

**B.Sc. 4th Semester (Honours) Examination, 2023 (CBCS)**

**Subject : Chemistry**

**Course : CC-X**

**Time: 2 Hours**

**Full Marks: 40**

*The figures in the margin indicate full marks.*

*Candidates are required to give their answers in their own words as far as practicable.*

**1. Answer any five questions:**

2×5=10

- (a) What do you mean by force constant and 'finger-print region' in I.R.-spectra?
- (b) Define 'synthon and synthetic equivalent' with example.
- (c) Why is excess of diazomethane used in Arndt-Eistert synthesis?
- (d) Arrange all-possible transitions in U.V.-spectroscopy in order of increasing energy.
- (e) What are the products you expect on reduction of nitrobenzene with Zn-dust, methanol, sodium hydroxide?
- (f) Give the NMR spectrum of pure ethyl alcohol in high resolution. What will happen if the spectrum is recorded in presence of D<sub>2</sub>O?
- (g) What change would you expect in the U.V.-spectral behaviour for the molecule 2-cyclohexen-1-one, when the solvent is changed from water to benzene?
- (h) Oxime of benzaldehyde does not give normal Beckmann rearrangement reaction. — Explain the statement.

**2. Answer any two questions:**

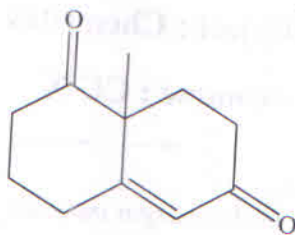
5×2=10

(a) (i) Predict the structure of the molecule from the following spectral data.

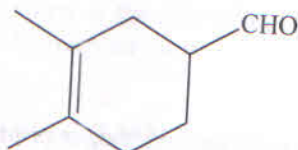
- Molecular formula: C<sub>4</sub>H<sub>10</sub>O.
- I. R. (cm<sup>-1</sup>): 3350 (disappear in presence of D<sub>2</sub>O), 2960.
- N.M.R.: (0.89, d, 6H), (1.3, triplet of heptet, 1H), (3.31, d, 2H), (4.33, s, 1H).
- U.V.: No λ<sub>max</sub> above 220nm.

(ii) Name one internal standard for NMR spectroscopy and explain its advantages for using as internal standard in that spectroscopic studies. 3+2

- (b) (i) Outline a synthesis of the following compound by using Robinson annulation:



- (ii) Give the retrosynthetic pathways and then synthesize the following compound: 3+2



- (c) (i) How would you differentiate between the following by spectroscopic method as indicated in the bracket?

(I) Benzaldehyde and acetaldehyde (I.R.),

(II) *o*-Xylene and *p*-Xylene (NMR),

(III) 2-methylbutadiene and 2-methyl-2-butene (U.V.).

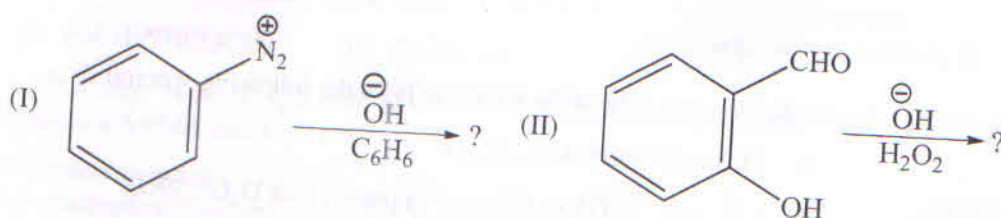
- (ii) Arrange the following in order of increasing stretching frequency: 3+2

(I) C—H, S—H, N—H, O—H.

(II) =C—H, —C—H, ≡C—H

- (d) (i) What happens when cyclohexanone is treated initially with hydroxylamine hydrochloride and subsequently with phosphorus pentoxide? Predict the product(s) with mechanism.

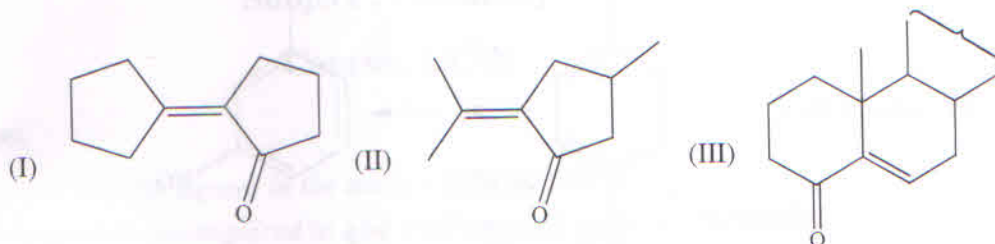
- (ii) Predict the product in each of the following reactions: (1+2)+(1+1)



