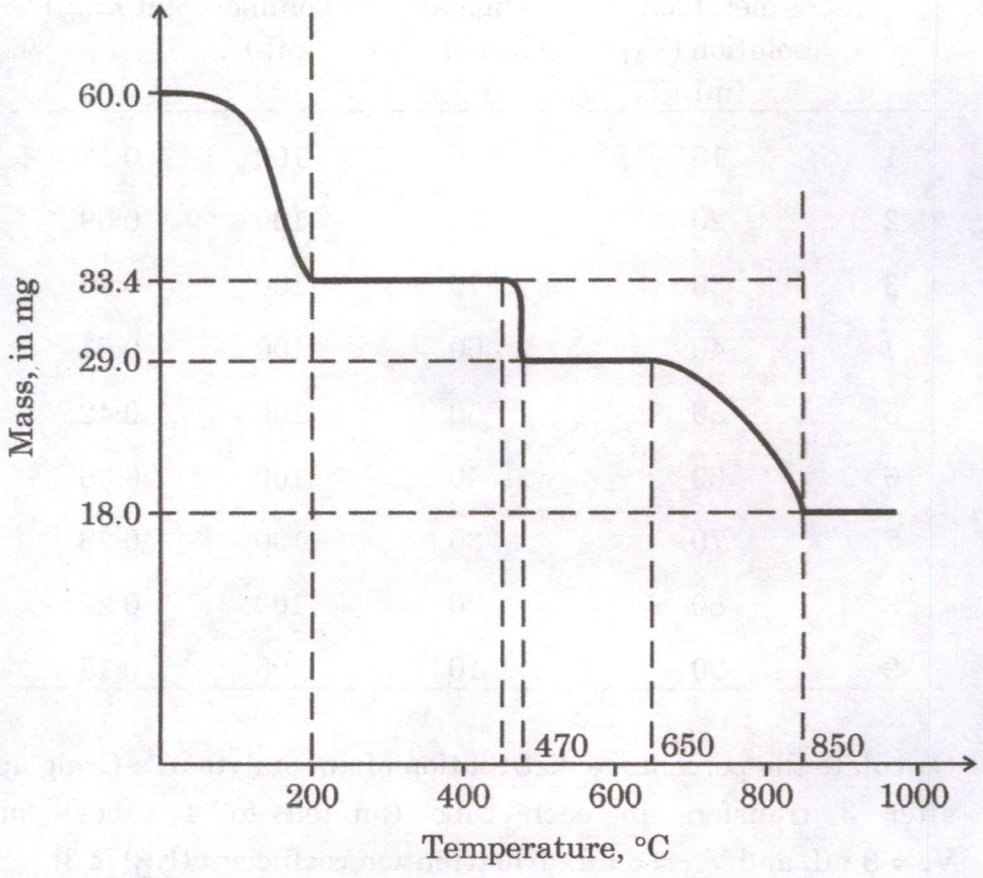
(g) How does high concentration of calcium interfere with ICP-MS analysis of iron ? *5*

(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 µL 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 $CaCO_3$ & $MgCO_3$ (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 Å

K emission line of Ag = 0·497 Å

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 λ_{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°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 kJ/kg/°C

Q4. (a) (i) Powder XRD of a crystalline material exhibited diffractions at 2θ 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 : $\sin 30° = 0{\cdot}5$, $\sin 60° = \frac{\sqrt{3}}{2}$ *5+10=15*

Molecular mass of the material = 60 g/mol

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

$\lambda = 1{\cdot}54$ Å

(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

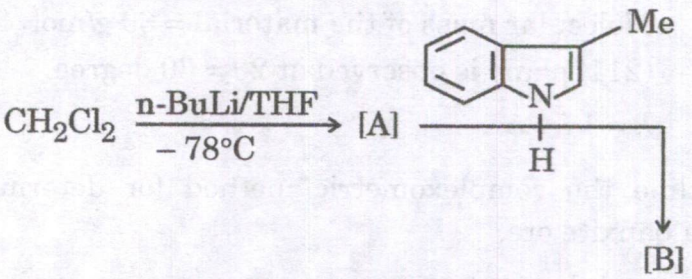
Decide by use of an appropriate 't'-test whether the different results of the two methods are significant at a confidence level of 90%. *10*

Sample Size	't'			
	CONFIDENCE LEVEL			
	90%	95%	99·9%	99·5%
6	1·943	2·447	3·707	4·317

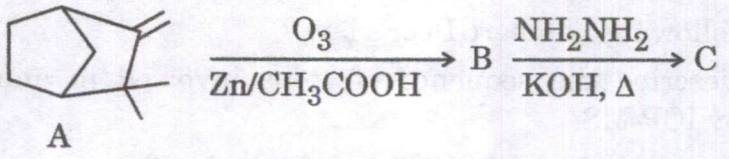
(d) What information is obtained in the analysis of petroleum product by Aniline point and Doctor test, respectively ? *3+2=5*

