

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.

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.

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

Answers must be written in ENGLISH only.

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.

SECTION—A

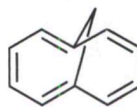
1. (a) Which one of the following is aromatic? Justify your answer. Give names of the given annulenes :



I



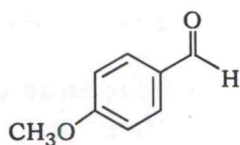
II



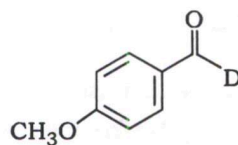
III

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- (b) What is secondary kinetic isotope effect? Explain it using the reaction of HCN with the following molecules :



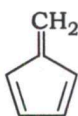
I



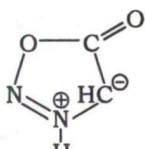
II

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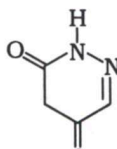
- (c) Comment on aromatic/non-aromatic/anti-aromatic behaviour of the following compounds and justify your answer :



I



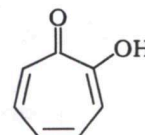
II



III



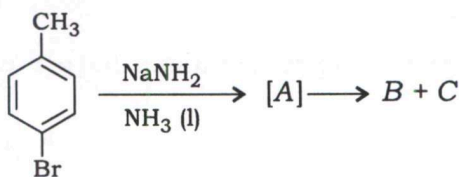
IV



V

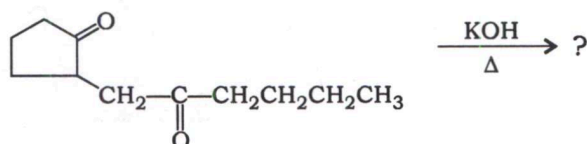
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- (d) Predict the products [A], B and C. Also give the reaction mechanism of the following reaction sequence :



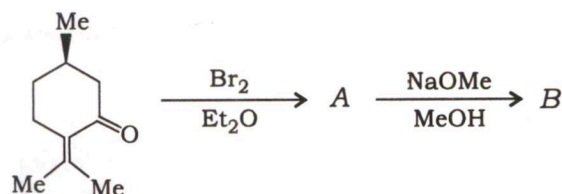
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- (e) Giving mechanism, write down the product(s) in the following chemical transformation :



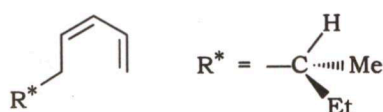
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(f) Identify A and B in the following reaction/rearrangement with mechanism :



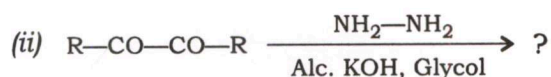
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(g) How does migration of R^* group involving photochemical [1, 5] sigmatropic rearrangement in the following compound proceed with inversion of configuration? Explain :



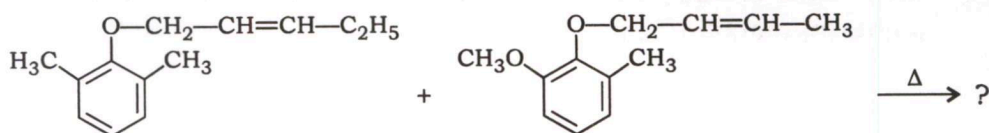
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(h) Give the products in the following reaction sequences :



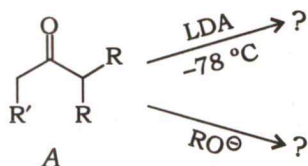
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2. (a) (i) Indicate the product(s) in the following reaction. What information is obtained about the reaction mechanism from the product(s) observed?



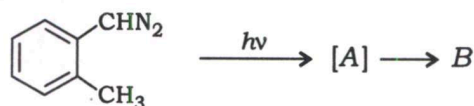
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(ii) Predict the generation of reactive chemical species giving suitable explanation in terms of thermodynamic/kinetic control in the following chemical equations :



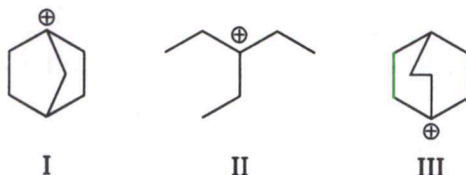
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- (b) (i) Identify the products [A] and B in the following reaction :



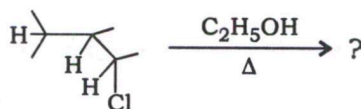
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- (ii) Arrange the following chemical entities in order of their decreasing stability :



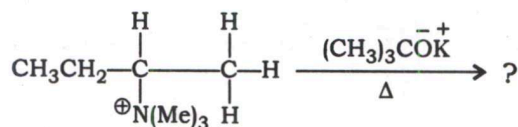
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- (iii) Complete the following reaction and justify the formation of the major product with emphasis on intermediate formed in situ :



