MPSC

Forest Service (Mains)

Previous Year Paper

(Chemistry)

15 May, 2025

महाराष्ट्र वन सेवा मुख्य परीक्षा - 2024 दिनांक - 9 5 मे, 2024

2024

K20

BOOKLET NO.
340051

Forest Services

Chemistry

Time Allowed : Three Hours **Maximum Marks : 200**

Medium : English **Type of Paper : Conventional**

Question Paper Specific Instructions

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

1. There are **EIGHT** questions divided in two Sections, out of which **FIVE** are to be attempted.
2. Questions no. 1 and 5 are compulsory. Out of the remaining questions, THREE are to be attempted choosing at least ONE question from each Section.
3. The number of marks carried by a question/sub question is indicated against it.
4. Keep in mind the word limit indicated in the question if any.
5. Wherever option has been given, only the required number of responses in the serial order attempted shall be assessed. Unless struck off, attempt of a question shall be counted even if attempted partly. Excess responses shall not be assessed and shall be ignored.
6. Candidates are expected to answer all the sub-questions of a question together. If sub-question of a question is attempted elsewhere (after leaving a few page or after attempting another question) the later sub-question shall be overlooked.
7. Any page or portion of the page left blank in the Answer Booklet must be clearly struck off.
8. Unless otherwise mentioned, symbol and notation have their usual standard meanings. Assume suitable data, if necessary and indicate the same clearly.
9. Neat sketches may be drawn, wherever required.
10. The medium of answer should be mentioned on the answer book as claimed in the application and printed on admission card. The answers written in medium other than the authorized medium will not be assessed and no marks will be assigned to them.

Note – 1. Candidates will be allowed to use Scientific (Non-programmable type) calculators.

SEAL

P.T.O.

SECTION – A

Q1. Solve **any five** from seven.

(a) Calculate the EAN value of the central metal cation the following. **(8×5=40)**

i) $[Zn(NH_3)_4]^{2+}$

ii) $[CoF_6]^{3-}$

iii) $[Ni(NH_3)_6]^{2+}$

iv) $[Fe(CN)_6]^{4-}$

(b) State and explain first law of thermodynamics.

(c) Write short notes on 'Galvanic cell'.

(d) i) A first order reaction takes 60.3 minutes for 50% completion. How much time will be needed for 80% completion ?

ii) The half life period of first order reaction is 60 minutes. Calculate the time required for 87.5% completion of the reaction.

(e) What are Quantum numbers ? What are their properties ? Explain the shape s, p, d and f orbitals with reference to structure of atom.

(f) What is phase rule ? What are its advantages and limitations ? Define the phase diagram one component system and explain the terms involved in it.

(g) Discuss the Born-Haber cycle for NaCl. What are the applications of Born-Haber cycle ? Derive the relation between lattice energy and 'Madelung' constant.

Q2. (a) Discuss the crystal field splitting of d-orbitals, in tetrahedral and Octahedral ligand field with suitable examples, what are the important postulates of crystal field theory ? Calculate crystal field stabilisation energy (Δo) for d^5 and d^6 configuration in octahedral ligand field. **15**

(b) State and explain third law of thermodynamics. How the evaluation of absolute entropies done on the basis of third law of thermodynamics ? Discuss chemical equilibrium in ideal gas reaction. **15**

(c) Derive 'Clausius – Clapeyron' equation and explain the relationship between the temperature of the liquid and its vapor pressure. **10**

Q3. (a) What is the relationship between 'EMF' of the cell and ionic concentration of the electrolyte ? Explain principle, instrumentation and applications of 'Voltametry' and Polarography. **15**

(b) Derive differential and integrated rate equation for zero, first and second order reactions. What is energy activation ? **15**

(c) What do you understand by the term Quantum mechanics ? Derive time independent 'Schrodingers' wave equation with the meanings of all the terms involved. **10**

Q4. (a) Discuss the basic principles of the united atom method in 'MOT' with suitable examples. Explain the polarity of the bond in the molecule and their dipole moment. **15**

(b) What is lanthanide contraction ? What are the consequences of lanthanide contraction on the properties of lanthanide elements ? Discuss the separation of lanthanide elements using Ion exchange and Solvent extraction method. **15**

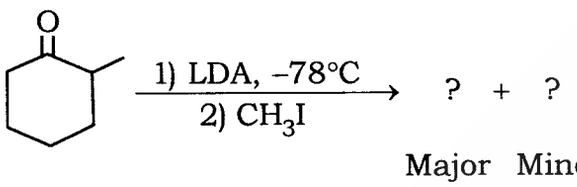
(c) How does 'BET' works ? Explain types of isotherms and surface area determination of Metal-Organic Frame work. **10**

P.T.O.

