CSM : 15

CHEMISTRY

PAPER - II

Time Allowed : 3 hours   Full Marks : 100

Marks for each question is indicated against it.

Attempt <u>any 5 (five)</u> questions taking not more than 3 (three) questions from each Part.

PART A

1. (a) Which of the following species is aromatic? Give justification for your answer.**(5×2=10)**
    - (i)   Cycloheptatrienyl radical
    - (ii) Cycloheptatrienyl cation
    - (iii) Cycloheptatrienyl anion
    - (iv) 18-annulene
    - (v)   Cyclopropenyl cation

    (b) Give the mechanism of the following reactions with the prediction of propen products:

    (2×5=10)
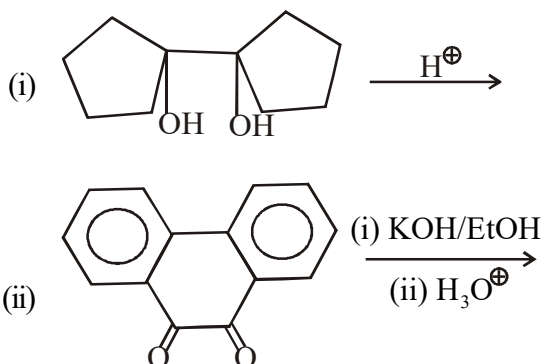
2. (a) The E2 elimination reactions of unsymmetrical substrates yield more than one Olefinic product. Two empirical rules, the Hofmann and the Saytzeff rules, govern the elimination in these reactions. State and explain these rules with suitable reactions.   **(10)**

    (b) Discuss briefly the four factors influencing the relative reactivity in substitution reactions:

    (4×2½=10)

    - (i)   The nature of the substrate
    - (ii) The nature of the solvent
    - (iii) The nature of the nucleophile
    - (iv) The nature of the leaving group

**3.** (a) There are two ways of stereochemical modes in the following electrocyclic transformations. Write structures of the products expected from both modes and tell which one is preferred and why? **(5)**
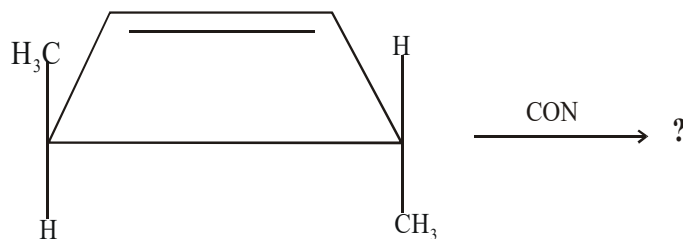
(b) With the help of FMO approach, explain whether the following reaction will be allowed thermally or photochemically. **(5)**
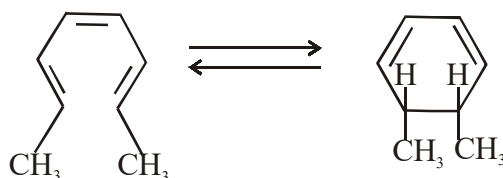

(c) Write the stereochemistry of the products of the following electrocyclic reactions and write whether the reaction proceeds in a conrotatory or disrotatory fashion. **(10)**
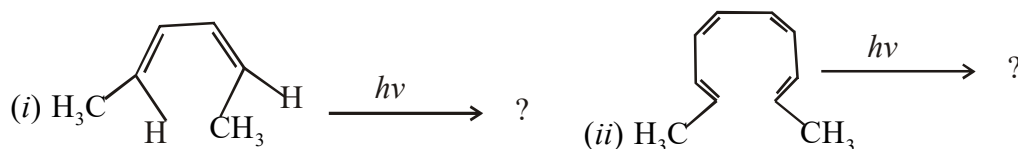

4. (a) How is terylene manufactured starting from dimethyl terephthalate? Give two properties and two uses of terylene. **(10)**

(b) What are polyamides? How is (a) nylon 6 and (b) nylon 6,6 manufactured? What does the "6,6" in nylon 6,6 stand for? **(10)**

PART B

**5.** (a) Complete the following reactions with mechanisms: **(5+5=10)**

(i)

(ii)
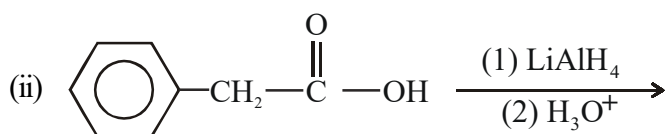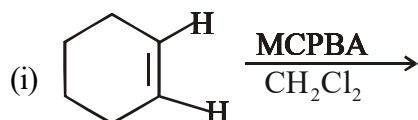
(b) Predict the products in the following reactions and give a plausible mechanism for each: **(5+5=10)**

