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) Define the terms "Accuracy" and "Precision" in quantitative analysis. *5*

(b) Mention the stationary phase and mobile phase in Gas Liquid Chromatography (GLC). What factors are involved in selecting a carrier gas in GLC ? *5*

(c) Some instrumental analytical techniques are listed in Column I. Name of sources and transducers or detection systems are listed in Column II. Items in Column I may match with one or more items in Column II. Match the items in Column I with those in Column II. *5*

Column I	*Column II*
(i) Infrared spectrophotometry	(p) Lead sulphide
(ii) X-ray fluorescence spectroscopy	(q) Photomultiplier tube
(iii) Atomic absorption spectroscopy	(r) In Ga As P
(iv) Inductively coupled plasma-mass spectrometry	(s) Electrode discharge lamp
	(t) Quadrupole magnetic analyzer
	(u) Deuterated triglycine sulphate
	(v) Molybdenum
	(w) Nernst glower
	(x) Faraday cup

(d) Describe the atomization method for determining mercury at parts per billion level concentrations by AAS. *5*

(e) Mention the different components in the instrument for thermogravimetric analysis. *5*

(f) How are X-rays generated by certain radioactive isotopes ? *5*

(g) How is plasma of required high temperature generated in ICP-MS ? *5*

(h) Describe the volumetric method for estimation of Mn in pyrolusite. *5*

Q2. (a) Describe the method (sample dissolution, chemical reactions and the steps involved) for estimating Cr and Mn in steel spectrophotometrically. *15*

(b) Compounds X and Y are separated by passing through a suitable chromatographic column of 30 cm length. Un-retained species passes through the column in 1·5 minutes.

Use the following data to determine the : *10*

(i) Column resolution

(ii) Average number of theoretical plates in the column

(iii) Plate height

(iv) Length of a new column to achieve a column resolution of 1·0

(v) Time required to elute the slowest moving compound through the new column

Compound	Retention Time	Peak width at the base
X	14·5 minutes	1·2 minutes
Y	15·2 minutes	1·3 minutes

(c) Determine the theoretical slit width (in mm, up to 3 decimal places) required for separating the sodium lines at wavelengths 588·9950 nm and 589·5924 nm, using grating monochromator with a reciprocal linear dispersion of 0·67 nm/mm. *5*

Q3. (a) Silver crystallizes in cubic form. The powder XRD pattern of silver recorded using Cu K_α (1·541 Å) exhibited first six lines at 2θ values of 38·16°, 44·34°, 64·52°, 77·48°, 81·64° and 98·00°.

Determine the density of silver in g/cm^3. *15*

Given : Atomic weight of Ag = 108 g/mol.

(b) Describe the direct and indirect methods for the estimation of lead in petrol. *10*

(c) What fuel and oxidant combination should be used in AAS for

(i) attaining flame temperature of 1800°C with maximum burning velocity of 40 cm/s ?

(ii) attaining flame temperature of 3000°C with burning velocity of 2000 cm/s ? $2\frac{1}{2}+2\frac{1}{2}=5$

Q4. (a) The equilibrium constant for the given conjugate acid-base pair is $2{\cdot}5 \times 10^{-5}$:

$$HIn + H_2O \rightleftharpoons In^- + H_3O^+$$

Determine the absorbance at 430 nm for the concentration of HIn = $3{\cdot}0 \times 10^{-4}$ M (up to 3 decimal places), using the following data : *15*

Species	Absorption Maximum (nm)	Molar Absorptivity	
		430 nm	600 nm
HIn	430	$4{\cdot}0 \times 10^3$	$7{\cdot}25 \times 10^2$
In^-	600	$3{\cdot}0 \times 10^2$	$9{\cdot}65 \times 10^3$

Given : Path length of the cuvette = 1 cm

Molar absorptivity in M^{-1} cm^{-1}

(b) Briefly describe the methods used for proximate analysis of coal. *10*

(c) Using a thermogram, describe the thermal decomposition events of calcium oxalate monohydrate in the temperature range between 25°C and 1000°C. *5*

Q5. (a) The accuracy of a new spectrophotometric method for determining uranyl ions in aqueous medium is tested by comparing with a reference method. The results are given below :

New Method (in ppm)	Reference Method (in ppm)
20·5	20·2
21·3	19·2
18·6	21·4
19·5	19·9
18·1	20·8
20·9	

Is there any statistical difference between the two methods at 95% confidence level ? Justify. *15*

(F-table and T-table are given)