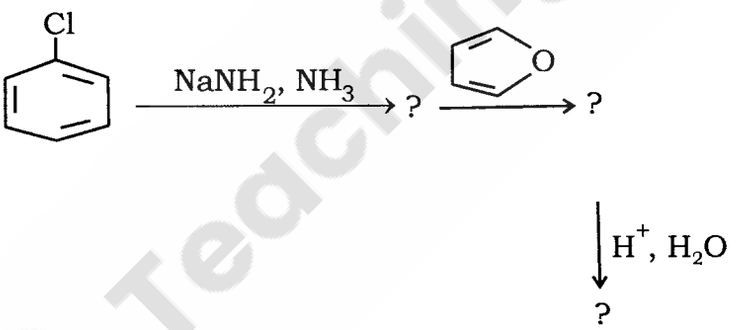
SECTION – B

Q5. Solve **any five** out of seven. **(8×5=40)**

(a) i) Draw the structure of LDA. Identify whether the reaction given below is kinetically or thermodynamically controlled and write the major and minor products formed. **4**



ii) Complete the following reaction and name obtained in step 1. **4**

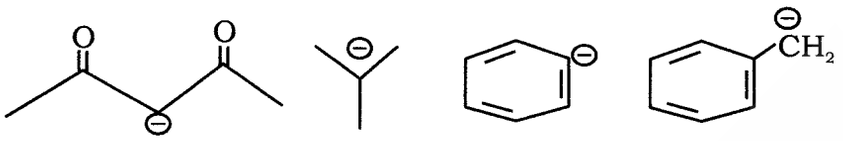


(b) i) Write any two methods for the generation of the following intermediates (write appropriate chemical equations) **4**

I) Carbenes

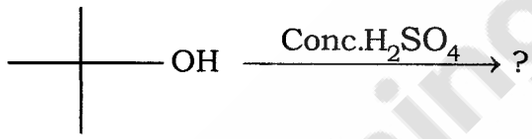
II) Carbocations

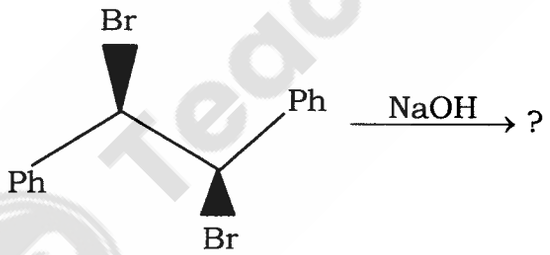
ii) Arrange the following carbanions in the increasing order of their stability and justify. **4**

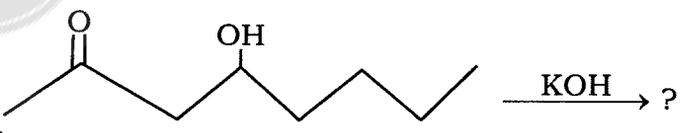


I II III IV

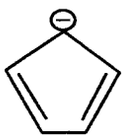
(c) Write the major product formed and explain the mechanism of the following reactions. Consider the stereochemical outcome of the reaction wherever applicable.

i)  **2**

ii)  **3**

iii)  **3**

(d) Identify whether the following structures are aromatic/antiaromatic/ nonaromatic. **8**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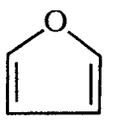
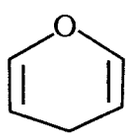
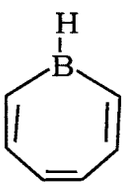
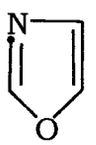

