

CHEMISTRY

PAPER—II

Time Allowed : Three Hours

Maximum Marks : 200

QUESTION PAPER SPECIFIC INSTRUCTIONS

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

There are EIGHT questions in all, out of which FIVE are to be attempted.

Question Nos. **1** and **5** are compulsory. Out of the remaining SIX questions, THREE are to be attempted selecting at least ONE question from each of the two Sections A and B.

All questions carry equal marks. The number of marks carried by a question/part is indicated against it.

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

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

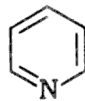
Neat sketches may be drawn, wherever required.

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.

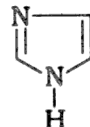
Answers must be written in ENGLISH only.

SECTION—A

1. (a) In the following molecules, which one is more basic and why?



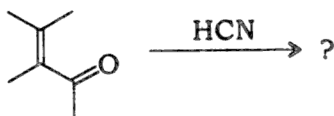
A



B

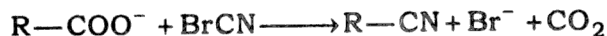
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- (b) Invoking the idea of kinetic and thermodynamic control, write the products (major and minor) in the following reaction :



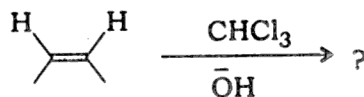
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- (c) Establish the origin of carbon in the cyano group of the product obtained in the following reaction by using isotopic labelling method :



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- (d) Giving the mechanism, write the product(s) of the following reaction. Prove the formation of intermediate involved in the reaction using a suitable trap :



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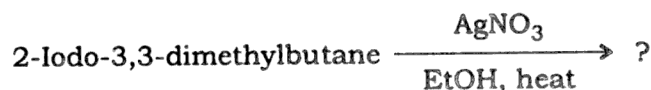
- (e) Why does $-\text{NH}_2$ at 'ortho' and 'para' position of the aromatic ring with respect to negatively charged groups cause their destabilization whereas $-\text{NO}_2$ at the same position has the stabilizing effect?

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- (f) Polar aprotic solvents like DMSO favour the $\text{S}_{\text{N}}2$ reactions. Why?

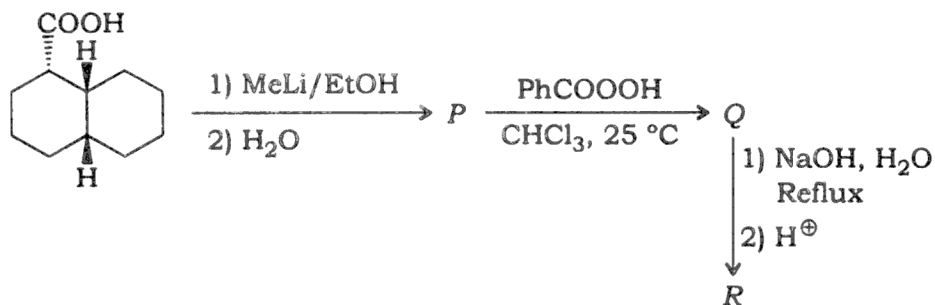
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- (g) Write the major product obtained in the following reaction. Also substantiate your answer with mechanism :



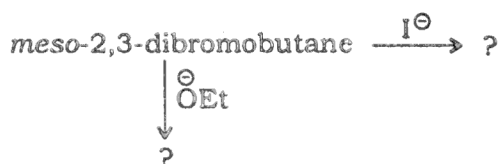
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(h) Identify the products *P*, *Q* and *R* in the following chemical sequence :



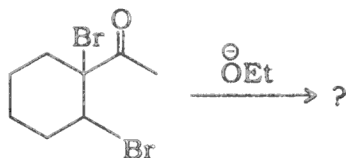
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2. (a) Indicating the stereochemistry of the products, complete the following reactions with their mechanisms :



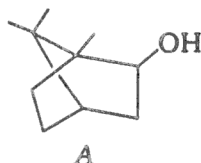
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(b) Complete the following reaction. Also write its possible mechanism along with the name of the reaction involved :