Values of t for v Degrees of Freedom for Various Confidence Levels

	Confidence Level			
v	90%	95%	99%	99·5%
1	6·314	12·706	63·657	127·32
2	2·920	4·303	9·925	14·089
3	2·353	3·182	5·841	7·453
4	2·132	2·776	4·604	5·598
5	2·015	2·571	4·032	4·773
6	1·943	2·447	3·707	4·317
7	1·895	2·365	3·500	4·029
8	1·860	2·306	3·355	3·832
9	1·833	2·262	3·250	3·690
10	1·812	2·228	3·169	3·581
15	1·753	2·131	2·947	3·252
20	1·725	2·086	2·845	3·153
25	1·708	2·060	2·787	3·078
∞	1·645	1·960	2·576	2·807

Values of F at the 95% Confidence Level

	$v_1 = 2$	3	4	5	6	7	8	9	10
$v_2 = 2$	19·0	19·2	19·2	19·3	19·3	19·4	19·4	19·4	19·4
3	9·55	9·28	9·12	9·01	8·94	8·89	8·85	8·81	8·79
4	6·94	6·59	6·39	6·26	6·16	6·09	6·04	6·00	5·96
5	5·79	5·41	5·19	5·05	4·95	4·88	4·82	4·77	4·74
6	5·14	4·76	4·53	4·39	4·28	4·21	4·15	4·10	4·06
7	4·74	4·35	4·12	3·97	3·87	3·79	3·73	3·68	3·64
8	4·46	4·07	3·84	3·69	3·58	3·50	3·44	3·39	3·35
9	4·26	3·86	3·63	3·48	3·37	3·29	3·23	3·18	3·14
10	4·10	3·71	3·48	3·33	3·22	3·14	3·07	3·02	2·98
15	3·68	3·29	3·06	2·90	2·79	2·71	2·64	2·59	2·54
20	3·49	3·10	2·87	2·71	2·60	2·51	2·45	2·39	2·35
30	3·32	2·92	2·69	2·53	2·42	2·33	2·27	2·21	2·16

(b) Calculate the weight of Fe(III) left unextracted from a 100 mL aqueous solution having 500 mg of Fe^{3+} ion in 6 N HCl after three extractions with 10 mL of diethyl ether in each go. *10*

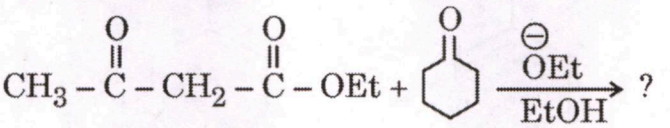
[Given : The distribution ratio between water and diethyl ether is 150]

(c) Draw a schematic diagram representing a typical double beam design of a flame type spectrophotometer used in AAS instrument. *5*

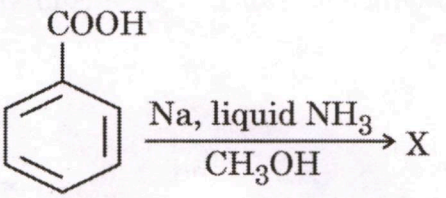
SECTION B

Q6. (a) Cyclohexanone is known to undergo self-condensation reaction when treated with aqueous NaOH. However, no such reaction is observed when treated with LDA (Lithium-diisopropylamide). Give proper reasoning. *4*

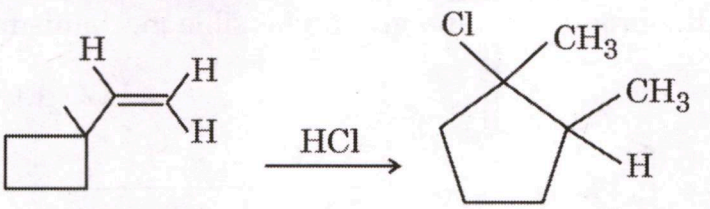
(b) Write the structure of product(s) formed in the following conversion and mention the steps involved. Identify the name of the reaction. *4*



(c) Identify the product (X). Name the reaction and give the plausible mechanism. *4*



(d) Write the mechanism for the following conversion : *4*

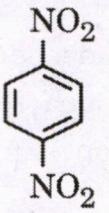


(e) The reaction of cyclopentadiene with maleic anhydride on heating can form two possible products, but only one is formed in major quantity. Write the structure of the two products and give suitable explanation. *4*

