

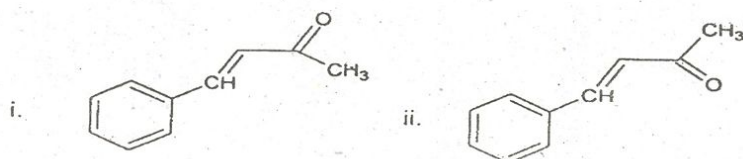
PG3S-389-A-23
M.Sc. III Semester (CBCS) Degree Examination
CHEMISTRY/ORGANIC CHEMISTRY-III Spectroscopy
(Common to Chemistry and Organic Chemistry)
Paper - HCT 3.1

Time : 3 Hours**Maximum Marks : 80****Instructions to Candidate:**

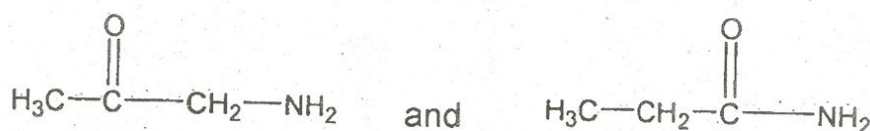
- i) Answer all questions
- ii) All questions carry equal marks.

1. Answer any Eight of the followings:**(8×2=16)**

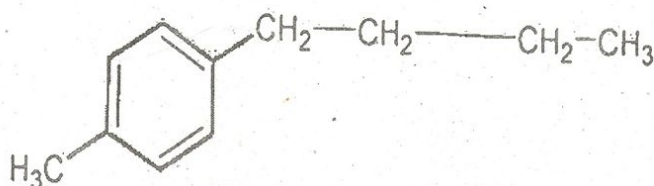
- a) Define the terms hypsochromic shift and bathochromic shift in Uv-Vis. Spectroscopy.
- b) Which of the following compound has the higher vibrational frequency? Justify your answer.



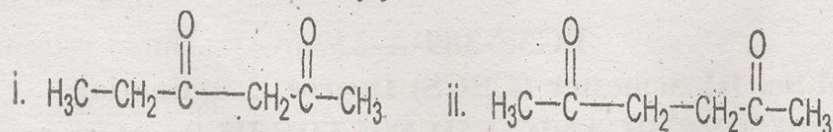
- c) Mention the range of function group region and fingerprint region in IR spectroscopy.
- d) How will you distinguish the following compounds using $^1\text{H NMR}$ spectroscopy? Justify your answer.



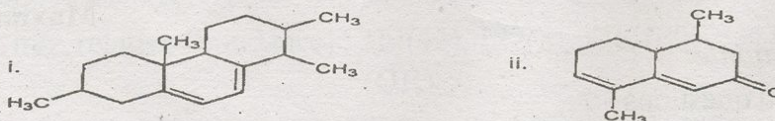
- e) Indicate the allowed transitions in UV-vis. Spectroscopy.
- f) Write the name and structure of internal standard used for water soluble compounds in $^1\text{H NMR}$ spectroscopy.
- g) Write the ^{13}C chemical shift values for the following compound:



- h) Sketch the ^1H NMR spectrum of the following compounds and assign the approximate chemical shift values. Justify your answer.



- i) Define the molecular ion peak and base ion peak.
 j) How will you distinguish the ethyl bromide and ethyl chloride using mass spectrometry.
 2. a) Using Woodward-Fieser rules calculate the λ_{max} for the followings:



- b) Explain with suitable examples how the vibration frequency of carbonyl group is influenced by mesomeric and inductive effects.
 c) Answer the followings:

- i) An organic compound with molecular formula $\text{C}_5\text{H}_{12}\text{O}_4$ exhibits broad band between $3400-3100\text{cm}^{-1}$ in its IR spectrum. The ^1H NMR spectrum showed two signals at 3.33 and 3.29 ppm with integral ratio 2:1, respectively. Deduce the structure of a compound.
 ii) Deduce the structure of a compound from the following data and assign the values.

Molecular formula: C_8H_{14}

UV (λ_{max}): no strong band $> 200\text{nm}$;

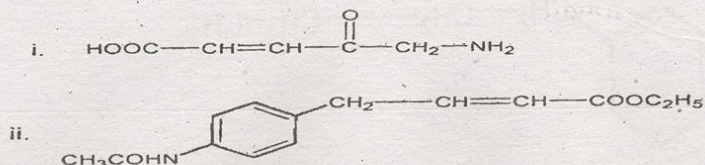
IR (cm^{-1}): 2983, 2938, 1484 and 1338.

