[This question paper contains 4 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 1744 **L**

Unique Paper Code : 2172013602

Name of the Paper : DSC: Polynuclear Hydrocarbons, Photochemistry, Pericyclic Reactions, and Spectroscopy of Organic Compounds

Name of the Course : **B.Sc. (Hons) Chemistry**

Semester : VI

Duration : 3 Hours Maximum Marks : 90

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **six** questions in all.
3. Each question carries **15** Marks.
4. Attempt sub-parts of each question together.

1. (a) Sulphonation of naphthalene with conc. H_2SO_4 at 40°C and 160°C yields two different products Explain using a suitable energy diagram.

   (b) (i) Anthracene is less aromatic and more reactive than benzene and naphthalene. Explain.

   (ii) How will you prepare anthracene from o-bromobenzyl bromide?

   (c) Carry out the following conversions : **(Any two)**

   (i) Anisole(methoxybenzene) to 7-methoxy-l-methylnaphthalene

   (ii) Naphthalene to anthracene

   (iii) Anthracene to 1-ethylanthracene (5,5,5)

2. (a) Define ξ_{max} and explain why the intensity of $\pi \rightarrow \pi^*$ transitions are 10 to 100 times higher than $n \rightarrow \pi^*$ transitions.

   (b) Differentiate between a bathochromic and a hypsochromic shift using a suitable example.

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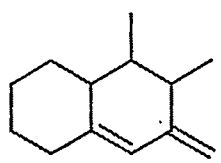
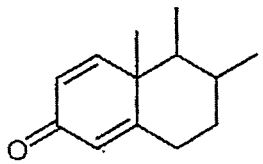
(c) Using Woodward-Fieser rules, calculate the λ_{max} values for the following compounds :

i. ii





Given :

Heteroannular Dienes	215 nm
Homoannular Dienes	253 nm
α, β-unsaturated ketones (six-membered)	215 nm
Alkyl group (dienes and polyenes)	+ 5 nm
Exocyclic Double bond	+ 5 nm
Increments for extended conjugation	+ 30 nm

α, β, γ, δ ring residues or alkyl groups for α, β–unsaturated carbonyl compound: + 10, 12, 18,18 nm respectively.

(d) Give the frequency ranges for the functional and fingerprint regions in the IR spectrum and explain their importance to IR spectroscopy, taking a suitable example.

(e) With the help of suitable diagrams, explain why alkenes absorb in the range 4.5 to 6.5 ppm, and aromatic compounds absorb in the range 6.5-8.0 ppm in the NMR spectrum, when both have C=C bonds. (3×5=15)

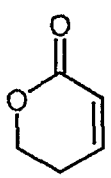
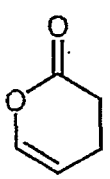
3. (a) What do you mean by the terms IR-active and IR- inactive? Give reasons and explain which of the following compounds would be IR active and which would be IR inactive?

(i) 2,3-Dimethylbut-2-ene

(ii) 1-Butyne

(b) How will you differentiate between the following compounds using IR spectroscopy?