II


III


IV

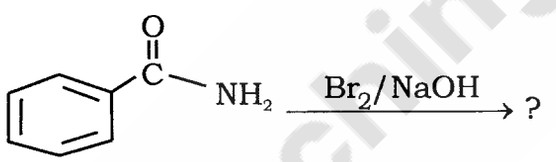

V

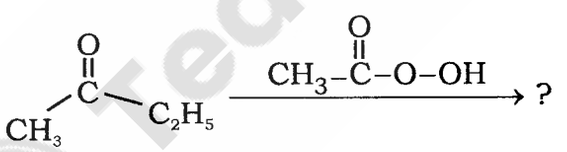

VI

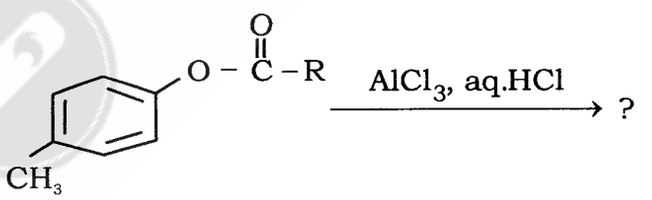

VII

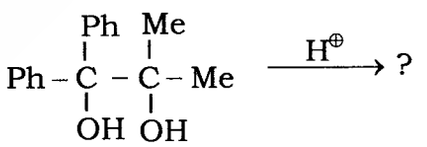

VIII

(e) Name the following rearrangement reactions and write the major product formed in each case.

i)  **2**

ii)  **2**

iii)  **2**

iv)  **2**

(f) i) Describe the instrumentation of EPR-Spectrophotometer with a neat and labelled block diagram explaining each component in detail. **4**

ii) Predict the number of ESR lines for the following radicals. **4**

I) $^{13}CF_2H$

II) Benzene

III) $CH_2(OCH_3)$

(g) i) Describe the use of Mark-Houwink equation and Ostwald viscometer for determination of molecular weight ($\overline{m}_v$) of the polymers. **4**

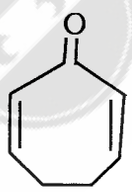
ii) A protein sample consists of an equimolar mixture of ribonuclease ($m = 13.7 \times 10^3$) Haemoglobin ($m = 15.5 \times 10^3$) and Myoglobin ($m = 17.2 \times 10^3$) calculate the number average and weight average molecular weights. **4**

Q6. (a) i) Explain why Azulene has large dipole moment. **3**

ii) Justify cyclo octatetraene has tub shaped structure and not a planar one. **2**

iii) Draw the structure of [18]-annulene. Explain why inner hydrogens in [18] annulene resonate at -1.9δ where as the outer hydrogens resonate at 8.2δ in ^1H NMR spectrum. **5**

iv)



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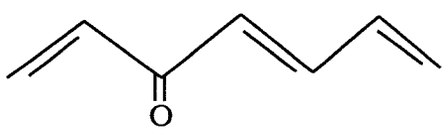
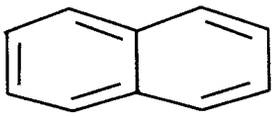


II

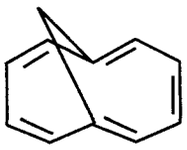
Explain why structure (I) is more basic than structure (II). **3**

P.T.O.

v) Identify whether the following structures are aromatic/antiaromatic/nonaromatic. **2**



I



II

(b) i) Draw the π molecular orbitals of 1, 3-butadiene. Indicate the electron occupancy of these orbitals. Mark the ground state and excited state. Illustrate the symmetry properties of HOMO and LUMO of this system. **7**

ii) With the help of Woodward-Hoffmann rules predict the stereochemistry of the following pericyclic reactions. **8**

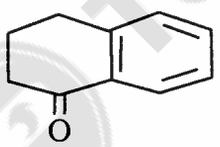
I) 2π + 4π thermal cycloaddition.

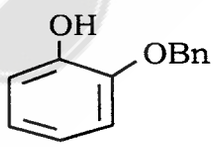
II) Photochemical electrocyclic ring closure of 1, 3-butadiene.

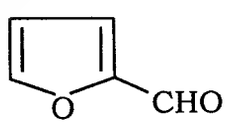
III) Thermal 1,5-sigmatropic rearrangement.