^1H NMR (δ , ppm): 2.12(t, 4H, $J=8\text{Hz}$), 1.48(sextet, 4H, $J=8\text{Hz}$), and 0.9(t, 6H, $J=8\text{Hz}$)

^{13}C NMR (δ , ppm): 80.2, 22.7, 20.9 and 13.5

(OR)

- c) Why the band position of both the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of a compound are shifted when the solvent is changed from hexane to ethanol? (5+5+6=16)
 3. a) Indicate the types of magnetically equivalent protons, their multiplicity for the following compounds. Sketch the ^1H NMR for each and write approximate chemical shift values:



- b) Describe the factors affecting the germinal and vicinal coupling using suitable examples.
- c) Deduce the structure of an organic compound from the following data and assign the values:

Molecular formula : C_9H_{10}

1H NMR (δ , ppm) : 7.30(M, 2H), 7.14(M, 2H), 2.62(T, 4H, $J = 7.5$ Hz)
and 2.04(quintet, 2H, $J = 7.5$ Hz)

(OR)

- c) Write the Karplus equation and sketch the Karplus curve. Discuss the usefulness of the curve. (5+5+6=16)
4. a) With suitable example, discuss 2D-homonuclear correlation experiment as applied to 1H NMR. Explain the terms 'cross peaks' and 'diagonal peaks'.
- b) Illustrate the 1H - ^{13}C HETCORE pulse sequence and sketch the 2D spectrum of bromoacetone and ethanol.
- c) Deduce the structure of an organic compound having molecular formula C_8H_{14} with the help of the following spectral data:

UV (λ max) : 275nm;

IR(cm^{-1}) : 2989, 2936, 2874, 2720, 1693, 1603, 1259 and 1101

1H NMR(δ , ppm) : 9.91(s, 1H), 7.90(d, 2H, $J = 8$ Hz), 7.04(d, 2H, $J = 8$ Hz), 4.10(t, 2H, $J = 7$ Hz), 1.85(m, 2H) and 1.06(t, 3H, $J = 7$ Hz)

^{13}C NMR(δ , ppm) : 193.10, 165.20, 132.40, 129.30, 112.20, 69.80, 32.20, 19.00 and 12.90

MS(m/z) : 178(M^+), 177(100%) and 76(46%)

(OR)

- c) How the number and Position of ^{13}C NMR signals can help in the identification of the four isomeric butyl alcohols $C_4H_{10}O$? (5+5+6=16)
5. a) Predict the masses of the ions produced in the mass spectrum of 1-hexene and 2-heptene by the McLafferty rearrangement. Are these radical cations? What happens to the alkene fragments produced in these rearrangements?
- b) Write notes on:
- Stevenson rule and its applications in mass spectrometry.
 - CI method for production of ions.

- c) Deduce the structure of an organic molecule with the help of the following data and assign the values:

Molecular formula : $C_{13}H_{10}O_2$

UV (λ_{\max}): 276nm;

IR (cm^{-1}): 3192, 1682, 1595, 1487, 1406 and 1100

1H NMR (δ , ppm): 10.51 (*s*, 1H, D₂O exchangeable), 8.04 (*d* / *d*, 1H), 7.59 to 7.38 (*m*, 3H), 7.34 to 7.18 (*m*, 4H) and 7.04 to 6.90 (*m*, 1H).

EIMS (m/z, relative abundance): 214(13), 122(8), 121(100), 93(9), 65(13) and 39(8).

(OR)

- c) Deduce the structure of an organic compound from the following data and assign the values:

Molecular formula : $C_4H_6O_2$

UV (λ_{\max}): 218nm;

IR (cm^{-1}): 3400 – 2800 (*M, br*), 1719, 1641 and 1111.

^{13}C NMR (δ , ppm): 172.4, 147.6, 122.4 and 18.00.

(5+5+6=16)

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PG3S-391-A-23
M.Sc.III Semester (CBCS) Degree Examination
CHEMISTRY
Physical Chemistry-III
Paper -HCT- 3.2

Time : 3 Hours

Maximum Marks : 80

Instructions to Candidates:

1. *Answer all the questions.*
2. *All questions carry equal marks.*

Answer any **Eight** of the following.

