

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 Booklet must be clearly struck off.

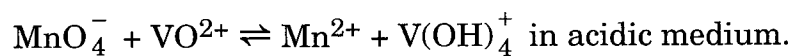
*Answers must be written in **ENGLISH** only.*

SECTION A

- Q1.** (a) Round the following answers so that only significant figures are obtained : 1×5=5
- (i) $2.4 + 0.010 + 6.24 = 8.65$
 - (ii) $3.6 - 0.020 - 5.14 = -1.56$
 - (iii) $(22 \times 5.42) \div 100.0 = 1.19$
 - (iv) $\log 5.000 \times 10^{-4} = -3.3010299$
 - (v) $\text{Antilog } 12.5 = 3.1622277 \times 10^{12}$
- (b) Particle diameter of stationary phase plays a critical role in chromatographic separations. Comment. 5
- (c) Draw and state schematic diagram of non-dispersive IR photometer for monitoring CO in the air sample. 5
- (d) Sketch the thermobalance used in TGA showing its key components. 5
- (e) In X-ray fluorescence technique, matrix effects interfere in sample analysis. Comment and justify your answer. 5
- (f) Describe three ways of introducing a sample into an ICP torch. 5
- (g) How does CaCl_2 transform into excited Ca^{0*} during process occurring in flame? Show schematically. 5
- (h) How will you determine chromium ions spectrophotometrically in a mineral sample? 5
- Q2.** (a) The solubility product (K_{sp}) of a salt is $(41.2 \pm 0.3) \times 10^{-8}$. The molar solubility of salt in water is
- $$\begin{aligned}\text{Solubility} &= (K_{sp})^{1/2} = (41.2 \times 10^{-8})^{1/2} \\ &= 6.418 \times 10^{-4} \text{ M}\end{aligned}$$
- What is the uncertainty in the calculated solubility of salt in water? 5
- (b) Describe the equilibrium processes involved in solvent extraction of metal ions through chelation. Write the effect of pH and reagent concentration on the solvent extraction of a metal chelate. 10
- (c) How will you determine the stoichiometry of metal : ligand in an iron (II) – 1,10-phenanthroline complex using slope-ratio and mole-ratio methods? 10
- (d) List the ways of calibrating TGA instrument. 5

- Q3.** (a) How will you analyse the mixture containing $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, $\text{BaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ by thermogravimetry ? State the strategy in brief. 10
- (b) What are the advantages of temperature programming and pressure programming in Gas Chromatography (GC) ? 5
- (c) In atomic/absorption spectrometry, plasma sources are preferred over flame sources. Why ? 5
- (d) How will you determine moisture content in a sample using Karl-Fisher reagent ? Describe the reactions involved in the method suggested. 3+7=10
- Q4.** (a) Define Specific Surface Area (SSA).
A solid cube weighing 2.0 g was divided into 1000 smaller cubes. If the solid cube is having volume 1 cm^3 , calculate SSA of the smaller cube. 5
- (b) A sample of feldspar weighing 0.5140 g was found to contain 0.0812 g of total of chlorides of sodium and potassium. On further treatment, it gave 0.1450 g of potassium hexachloroplatinate precipitates [FW = 485.95]. Find out % of Na_2O in the feldspar sample. 10
[$\text{K}_2\text{O} = 94$, $\text{Na}_2\text{O} = 62$, $\text{NaCl} = 58.5$, $\text{KCl} = 75.5$]
- (c) (i) Write the common practice to prepare TLC plates in laboratory. Name the reagents used for spot detection. 5
- (ii) Discuss the advantages and disadvantages of alumina (Al_2O_3) as stationary phase in TLC. 5
- (d) A 5.00 mL sample was treated with reagent to generate a colour with phosphate. Subsequently the sample was diluted to 100 mL. To a second 5.00 mL sample was added exactly 10.00 mL of a phosphate solution containing 0.05 mg phosphate/mL, which was treated in the same way as the original sample. The absorbance of the first solution was 0.525 and that of the second was 0.635. Calculate the concentration of phosphate in mg/mL of the sample. 5
- Q5.** (a) A mixture containing 8-hydroxyquinoline-complexes (AlQ_3 and MgQ_2) of aluminium and magnesium weighed 1.0981 g. They left the mixture of Al_2O_3 and MgO as a residue weighing 0.1354 g, when ignited in the air. [$\text{Al}_2\text{O}_3 = 101.96$, $\text{MgO} = 40.30$, $\text{AlQ}_3 = 459.44$, $\text{MgQ}_2 = 312.61$] 5
- (b) Describe spectrophotometric analysis of
- (i) A sample containing one absorbing component.
- (ii) A sample containing two absorbing components. 10