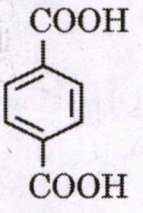
(f) Aniline absorbs at 280 nm (ε_{max} 8600), but in acidic solution, the main absorption band is observed at 203 nm (ε_{max} 7500). Provide a suitable explanation. *4*

(Unit of ε_{max} is $M^{-1}\ cm^{-1}$)

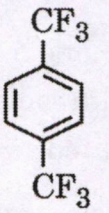
(g) Arrange the following compounds in the increasing order of chemical shift value (δ) of aromatic protons. Justify your answer. *4*



I

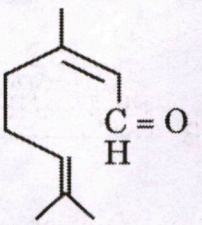


II

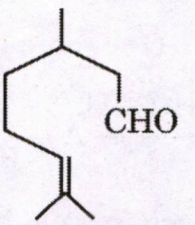


III

(h) How can you distinguish between citral and citronellal on the basis of their IR spectra ? *4*

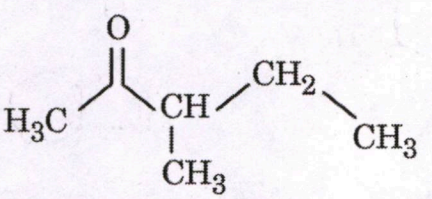


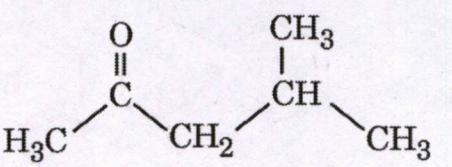
Citral



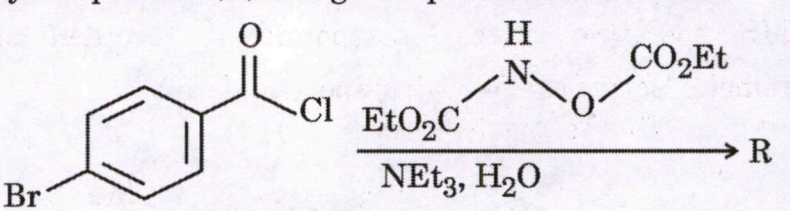
Citronellal

(i) How can the following pairs of isomeric compounds be differentiated by mass spectrometry ? *4*



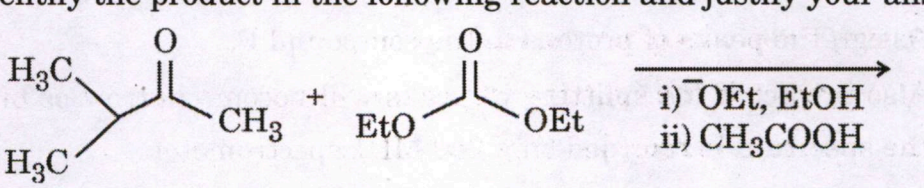
and


(j) Identify the product (R) and give a plausible mechanism. *4*

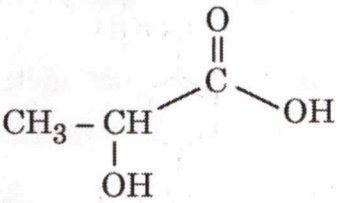


Q7. (a) Write the structure of the polymer formed and the stepwise mechanism involved when acetylene is treated with Ziegler-Natta catalyst. Comment if the product formed is conducting or non-conducting. *10*

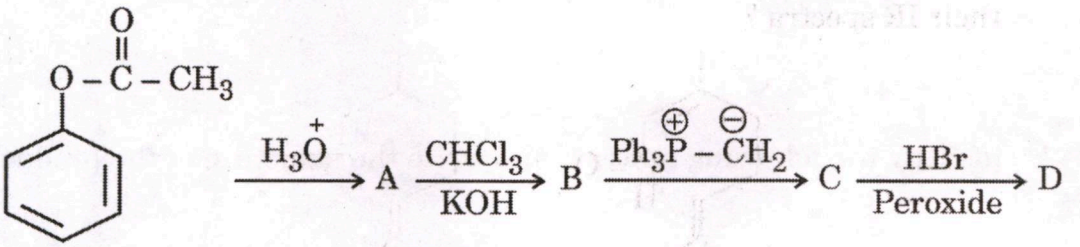
(b) Identify the product in the following reaction and justify your answer : *5*



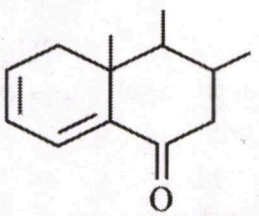
(c) How can the following compound be prepared from a carbonyl compound that has one less carbon than the designed product ? *5*