(8×2=16)

1.
 - a) Define γ space and μ space.
 - b) What is partition function? Give its equation.
 - c) Discuss briefly Harmonic Oscillator.
 - d) Discuss bonding and antibonding molecular orbitals.
 - e) Give general principles of solid state reactions.
 - f) Give differences between Ferro and Ferrimagnetic materials with examples.
 - g) Define ensembles.
 - h) Comment on stationary states.
 - i) Give classification of surface active agents.
 - j) Give principle of minimum entropy production.
2.
 - a) Discuss Bose-Einstein and Fermi-Dirac statistics. (5+5+6=16)
 - b) Explain Translational and Vibrational partition function.
 - c) Explain Maxwell-Boltzman distribution for ideal gases.

(OR)

Calculate internal energy thermodynamics quantities in terms of partition function.

3. a) Explain Huckel theory application to benzene molecule. (5+5+6=16)
b) Explain MO theory of hydrogen ion.
c) Explain the applications of Schrodinger wave equation to hydrogen like atom.

(OR)

Discuss the comparison of VBT and MO theories.

4. a) Discuss single crystal growth method of solid state reaction. (5+5+6=16)
b) Explain differential thermal analysis (DTA) for characterization of compound.
c) Write notes on optical properties and photoconductance structure of amorphous glasses.

(OR)

Explain Hall and Sebeck effect in semiconductor materials.

5. a) Explain a method for determination of surface tension. (5+5+6=16)
b) Explain energy production in irreversible process.
c) Discuss Onsager's reciprocity relations.

(OR)

State and derive Gibbs-Duham equation.

Roll No. _____

[Total No. of Pages : 2

PG3S-390-A-23
M.Sc. III Semester (CBCS) Degree Examination
ORGANIC CHEMISTRY
Reaction Mechanisms
Paper : HCT 3.2

Time : 3 Hours

Maximum Marks : 80

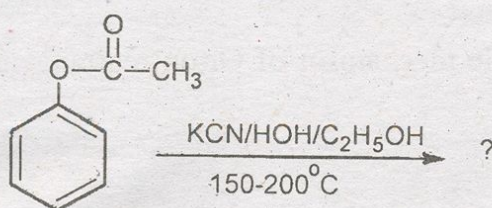
Instructions to Candidates:

- 1) Answer all questions.
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Answer any **Eight** of the followings:

(8×2=16)

1.
 - a) Write any one reaction involving aryne intermediate.
 - b) Give any two methods for the generation of free radicals.
 - c) Write an example of neighbouring group participation involving alkyl group.
 - d) What is trans annular rearrangement? Give an example.
 - e) What is Chugave reaction? Sketch its mechanism.
 - f) Explain the mechanism of Aldol condensation using suitable example.
 - g) What is Push-Pull reaction? Outline its mechanism.
 - h) Give the mechanism of Von-Richter rearrangement by taking appropriate example.
 - i) What is eclipsing effect in elimination reactions?
 - j) Predict the product and suggest suitable mechanism for the following transformation:



2.
 - a) Write an account on geometry of carbenes. Explain how the singlet and triplet carbenes are distinguished.
 - b) Write briefly on formation and reactions of enamines.
 - c) Write notes on:
 - i) Geometry, stability and reactions of free-radicals.
 - ii) Formation and synthetic applications of nitrenes.

(OR)

- c) Describe the reactions and applications of phosphorus and nitrogen ylides.

(5+5+6=16)

3. a) Discuss the nucleophilic substitution at allylic and trigonal carbon atom.
b) Explain the reactions involving nitrogen and cycloalkyls as neighbouring group participation.
c) Give an account of the neighbouring group participation in the addition and elimination reactions.

(OR)

- c) Write briefly on Intramolecular displacement by oxygen in neighbouring group participation reactions. (5+5+6=16)

4. a) What is Cram's rule? Illustrate with appropriate example how the open-chain model is useful to determine the stereochemistry of the product formed in the addition reactions of carbonyl compounds.
b) Discuss the stereochemistry of elimination in non-cyclic compounds with suitable examples.
c) Write notes on:
i) Hoffmann and Saytzeff eliminations
ii) Cope reaction.

(OR)

- c) Write briefly on:
i) Cannizzaro's reaction and its applications.
ii) Elimination by carbanions mechanism. (5+5+6=16)

5. a) What is Claisen Condensation? Outline its mechanism by taking appropriate example?
b) Illustrate with suitable example mechanism of Orton rearrangement. Mention its applications.
c) Write notes on:
i) Schmidt rearrangement.
ii) Perkin reaction.

(OR)

- c) Write briefly on:
i) Mc Murry reaction
ii) Free radical mechanism in allylic rearrangements. (5+5+6=16)