- (c) Derive a balanced chemical reaction for the redox reaction



5

- (d) Determination of vitamin in a food sample was carried out by a routine voltammetric method and by Flow Injection Analysis (FIA). Following results were obtained :

Sample	Voltammetry	FIA
1	32.1	31.9
2	32.3	31.8
3	31.9	31.7
4	32.1	31.8
5	32.0	31.6
6	32.1	31.9
7	31.8	31.8

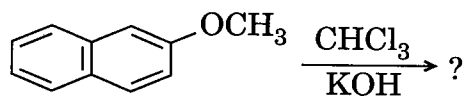
Compare the precision of two methods by means of an 'F'-test at a significant level of $\alpha = 0.05$. Decide by use of an appropriate 't'-test whether the different results of the two methods are significant at a level of $\alpha = 0.05$.

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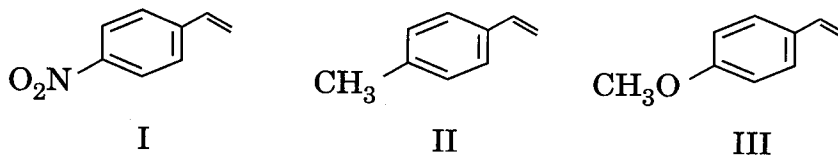
Sample size	t		
	$\alpha = 0.10$	$\alpha = 0.05$	$\alpha = 0.025$
7	1.415	1.895	2.365

SECTION B

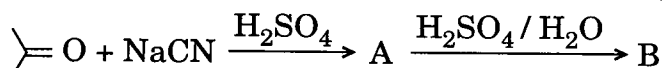
- Q6. (a) Give the product in the following transformation : 4



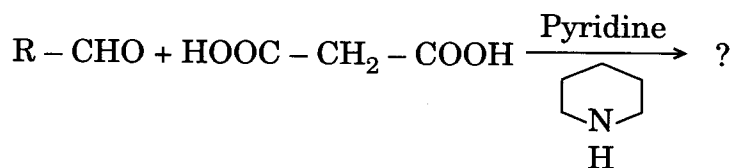
- (b) List the following monomers in order of decreasing ability to undergo anionic polymerisation : 4



- (c) Identify the compounds A and B in the following sequence of reactions : 4

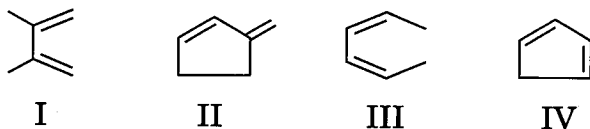


- (d) Write the possible product(s) in the following chemical reaction : 4

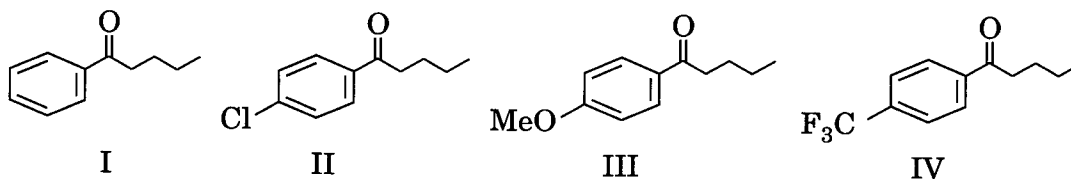


- (e) What product is formed by the treatment of 3,3-dimethylbut-1-ene with aq. H_2SO_4 ? 4

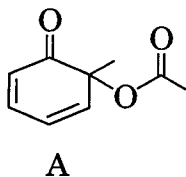
- (f) List the following dienes in order of decreasing reactivity in a Diels-Alder reaction : 4



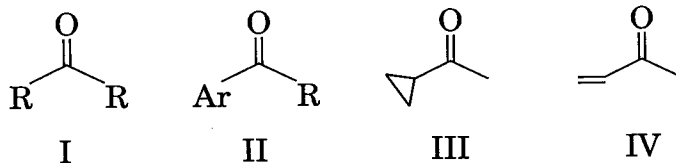
- (g) Arrange the following compounds in order of their decreasing reactivity towards Norrish type-II process : 4