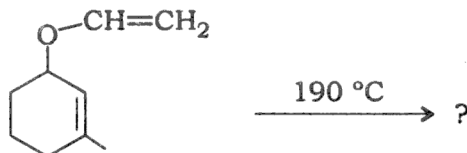
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(c) Write the product(s) of the reaction of alcohol (*A*) with acid (H^\oplus) along with the mechanism. Also give the name of the reaction :



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(d) While naming the process involved, complete the following reaction along with its push and pull arrows mechanism :



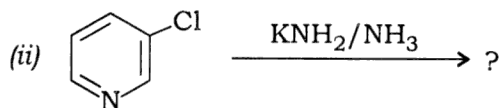
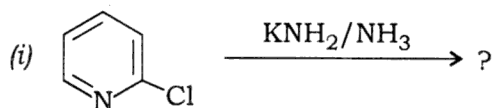
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(e) The compounds *A* and *B* undergo hydrolysis in the presence of water. Compare their hydrolysis behaviour giving appropriate explanation :



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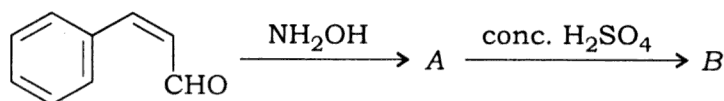
3. (a) Complete the following reactions with their mechanisms :



5+10

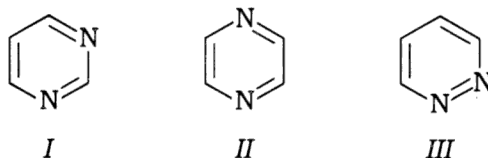
(b) Explain the reactive behaviour of 2,3-di-*t*-butylbuta-1,3-diene (A) and 1,3-di-*t*-butylbuta-1,3-diene (B) as dienes for Diels-Alder reaction. 5

(c) Write the products A and B in the following sequence of reactions. Give the mechanism of second reaction only and also write the name of this reaction :



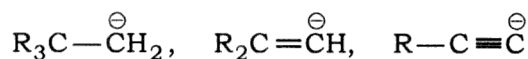
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(d) Arrange the following molecules in the decreasing order of their aromatic character :



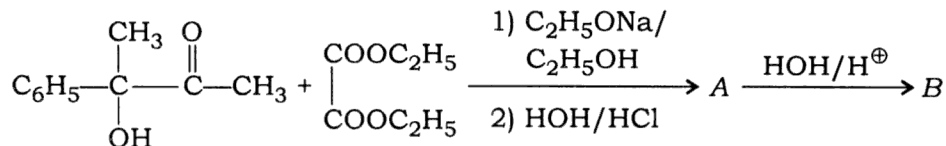
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(e) Arrange the following according to their stability with proper justification :



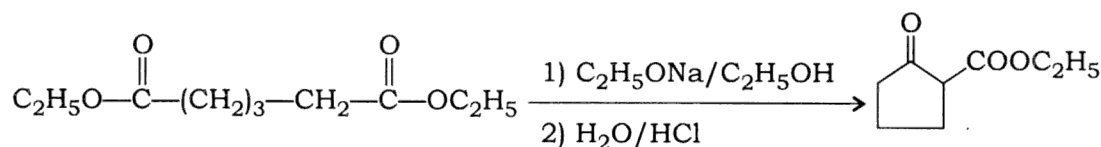
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4. (a) Complete the given reaction and provide mechanism for each step :



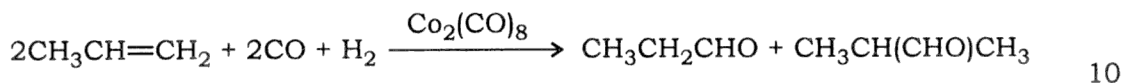
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(b) Provide the name and mechanism for the given reaction :

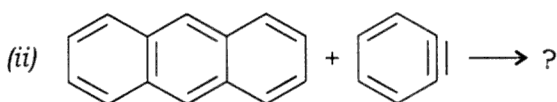
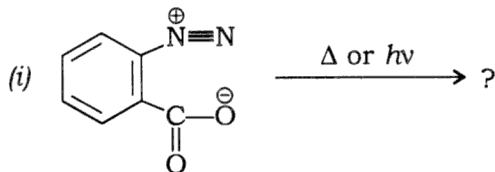