(i)

$\xrightarrow[h\nu]{CCl_4}$

(ii)

$\xrightarrow[EtOH]{SeO_2}$
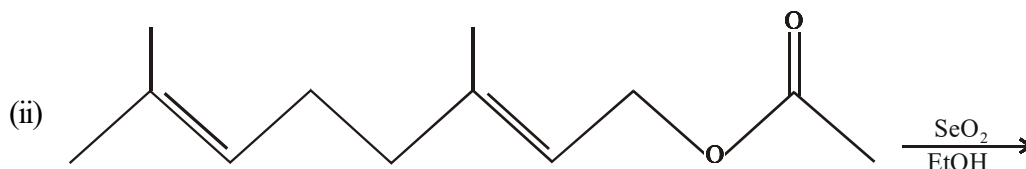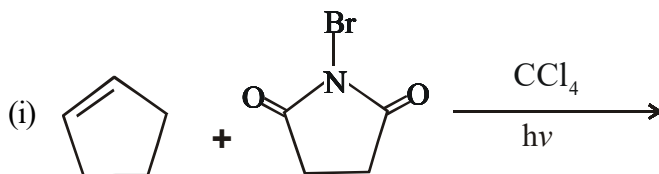
6. (a) Draw Jablonski diagram and define the following: **(10)**

   (i) ground state   (ii) singlet excited state

   (iii) triplet excited state   (iv) inter system crossing

   (b) Complete the following reactions with suitable mechanisms: **(5+5=10)**

   (i)

   $\xrightarrow[\text{gas phase}]{h\nu}$ **?**

   (ii)

   $\xrightarrow[\text{solution}]{h\nu}$ **?**
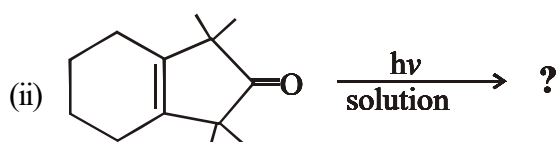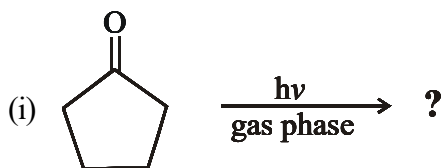
7. (a) The first line in the rotation spectrum of carbon monoxide has a frequency of 3.8424 cm⁻¹. Calculate the rotational constant and hence the C-O bond length in carbon monoxide. (given: Avogadro number $= 6.023 \times 10^{23}$ and $c = 3 \times 10^{10}$ m/s) **(5)**

   (b) Molecules having permanent dipole moment are microwave active and those not having permanent dipole moment are microwave inactive. Comment. **(5)**

   (c) State the rule of mutual exclusion with the help of an example. **(5)**

   (d) Which of the following molecules will show a rotational Raman spectrum and why? H_2, HCl, CO, CH_4, SF_6. **(5)**

8. (a) Using Woodward-Fieser rules calculate wavelengths maximum UV absorptions for the following compounds: **(5+5=10)**

(i)

(ii)
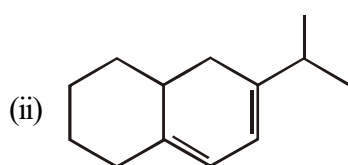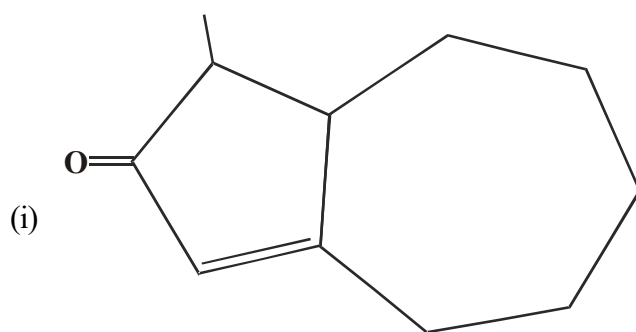
(b) Using nmr spectroscopy, distinguish the following pairs: **(2×5=10)**

   (i) Acetone and methylacetate

   (ii) 1-methyl cyclohexane and Toluene

Give approximate δ values also.

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