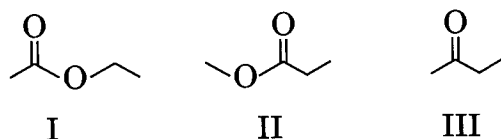
- (h) Predict the λ_{max} for the compound A : 4



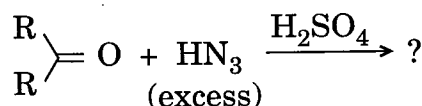
- (i) Arrange the following compounds in order of their decreasing C = O stretching vibrational frequencies : 4



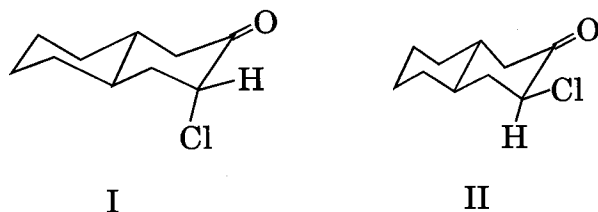
- (j) How can you distinguish the following compounds by ^1H NMR spectroscopy ? 4



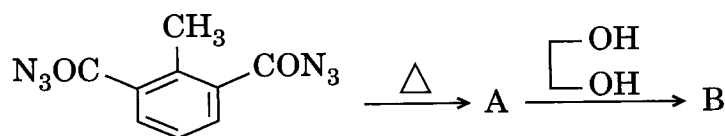
- Q7.** (a) Complete the following reaction giving the plausible mechanism : 10



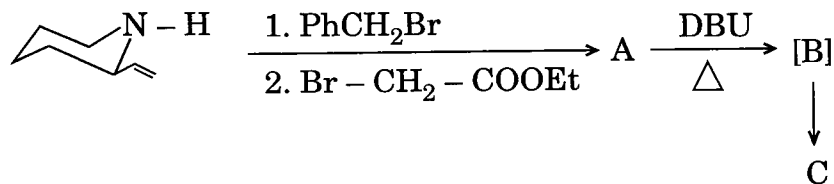
- (b) Distinguish the following compounds by IR spectroscopy : 5



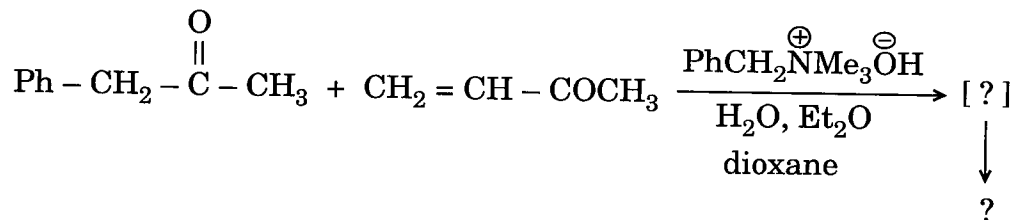
- (c) Identify the species A and B in the following reaction sequence : 5



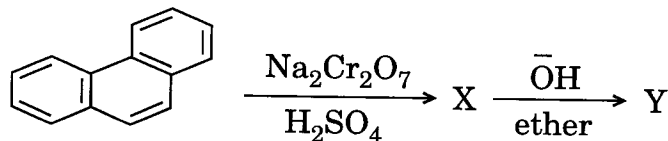
- (d) Complete the following reaction along with the mechanism of formation of B and C from A : 10



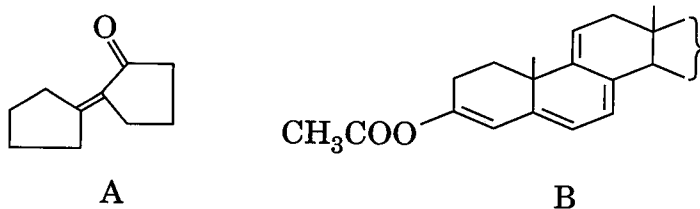
- Q8. (a) Complete the following sequence of reactions with mechanism : 10