SECTION B

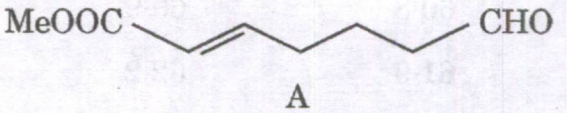
Q6. (a) Predict the product(s) A and B in the following reaction and explain the mechanism involved. *4*



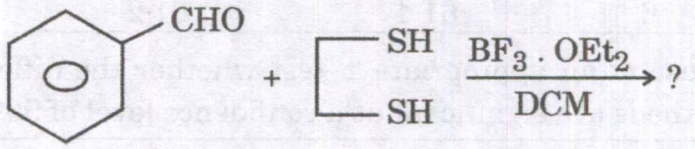
(b) Complete the following reaction and sketch a suitable mechanism for conversion of B → C. *4*



(c) In the following reaction sequence, reaction of aldehyde A with benzylamine followed by sodium borohydride ($NaBH_4$) 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 ? *4*



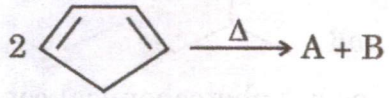
(d) Predict the product of the following reaction and give the plausible mechanism. *4*



(e) Write the product and propose a suitable mechanism for the following reaction : *4*

$$CH_3 - (CH_2)_3 - CH = CH_2 \xrightarrow[NaBH_4, H_2O]{Hg(OAc)_2, CH_3CN} ?$$

(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}H NMR spectrum of two isomeric esters P & Q with molecular formula $C_7H_{14}O_2$ are given below. Identify the structures of P & Q. *4*

Compound P

^{1}H NMR ($CDCl_3$ δ) : 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

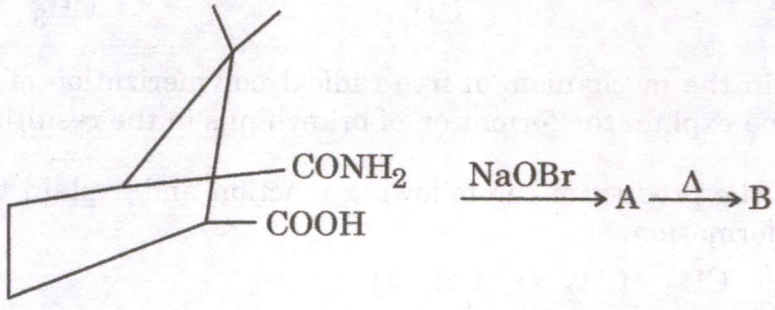
^{1}H NMR ($CDCl_3$ δ) : 2·3 – 2·6 (q, 2H), 1·45 (s, 9H), 1·1 – 1·3 (t, 3H)

(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*

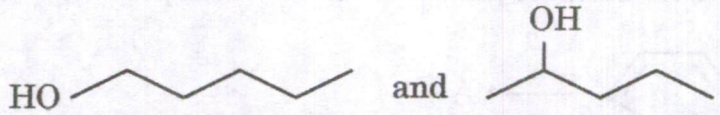
(i) Acetone absorbs at 279 nm in hexane whereas the value of λ_{max} in water is 264·5 nm. Provide a suitable justification to your answer. *4*

(j) Mass spectrum of Butyrophenone shows two peaks m/z 106 and 120 due to McLafferty rearrangement. Justify your answer. *4*

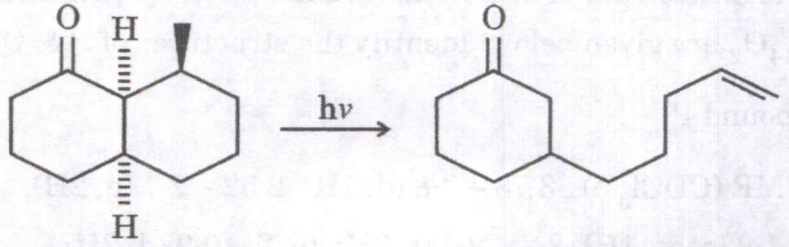
Q7. (a) Complete and outline the mechanism of the following reaction. How will you establish that Hofmann rearrangement is intermolecular in nature ? *10*



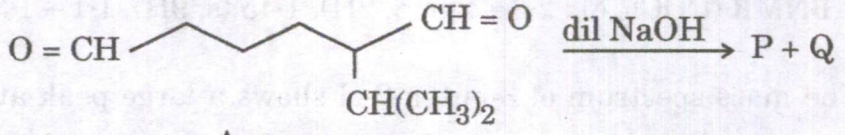
(b) How would you differentiate between the following pairs of alcohols with the help of mass spectrometry ? 5