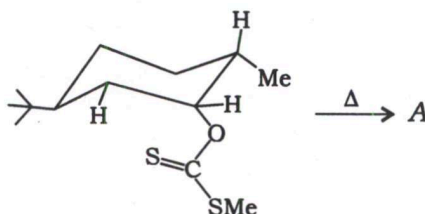
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- (c) (i) Define Hofmann product. Explain the formation of the major product with the help of Newman projection formulae by taking the example given below :



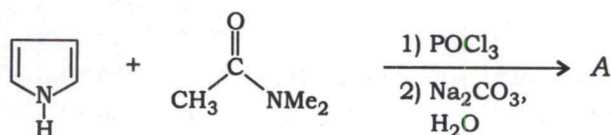
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- (ii) Predict the major product and identify the reaction given below by giving its name :



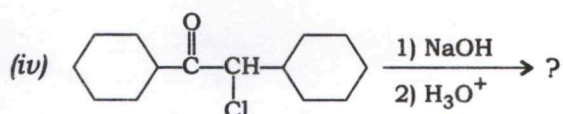
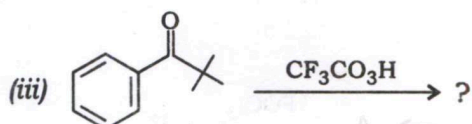
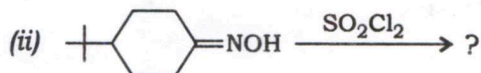
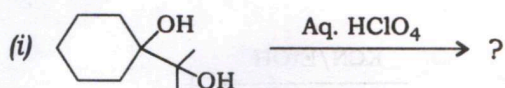
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3. (a) Complete the following reaction with detailed reaction mechanism :



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(b) Write the major product(s) of each of the following rearrangements with justification :



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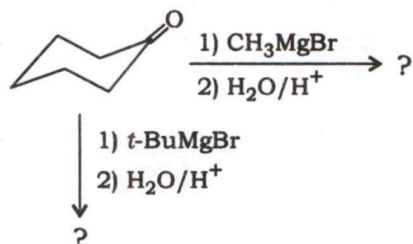
(c) (i) In the cycloaddition reaction of cyclopentadiene with maleic anhydride, the endo product is preferred even though the endo product is less stable than the exo product. Explain.

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(ii) Write the product indicating stereochemistry when 2*E*, 4*Z*-hexadiene is undergoing thermal as well as photochemical reaction.

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4. (a) Complete the following reactions giving proper explanation for the formation of products with their spread :

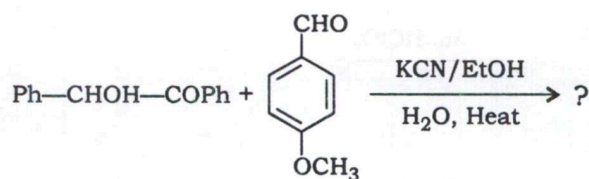


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(b) Write the product of the reaction between cyclohexanone and diethyl succinate in the presence of a strong base followed by treatment with aqueous acid. Also give the mechanism of this transformation.

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- (c) (i) Write the product(s) in the following reaction sequence along with the mechanism :



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- (ii) Identify the products A and B in the following reaction sequence. Also write the mechanism of Step II :



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SECTION—B

5. (a) Calculate $\bar{M}_w$ for a polydispersed polymer having three fractions with molecular weights and mass % as follows :

Molecular weight	:	200000	50000	100000
Mass %	:	50	20	30

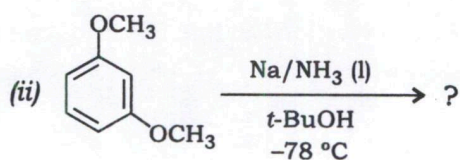
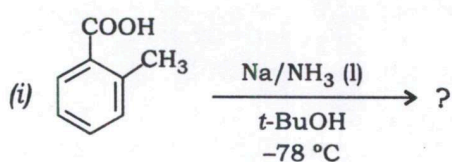
where $\bar{M}_w$ is average molecular weight of the polymer.

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- (b) What is the energy of the lowest vibrational level of the simple harmonic oscillator? Justify your answer.

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- (c) Complete the following reactions :

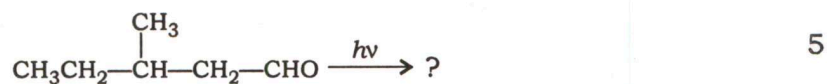


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- (d) Draw the structure of a peptide bond giving the values of bond angles and bond lengths.

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(e) Indicating the major/minor product(s), complete the following reaction :



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(f) Distinguish between acetanilide and N-methyl benzamide on the basis of IR spectroscopy.

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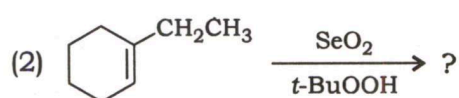
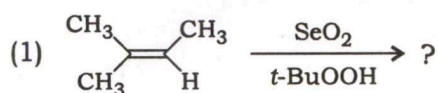
(g) How can you identify the presence of (i) chlorine, (ii) bromine and (iii) both chlorine and bromine atoms in the molecule based on the percentage intensity of isotope peaks relative to the intensity of molecular ion peak?