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(c) Propose the mechanism for the following reaction :

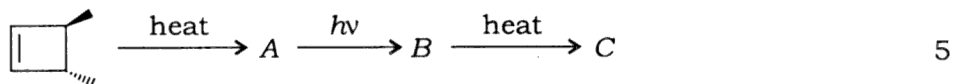


(d) Complete the following reactions :



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(e) Identify A, B and C in the following chemical sequence :

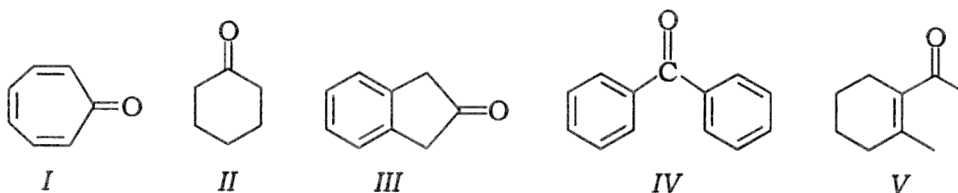


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SECTION—B

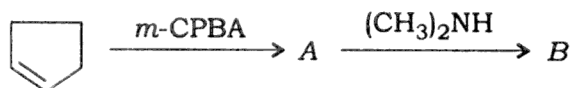
5. (a) What are hydrophobic attractions? How do such attractions alter the conformation of proteins and nucleic acids? 5
- (b) Polystyrene is largely used thermoplastic material. For preparation of polystyrene, monomers of styrene are polymerized in the presence of BPO. After attainment of desired molar mass, the living polymer is subjected to react with DPPH to become dead polymer. Explain the above process of conversion of living polymer to dead polymer through chemical reactions. 5
- (c) In a strand of DNA, a sequence 5'-CGCATC-3' is found. Suggest sequence of its complementary strand and also predict the sequence of RNA strand synthesized from the above complementary strand. 5
- (d) When rotational spectra of CO molecule are studied, a series of equidistant lines at a gap of 3.84 cm^{-1} is observed. Calculate the bond length of CO. 5
- (e) C—H stretching frequency of an alkane is found at 2900 cm^{-1} . What will be the change in stretching frequency, if deuterium replaces hydrogen? Calculate $\bar{\nu}$. 5

- (f) Arrange the following carbonyl compounds in order of increasing C—O stretching frequencies (cm^{-1}):



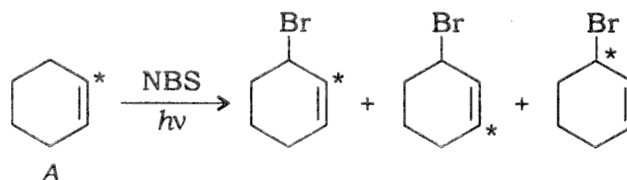
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- (g) Write the products of the following reaction and predict the mechanism:



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- (h) How will you account for the formation of the following products on treatment of labelled ($\ast = {}^{14}\text{C}$) A with NBS?



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6. (a) In local hardware stores, now-a-days epoxy resins are commonly sold. What are these? Give one method of preparation of epoxy resin. Write three uses of it.

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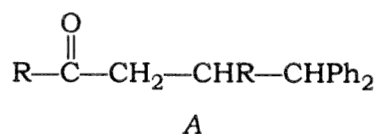
- (b) What is group analysis method of determination of molar mass of polymers? Which spectroscopic technique is used in this quantitative estimation method?

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- (c) Hydrogen bonding plays an important role in explaining the structure of biomolecules. Can you predict, which type of hydrogen bonding is responsible for the formation of α -helix and β -pleated sheets of proteins? If yes, draw the structures and represent hydrogen bonds.