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

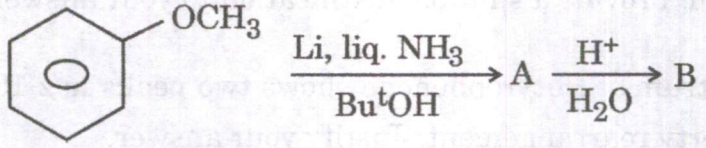


(d) Base catalyzed condensation of dialdehyde A can result in the formation of two products (P, Q). Identify the two products. Which one is actually obtained and why ? Also give the mechanism of its formation. 10

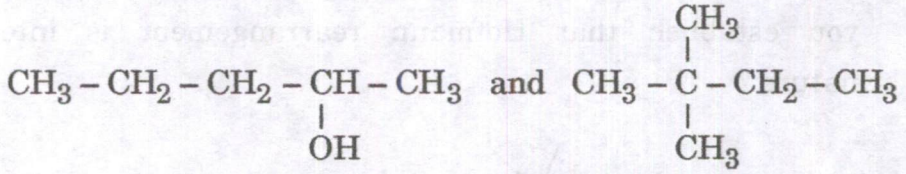


A

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

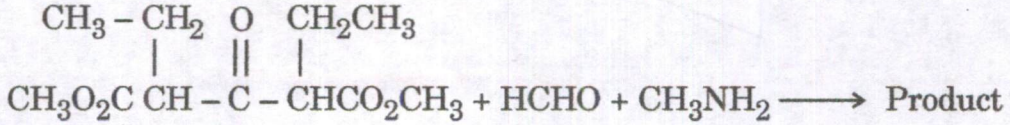


(b) How could the following pairs of isomeric compounds be differentiated by mass spectrometry ? 5

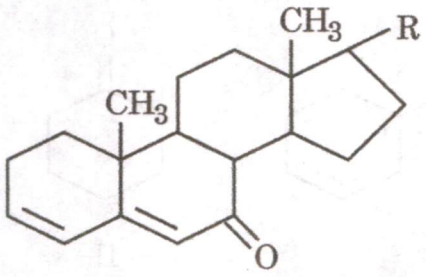


(c) Explain the mechanism of free radical polymerization of ethylene. How will you explain the formation of branchings in the resulting polymer ? 5

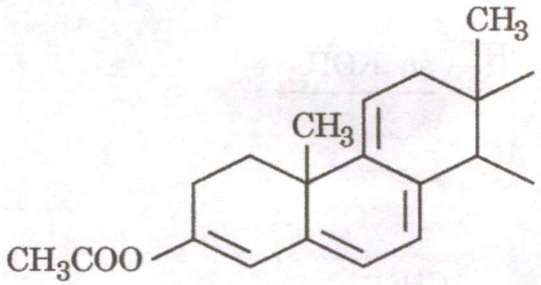
(d) Write the product of the following reaction and explain the mechanism of its formation. 10



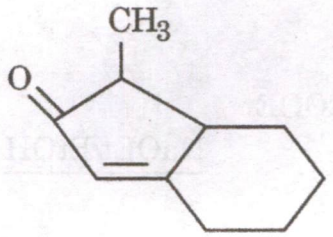
Q9. (a) Using Woodward's rules, calculate the λ_{max} value for the following compounds : *10*



I



II



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 ? *10*

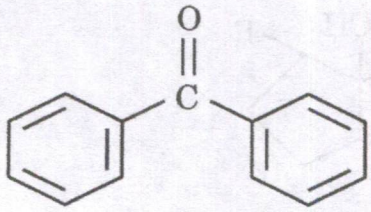
(i) $R - CH_2 - CH_2 - CHO$

(ii) $R - CH_2 - CH_2 - \overset{\overset{O}{\|}}{C} - CH_2 - CH_2 - R$

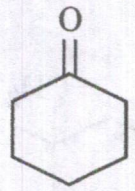
(iii) $R - CH_2 - CH_2 - OH$

(iv) $(R - CH_2\,CH_2)_3 - C - OH$

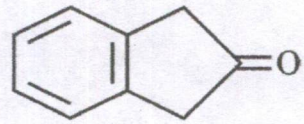
(c) Arrange the following carbonyl compounds in order of their increasing carbonyl stretching frequency. Justify your answer. 5