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(h) Define spin labels. Write the name and structure of the most commonly used spin label for macromolecules' structure investigation.

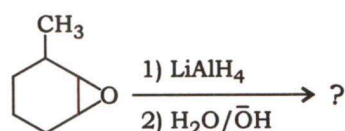
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6. (a) (i) Write the structures of the products formed in the following reactions :



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(ii) Giving mechanism, complete the following reaction :



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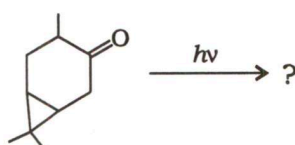
(b) (i) What is living polymer? Explain the reaction mechanism by taking example of a reaction of monomer styrene with BuLi.

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(ii) Give the representative structure of silicone. Comment on its stability.

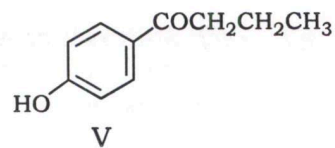
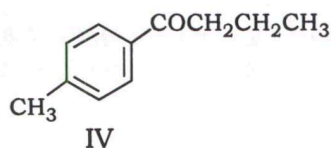
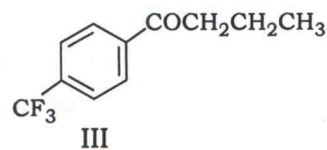
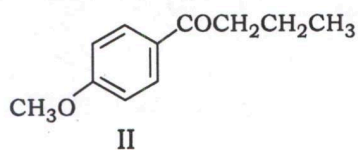
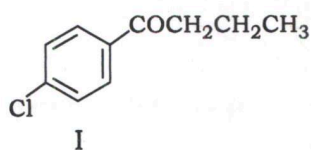
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(c) (i) Complete the following photochemical reaction giving the most probable mechanism :



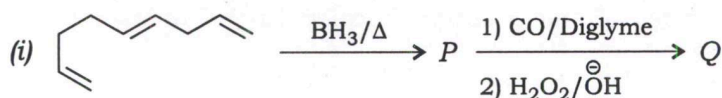
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- (ii) Arrange the following compounds in order of their decreasing Norrish type II potential. Give the proper reason for the order you have given :

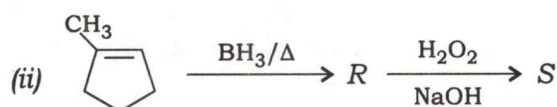


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7. (a) Write the structures of the products in the following reaction sequences :



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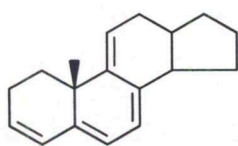


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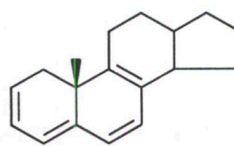
- (b) (i) Give and compare the approximate values of λ_{max} and ϵ of 3-pentanone and 3-penten-2-one due to $\pi-\pi^*$ and $n-\pi^*$ transitions.

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- (ii) Predict λ_{max} of the following molecules based on Woodward-Fieser rules :



and



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- (c) Identify the structure of a compound having molecular formula $\text{C}_6\text{H}_{13}\text{NO}_2$ and displaying the following spectral data :

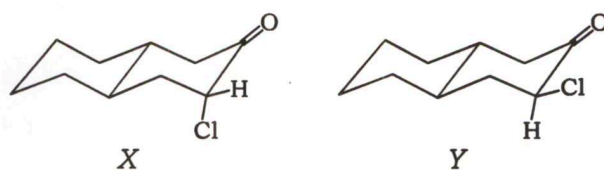
IR : ν_{max} 2981 cm^{-1} and 1736 cm^{-1}

$^1\text{H NMR}$: δ 1.31 (t, 3H), 2.42 (s, 6H), 3.20 (s, 2H), 4.18 (q, 2H)

Explain the mass spectral fragmentation of the identified compound for m/z 131, 116, 103, 86 and 84 peaks.

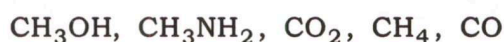
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8. (a) (i) How can you distinguish the following compounds on the basis of IR spectroscopy?



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- (ii) State which of the following molecules are infrared active :



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- (b) Differentiate between benzyl alcohol and anisole on the basis of mass spectral fragmentation.

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- (c) (i) Distinguish between (1) ethyl acetate and methyl propionate and (2) 2-nitroacetophenone and 4-nitroacetophenone with reference to number of signals, approximate chemical shift values and spin-spin couplings (multiplicity) in their ^1H NMR spectra.

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- (ii) Deduce the structure of the compound obtained by condensation of benzaldehyde and acetone in the presence of a base based on the following ^1H NMR spectral data :

δ 2.31 (s, 3H), 6.73 (d, 1H, $J = 16$ Hz), 7.32–7.40 (m, 5H),
7.52 (d, 1H, $J = 16$ Hz)

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