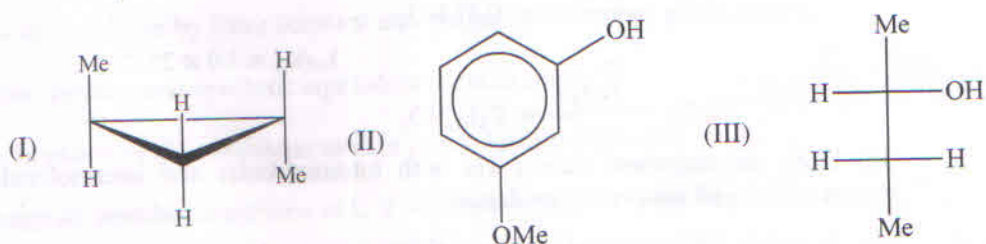
3. Answer any two questions:

- (a) (i) Compound 'P' is asymmetric (MF = C<sub>5</sub>H<sub>10</sub>O), and contains two methyl groups and one *tert* functional group. IR: broad band in the 3200-3550 cm<sup>-1</sup> region, no absorption at 1620-1680 cm<sup>-1</sup>. Propose a structure for 'P'. Is your suggested structure capable of showing stereoisomerism? 10×2=20

- (ii) The  $\lambda_{\max}$  values of the following compounds are 242 nm, 254 nm and 259 nm. Which is for which?

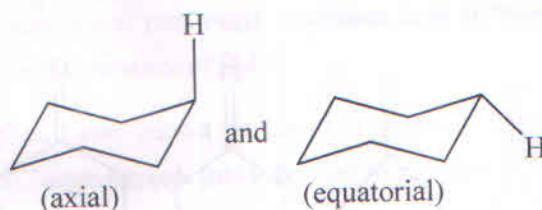


- (iii) How many  $^1\text{H-NMR}$  signals will be observed for each of the following compounds?



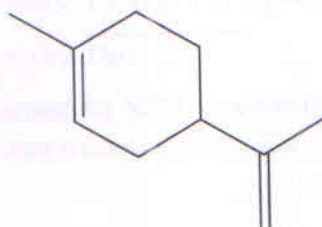
- (iv) Distinguish the following pair by  $^1\text{H-NMR}$  analysis:

3+3+3+1

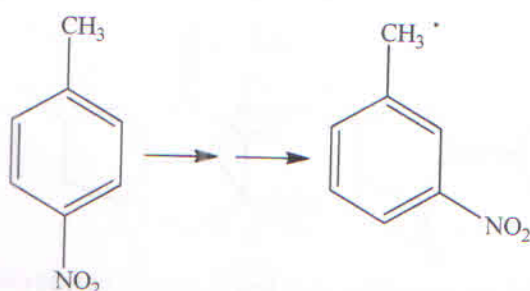


- (b) (i) What do you mean umpolung reaction? Account for the use of 1,3-propanedithiol over ethylene glycol in these reactions. Show how would you convert benzaldehyde to acetophenone.
- (ii) Show how could you prepare 1-phenyl-1,4-pentanedione from ethyl acetoacetate and any necessary reagents.
- (iii) Give the retrosynthetic pathways and then synthesize the following compound.

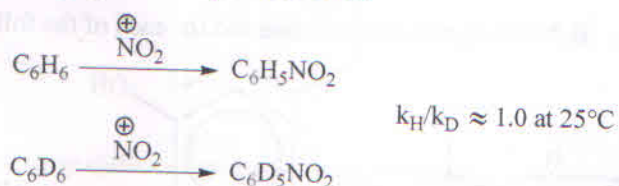
(1+1+2)+3+3



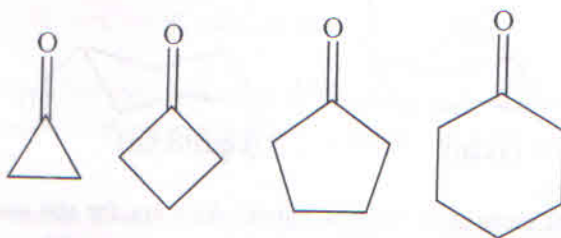
- (c) (i) Convert the following:



- (ii) Indicate the rate-limiting step of the following reactions from their
- $k_H/k_D$
- ratio and then show the energy profile diagram for each.



- (iii) Fries rearrangement occurs via both intramolecular and intermolecular. Explain the reaction with supporting evidences.
- (iv) In which rearrangement  $\alpha$ -diketones are converted into  $\alpha$ -hydroxy acids in presence of a base?  
2+3+(2+2)+1
- (d) (i) Arrange the following cyclic ketones in decreasing order of 'C=O' stretching frequencies. Explain your answer.



- (ii) Predict the products formed by the action of  $\text{HNO}_2$  on the following compound:  
(I)  $\text{PhCH}_2\text{NHCOCH}_3$       (II)  $\text{PhCH}_2\text{NHMe}$
- (iii) Explain why  $^1\text{H-NMR}$  spectrum of  $\text{CH}_3\text{OH}$  in  $\text{CCl}_4$  shows two singlets but in  $(\text{CD}_3)_2\text{SO}$  it shows a doublet and a quartet.
- (iv) Benzenediazonium chloride does not couple with anisole whereas 2,4-dinitrophenyldiazoniun chloride does—explain.  
3+2+2+3