(i) CH_2CO_2H and CH_3COCH_3

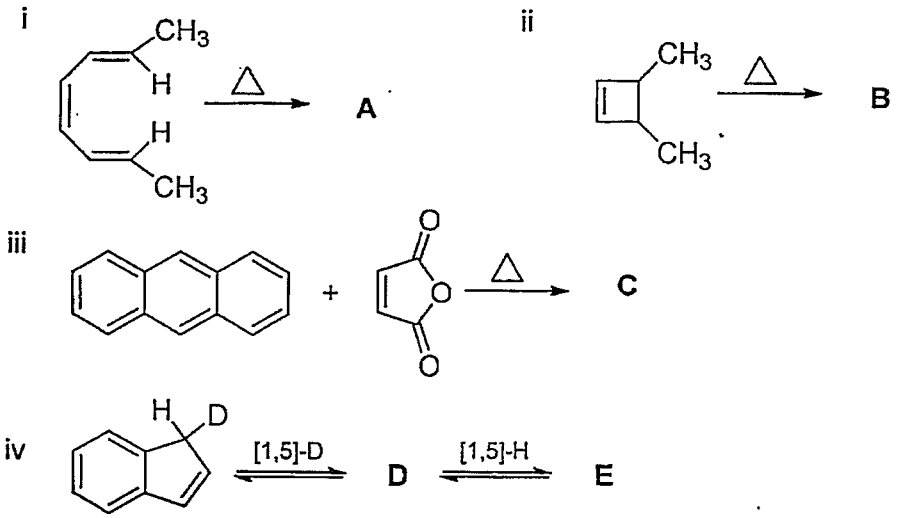
(ii)  and 

(c) Define chemical shift in ppm and give its mathematical expression. Explain why all protons in a molecule do not absorb at the same frequency in the NMR region? (5,5,5)

4. (a) Define coupling constant. Explain how you will distinguish between *cis* and *trans*-crotonic acid (MeCH=CHCOOH) by their NMR spectra?

(b) Discuss the correlation diagram for conrotatory and disrotatory cyclization of butadiene to cyclobutene.

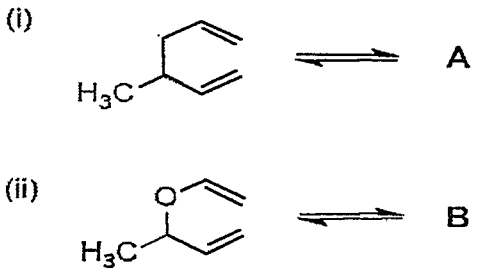
(c) Predict the product(s) of the following reactions :



(5,5,5)

5. (a) The combination of a carbonyl compound and an alkene leads to the formation of a photoadduct. Give the name and discuss the mechanism of this reaction in detail.

(b) Complete the following reaction :



Draw the aromatic transition state for each reaction and illustrate the product formation using curved arrow notation. Mention the name of the reactions.

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(c) Thermal [4+2] cycloaddition of 1,3-butadiene and ethylene is symmetry-allowed. Explain. (5,5,5)

6. (a) Calculate DBE and write the structural formulae for the compounds with the following molecular formulae, showing the mentioned signals in their NMR spectra :
   (i) $C_2H_4Cl_2$; one
   (ii) C_8H_{18}; one
   (iii) C_9H_{12}; two

   (b) How would you distinguish between the following pairs of compounds based on their NMR spectra?
   (i) Geometric isomers of 1,2-dimethylcyclopropane
   (ii) But-1-yne and but-2-yne

   (c) Draw the PMR spectrum of ethyl acetate and explain multiplicity and approximate chemical shift values for each signal. (5,5,5)

7. (a) An organic compound, A, with molecular formula $C_{10}H_{12}O_2$, shows the following spectral data: UV absorption at λ_{max} 220 nm (ξ_{max} 1800); IR absorption bands at 3077, 2976, 1745, 1608, 1497, 1456 cm^{-1}; PMR absorption bands at δ 7.3 s; 4.3 (t, J=7 Hz); 3.0 (t, J=7 Hz); 2.1 (s) in the ratio 2.5:1: 1: 1.5.
   (i) Calculate DBE.
   (ii) Explain UV, IR, and PMR Data.
   (iii) Give the structure of the compound A.
   (iv) Write the products (B) obtained when A is hydrolyzed with concentrated sulphuric acid.

   (b) Paracetamol is hydrolyzed in a basic medium to a compound, A, with molecular formula C_6H_7NO. Write the structure of A and explain how IR and NMR data (only main peaks) can be used to distinguish between the reactant and the product. (10,5)

8. Write short notes on the following **(Any three)** :
   (a) Molecular orbital theory of color and constitution
   (b) Effect of inter- and intramolecular H-bonding on IR absorptions
   (c) Photosensitization
   (d) Howarth's synthesis of anthracene (5,5,5)

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