I

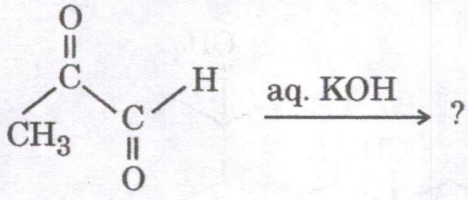


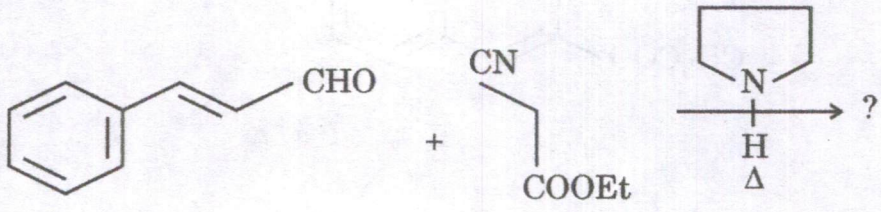
II

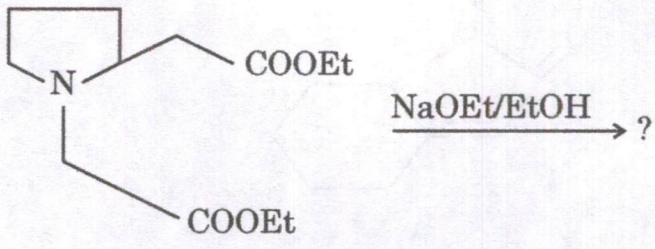


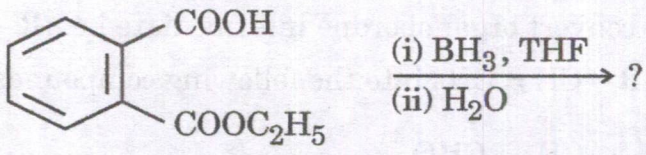
III

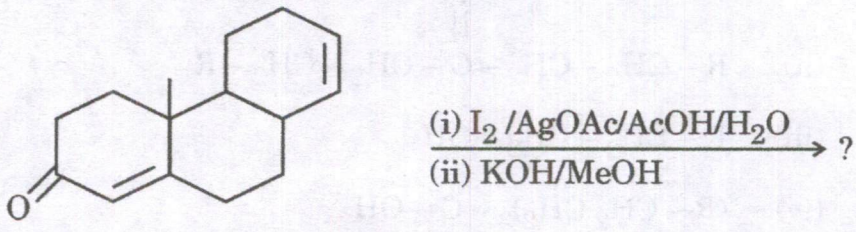
(d) Identify the structure of the product(s) in the following reactions : 5

(i) 

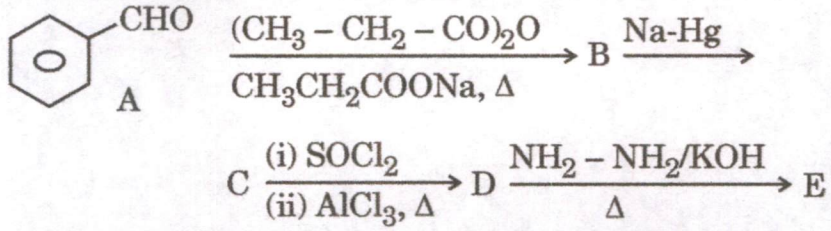
(ii) 

(iii) 

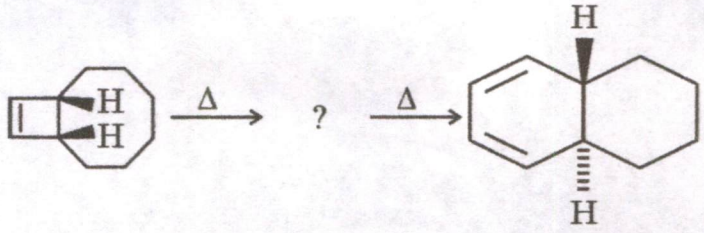
(iv) 

(v) 

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*

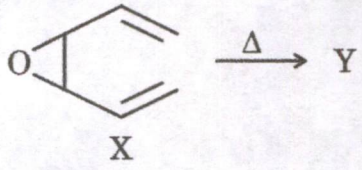


(b) Predict the intermediate II in the following electrocyclic reaction which involves 4π and 6π electron system. Propose mechanism with suitable explanation. *5*



I II III

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



X

(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, ν cm^{-1} : 3500 – 2500, 2942, 1711, 1195

^1H NMR ($CDCl_3$) δ : 10·6 (1H, D_2O exchangeable), 3·4 (t, 2H), 2·59 (t, 2H), 1·87 – 1·82 (m, 2H), 1·65 (pent., 2H), 1·55 (pent., 2H).

^{13}C NMR ($CDCl_3$) δ : 179, 33·6, 33·4, 32·3, 27·5, 23·7