

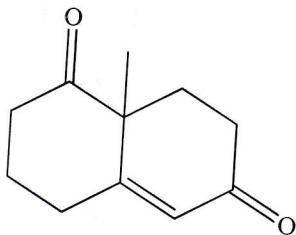
B.Sc. 4th Semester (Honours) Examination, 2023 (CBCS)**Subject : Chemistry****Course : CC-X****Time: 2 Hours****Full Marks: 40***The figures in the margin indicate full marks.**Candidates are required to give their answers in their own words as far as practicable.***1. Answer any five questions: 2×5=10**

- (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 D₂O?
- (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.

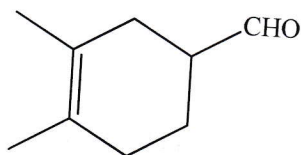
2. Answer any two questions: 5×2=10

- (a) (i) Predict the structure of the molecule from the following spectral data.
 - Molecular formula: C₄H₁₀O.
 - I. R. (cm⁻¹): 3350 (disappear in presence of D₂O), 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_{max} 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

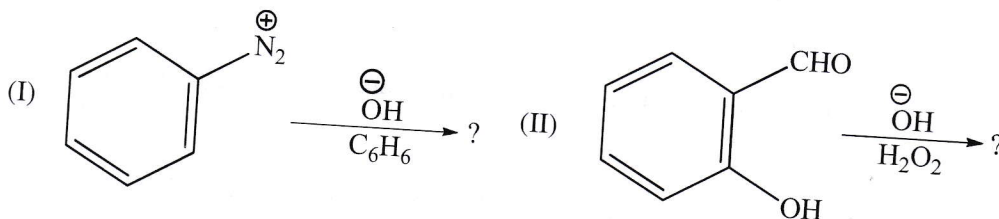
(I) C—H, S—H, N—H, O—H.

(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:

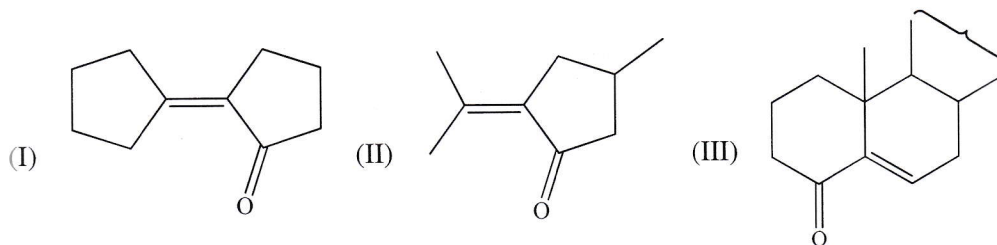
(1+2)+(1+1)



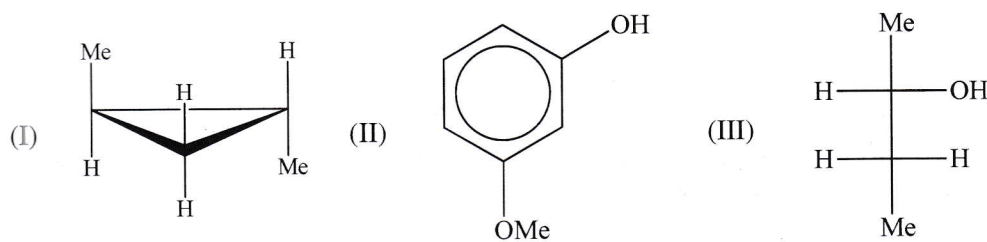
3. Answer any two questions:

- (a) (i) Compound 'P' is asymmetric (MF = C₅H₁₀O), and contains two methyl groups and one *tert* functional group. IR: broad band in the 3200-3550 cm⁻¹ region, no absorption at 1620-1680 cm⁻¹. Propose a structure for 'P'. Is your suggested structure capable of showing stereoisomerism? 10×2=20

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

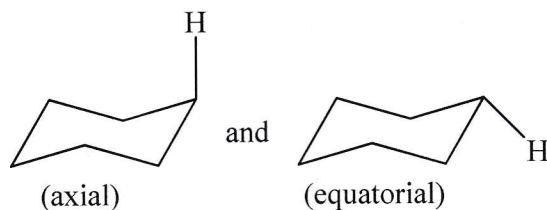


- (iii) How many $^1\text{H-NMR}$ signals will be observed for each of the following compounds?



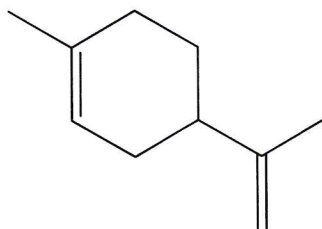
- (iv) Distinguish the following pair by $^1\text{H-NMR}$ analysis:

3+3+3+1

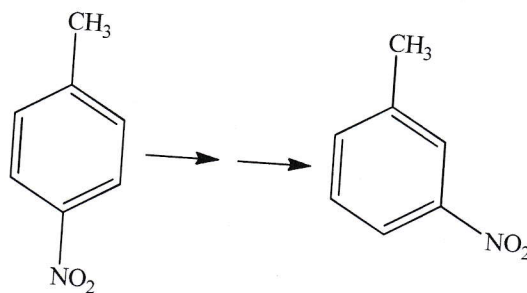


- (b) (i) What do you mean umplung reaction? Account for the use of 1,3-propanedithiol over ethylene glycol in these reactions. Show how would you convert benzaldehyde to acetophenone.
- (ii) Show how could you prepare 1-phenyl-1,4-pentanedione from ethyl acetoacetate and any necessary reagents.
- (iii)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

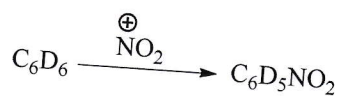
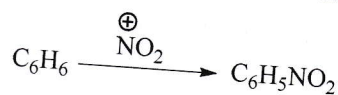
(1+1+2)+3+3



(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.

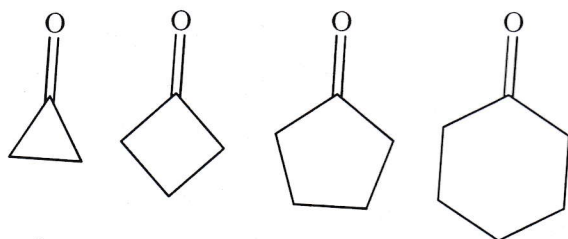


$$k_H/k_D \approx 1.0 \text{ at } 25^\circ\text{C}$$

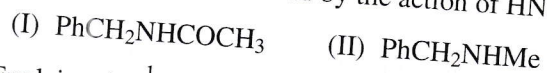
(iii) Fries rearrangement occurs via both intramolecular and intermolecular. Explain the reaction with supporting evidences.

(iv) In which rearrangement α -diketones are converted into α -hydroxy acids in presence of a base?

(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 HNO_2 on the following compound:



(iii) Explain why $^1\text{H-NMR}$ spectrum of CH_3OH in 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-dinitrophenyldiazonium chloride does—explain.

3+2+2+3