(b) Differentiate between 1-butene and 1-butyne using IR spectroscopy.

(c) Explain, why [2+2] cycloaddition reaction are photochemically allowed and thermally forbidden. (5,5,5)

8. Write short notes on **(Any three)** :

(a) Haworth synthesis of naphthalene

(b) Norrish Type II reaction

(c) Witt's theory of colour

(d) Claisen rearrangement (5,5,5)

[This question paper contains 8 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 5546 **J**

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. (H) Chemistry**

Semester : VI

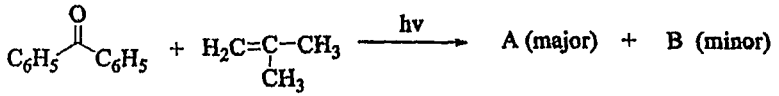
Duration : 3 Hours Maximum Marks : 90

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **six** questions. **All** parts of a question should be attempted together.
3. Each question carries **15** marks.

P.T.O.

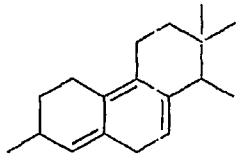
1. (a) Complete the following reaction

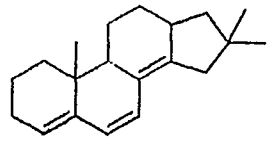


(i) Write the name of the reaction.

(ii) Explain the formation of products.

(b) Calculate the λ_{max} value for the following compounds

i) 

ii) 

Base value for homo annular diene = 253 nm, Base value for heteroannular diene = 215 nm; Alkyl group or Ring residue = 5 nm, Exocyclic double bond = 5 nm, Double bond extended conjugation = 30 nm

(c) Acetylenic protons are more shielded as compared to ethylenic protons. Explain. (5,5,5)

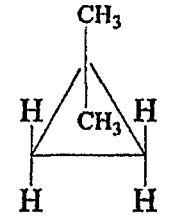
2. (a) An organic compound with molecular formula $C_6H_{12}O$ showed the following spectral data:

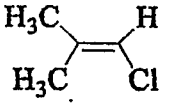
(c) In an organic compound, three kinds of protons appear at 60,100 and 180 Hz when the spectra are recorded at 60 MHz spectrometer.

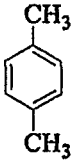
(i) Determine the chemical shift.

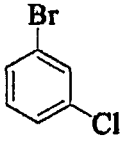
(ii) Relative position (in Hz) when 90 MHz spectrometer is used. (5,5,5)

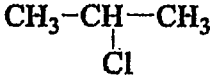
7. (a) Give the number of PMR signal in each of the following :

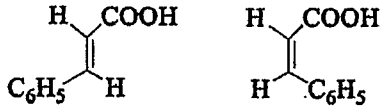
(i) 

(ii) 

(iii) 

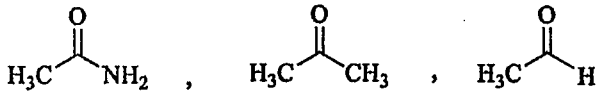
(iv) 

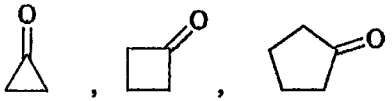
(v) 



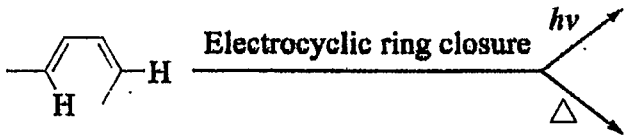
(c) Draw the PMR of pure and impure ethanol. Give reasons for the difference.

6. (a) Arrange the following compounds in order of increasing order of carbonyl absorption frequency in IR spectroscopy. Give reasons.

(i) 

(ii) 

(b) Complete the following reaction and explain the formation of products



(2E,4Z) 2,4-Hexadiene

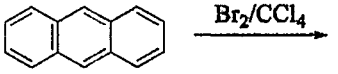
UV: λ_{max} = 288 nm, ε = 24; IR: A very strong band at 1715 cm^{-1}; ^{1}HNMR: δ values 2.0 (3H, s) and 1.0 (9H, s)

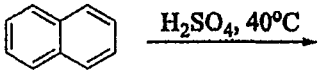
(i) Calculate the double bond equivalence

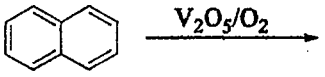
(ii) Deduce the structure of the compound

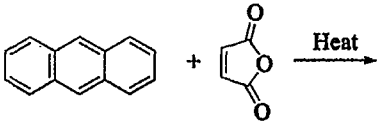
(iii) Explain (a) UV transition (b) IR absorption band (c) NMR peaks along with splitting patterns

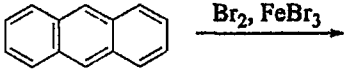
(b) Complete the following reactions :

(i) 

(ii) 

(iii) 

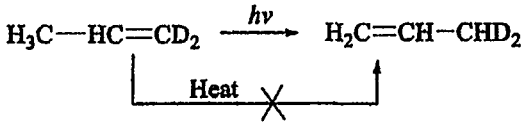
(iv) 

(v) 

P.T.O.

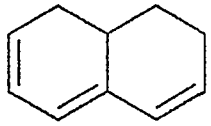
(c) Explain giving reason. Why IR spectrum of liquid *t*-butyl alcohol shows a strong absorption at 3360 cm^{-1}? Whereas a very dilute solution of the same compound in CCl_4 shows a strong absorption band at 3620 cm^{-1} instead of 3360 cm^{-1}. (5,5,5)

3. (a) Using the Frontier Molecular orbital approach, explain why [1,3] sigmatropic hydrogen shift is photochemically allowed and thermally forbidden.



(b) Write the full form and structure of TMS. Why it is used as internal reference?

(c) An organic compound (A) on partial hydrogenation with one equivalent of H_2 gives three isomers with molecular formula $C_{10}H_{14}$. Show how UV can distinguish these isomers.



Compound (A)

(5,5,5)

4. (a) How will you establish that in naphthalene two benzene rings are fused at *ortho* positions.

(b) Write the structural formula for the compounds with the following molecular formula that shows only one signal in their PMR spectra

(i) $C_3H_6Cl_2$ (ii) C_5H_{12}

(iii) C_4H_6 (iv) C_5H_{10}

(v) C_2H_6O

(b) A carbonyl compound shows the following data:

Solvent	λ_{max} (ε)	λ_{max} (ε)
Hexane	230 (12,600)	327 (98)
Water	245 (10,000)	305 (60)

Assign the various transitions. Explain the shift when the solvent is changed from hexane to water. (5,5,5)

5. (a) Explain, why electrophilic substitution in anthracene occurs at C-9 and C-10 position.

(b) Explain, which one is having higher λ_{max} (in UV spectroscopy) and higher value of $\nu_{c=o}$ (in IR spectroscopy)

P.T.O.