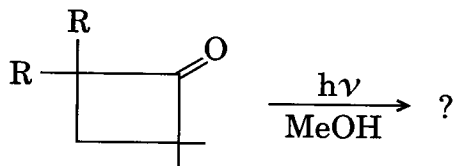
- (b) Identify the products X and Y below. And predict the plausible mechanism for the formation of "Y" from "X". 10



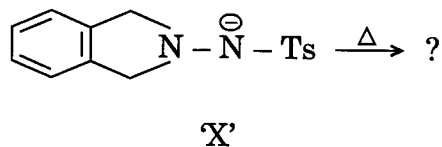
- (c) Calculate the λ_{max} of A and B using Woodward-Fieser rules. 10



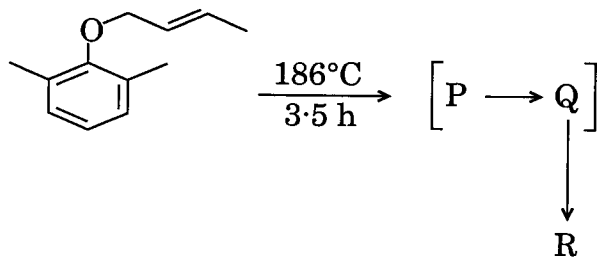
- Q9. (a) Complete the following reaction and give its mechanism : 10



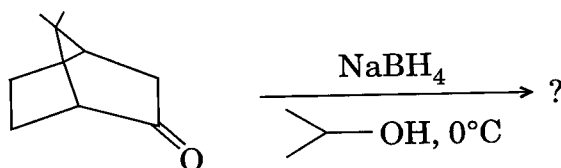
- (b) What happens when the anion 'X' is subjected to heating? Complete the reaction with mechanism. 5



- (c) Identify P, Q and R in the following sequence along with suitable mechanism description : 5



- (d) Invoking the idea of stereoselectivity, write the product(s) with proper justification in the following transformation : 10



- Q10.** (a) Identify the organic compound which exhibits the following spectral data : 10

UV ($\lambda_{\text{max}}^{\text{EtOH}}$) at pH 7.0 = 263 nm ($\log \epsilon_{\text{max}} = 4.2$); 300 nm ($\log \epsilon_{\text{max}} = 3.6$)

at pH 13.0 = 288 nm ($\log \epsilon_{\text{max}} = 4.0$); 315 nm ($\log \epsilon_{\text{max}} = 3.8$)

IR ($\nu_{\text{max}}^{\text{cm}^{-1}}$) = 3510, 3030, 2910, 1595, 1430, 1220, 1010.

Mass (m/z) = 164 (M^+ , 100%), 165 ($M+1$), 166 ($M+2$)

$^1\text{H NMR}$ (500 MHz, CDCl_3) = δ 6.82 (dd, $J = 8.3, 2.0$ Hz, 1H)

6.78 (d, $J = 2.0$ Hz, 1H),

6.74 (d, $J = 8.3$ Hz, 1H),

6.35 (d, $J = 14.5$ Hz, 1H), 6.0 (s, 1H)

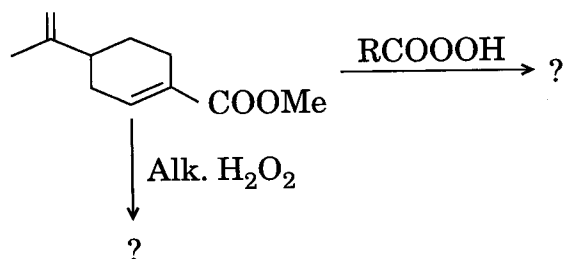
5.67 (dq, $J = 14.5, 6.3$ Hz, 1H)

3.93 (s, 3H), 1.87 (d, $J = 6.3$ Hz, 3H)

$^{13}\text{C NMR}$ (125 MHz) = δ 146.67, 144.94, 130.92, 130.78, 123.35,

119.44, 114.50, 108.10, 55.86, 18.26

- (b) Explain the reactive behaviour of 2,3-di-*t*-butylbuta-1,3-diene and 1,3-di-*t*-butylbuta-1,3-diene as diene for Diels-Alder reaction. 5
- (c) Carry out the following transformations with proper reasoning : 10



- (d) Outline the mass spectral fragmentation of cyclohexanone for the peaks at $m/z = 98, 70, 83, 55$ and 42 . 5