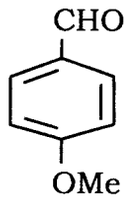
IV) 2π + 2π photochemical cycloaddition.

(c) Name the following reactions and predict the product. **10**

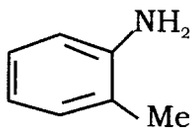
I)  $\xrightarrow[\text{Conc.HCl}]{\text{Zn/Hg}}$?

II)  $\xrightarrow[CHCl_3]{NaOH}$?

III)  $\xrightarrow[H^+]{NaOH}$?

IV) 

$\xrightarrow[EtOH, H_2O]{KCN}$?

V) 

$\xrightarrow[2)\ CuCN]{1)\ HNO_2}$?

Q7. (a) Discuss the preparation, properties and uses of the following polymers. **15**

1) Teflon

2) Polycarbonates

3) Polyvinyl Chloride

4) Silicones

5) Borazines

(b) i) Deduce the structure of following organic molecules using the NMR Data. **9**

I) Molecular formula : C_9H_{12}
NMR signals : (δ ppm) – 2.2 (s, 9H), 6.7 (s, 3H)

II) Molecular formula : $C_5H_{10}O$
NMR signals : (δ ppm) – 1.05 (t, 6H), 2.5 (q, 4H)

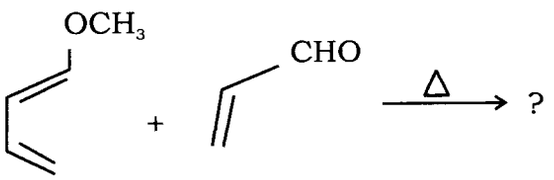
III) Molecular formula : $C_3H_5Cl_3$
NMR signals : (δ ppm) – 2.2 (s, 3H), 4.02 (s, 2H).

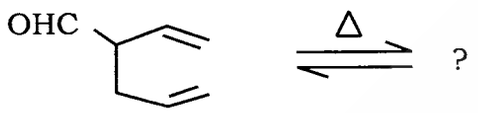
ii) Predict the chemical shift positions, number of signals and multiplicities of the signals in the proton NMR spectrum of **6**

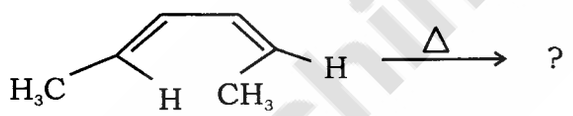
IV) I-propanol

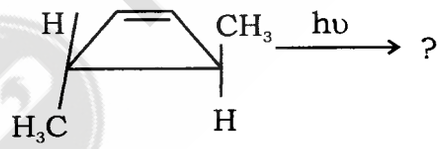
V) Phenyl acetic acid.

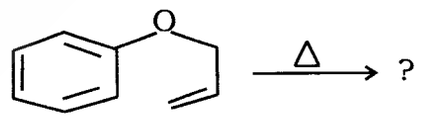
(c) Complete the following pericyclic reactions and classify them into electrocyclic (4n/4n + 2 e^- system), cycloaddition (m + n)/, sigmatropic reaction [i, J] **10**

I) 

II) 

III) 

IV) 

V) 

Q8. (a) i) Explain with mechanism the Norrish Type I and Type II photochemical cleavage of carbonyl compounds. **10**

ii) Discuss the fate of excited molecule with the help of Jablonski diagram. **5**

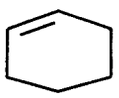
(b) i) Explain Mclafferty Rearrangement giving two suitable examples. **3**

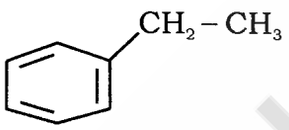
ii) Describe the significance of base peak and molecular ion peak in Mass spectrum. **2**

iii) Give the fragmentation patterns of the following molecules. **10**

I) $CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$

II) $CH_3-CH_2-CH_2-CH_2=CH_2$

III) 

IV) 

V) $CH_3-CH_2-O-CH_2-CH_3$

(c) With suitable examples discuss the mechanism of – **10**

a) Fisher Indole synthesis

b) Skraup quinoline synthesis.

SEAL