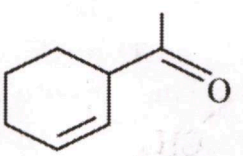
(d) Complete the following reaction and sketch a suitable mechanism for conversion of A → B and B → C : *10*



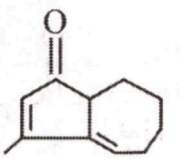
Q8. (a) Calculate the λ_{max} value for the following compounds, using Woodward rules : *10*



I

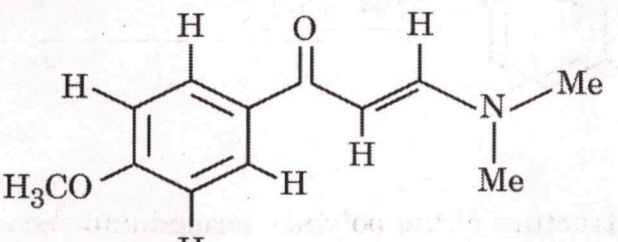


II



III

(b) ^{1}H NMR spectrum of the compound P recorded on a 90 MHz spectrometer shows the following spectral data :



P

δ 3·02 (s, 6H), 3·91 (s, 3H), 5·80 (d, J = 12·3 Hz, 1H),

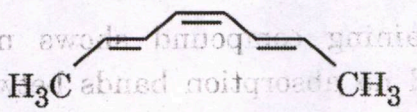
6·95 (d, J = 8·8 Hz, 1H), 7·80 (d, J = 8·8 Hz, 1H), 8·00 (d, J = 12·3 Hz, 1H)

Assign the peaks of protons in the compound P.

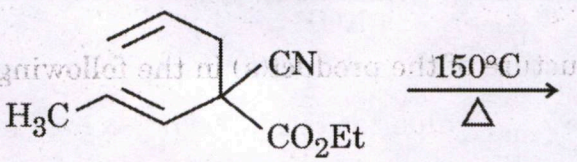
Also predict if the splitting in peaks will become narrow or broad when the spectrum is recorded on a 300 MHz spectrometer. *5*

(c) Will a concerted reaction take place between 1,3-butadiene and 2-cyclohexenone in the presence of ultraviolet light ? Explain. *5*

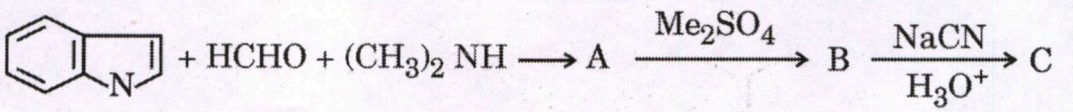
(d) Predict the structure of the product including stereochemical aspects based on orbital symmetry principles for the following reaction : *5*

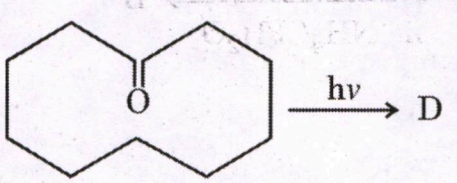


(e) Identify the following reaction and write the structure of the product. *5*

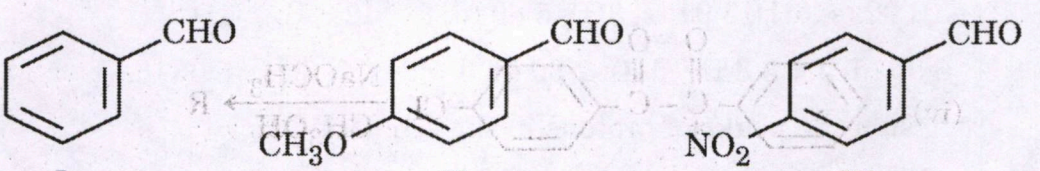


Q9. (a) Predict the products C and D in the given reaction schemes (i and ii). Provide suitable mechanisms for both the schemes. *10*

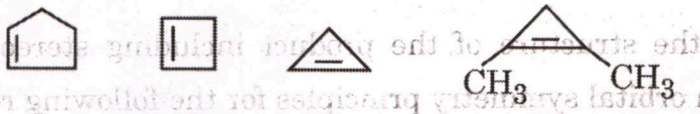
(i) 

(ii) 

(b) Compare the rate of Cannizzaro's reaction for the following aromatic aldehydes and justify your answer : *5*