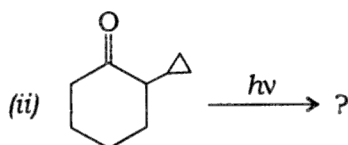
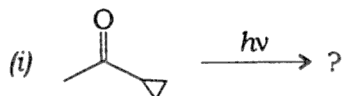
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- (d) The compound A undergoes H-abstraction under photochemical conditions. Give the major/minor products and their mechanism of formation along with proper explanation:



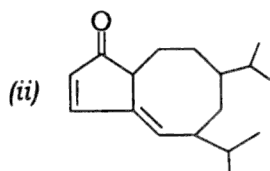
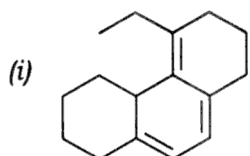
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(e) Giving their plausible mechanisms, complete the following reactions :



5+10

7. (a) Calculate λ_{\max} for the following compounds using Woodward-Fieser rules :

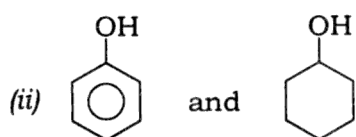
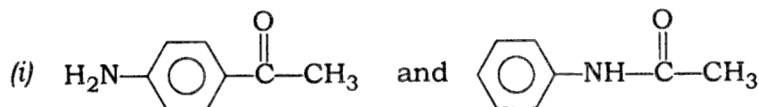


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(b) Draw tautomers of but-3-en-2-one and identify auxochromic and chromophoric groups in both forms. 5

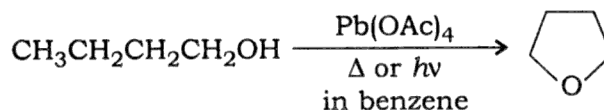
(c) Predict ESR peaks for pyrazine. Represent their intensity ratio also. 5

(d) How do IR spectra help to distinguish the following pairs of compounds?



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(e) Propose the mechanism for the following reaction :

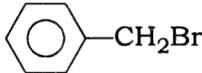
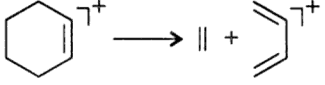
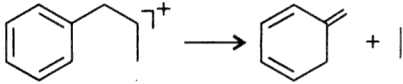
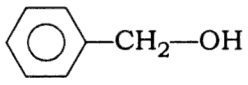
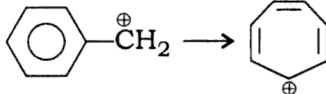


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8. (a) HMDA is a starting material of polymer Nylon-6. How can we prove the presence of N—H bond in HMDA through PMR spectroscopy? 5

(b) Do *ortho*-, *meta*- and *para*-hydrogens of monosubstituted benzene show spin-spin coupling? Predict the approximate values of their coupling constants. 5

(c) Match the following columns :

Column—A	Column—B
(A) Scrambling	I. 
(B) M-18 peak	II. 
(C) M and M+2 peak (1:1)	III. 
(D) Retro-Diels-Alder	IV. 
(E) McLafferty rearrangement	V. 

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(d) Phenol reacts with bromobenzene in the presence of catalytic amount of copper and gives compound A, which is a sweet smelling liquid. In mass spectral analysis of A, prominent peaks are observed at $m/z = 170, 141$ and 71 . Predict the structure of A and also represent its fragmentation pattern. 10

(e) An organic compound A having molecular formula $C_8H_8O_3$ burns with sooty flame. It is fragrant solid with the following spectroscopic data. Predict its structure :

UV : λ 275nm, 292nm, 295nm

IR : 3250 cm^{-1}

3060 cm^{-1}

2950 cm^{-1}

2840 cm^{-1}

2760 cm^{-1}

2720 cm^{-1}

1700 cm^{-1}

1600 cm^{-1}

1580 cm^{-1}

1500 cm^{-1}

1250 cm^{-1}

1050 cm^{-1}

NMR : δ 5.75 (s)

δ 7.1 (d), 8 Hz

δ 7.1 (dd), 2 Hz, 8 Hz

δ 8.05 (s)

δ 9.80 (s)

Mass (m/z) : 152, 151, 123, 137, 109, 89

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