(c) (i) Arrange the following compounds in order of increasing value of C = C stretching frequency :

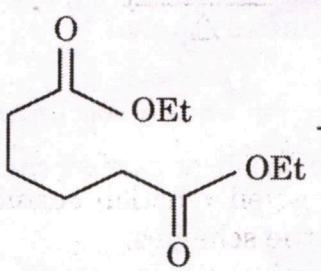


I II III IV

(ii) A nitrogen containing compound shows no absorption band at 3400 cm^{-1} and no absorption bands between 1700 cm^{-1} and 1600 cm^{-1}. What class of compound is it ? *5*

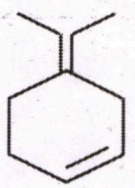
(d) Write the structure of the product(s) in the following conversions : *10*

(i)



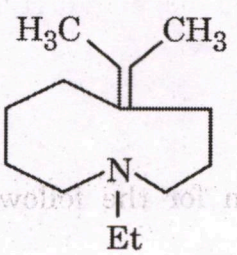
$\xrightarrow[EtOH]{NaOEt}$ P $\xrightarrow[\Delta]{\text{dilute HCl}}$ Q

(ii)



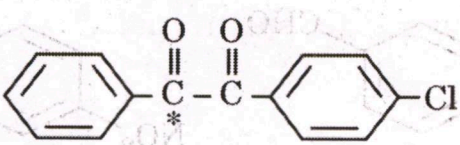
$\xrightarrow{mCPBA}$ A $\xrightarrow[ii.\ NH_4Cl/H_2O]{i.\ LiAlH_4}$ B

(iii)



$\xrightarrow{OsO_4}$ M $\xrightarrow{NaIO_4}$ N

(iv)

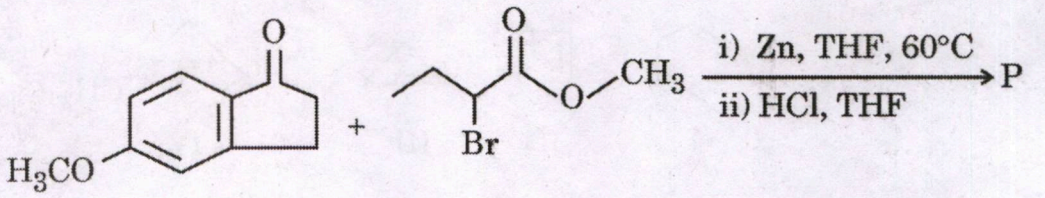


$\xrightarrow[CH_3OH]{NaOCH_3}$ R

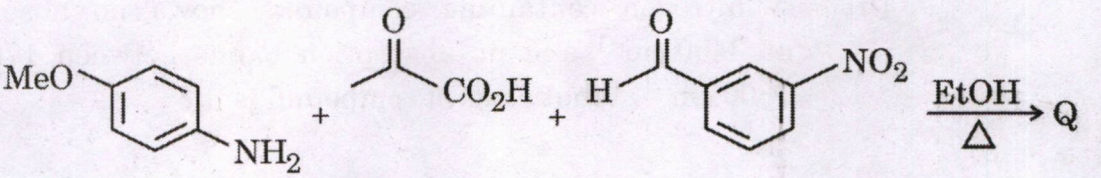
* : Labelled carbon

Q10. (a) Write the structure of final products (P and Q) in the following reactions : *10*

(i)



(ii)



(b) Describe the electronic transitions in acrylaldehyde. Comment if these are allowed or forbidden and the changes observed in UV spectrum when the solvent is changed from hexane to ethanol. *5*

(c) [1, 3] sigmatropic migration of hydrogen cannot occur under thermal conditions, but [1, 3] sigmatropic migration of carbon can. Justify your answer. *5*

(d) On treating acetone with a base, a higher-boiling liquid (b.p. 130°C) can be isolated from the reaction mixture. The spectral data of this liquid are :

IR : 1620 cm^{-1} (m), 1695 cm^{-1} (s)

^1H NMR : δ 1·9 (3H, singlet), 2·1 (6H, singlet), 6·15 (1H, singlet)

UV : λ_{max} 235 nm

^{13}C NMR : δ 20, 27, 31, 124, 154 and 197

Mass : m/z (RA) 55 (100), 83 (90), 43 (78), 98 (49), 29 (46), 39 (43), 27 (42), 53 (13), 41 (13), 28 (8)

Deduce the structure and interpret the spectral data. *10*