

Seat No.	
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**M.Sc. (Part - II) (Semester - III) Examination, November - 2019**

**ORGANIC CHEMISTRY (CBCS) (Paper - OCH - X)**

**Advanced Spectroscopic Methods**

**Sub. Code : 60841**

**Day and Date : Thursday, 14 - 11 - 2019**

**Total Marks : 80**

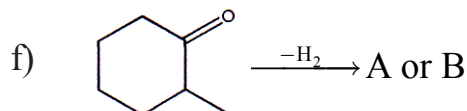
**Time : 11.00 a.m. to 02.00 p.m.**

- Instructions :**
- 1) Question No. 1 is compulsory.
  - 2) Answer any two questions from each section.
  - 3) Answers to the all the questions should written in the same answer book.
  - 4) Figures to the right indicate marks.

**Q1) Answer the following.**

**[16]**

- a) State the significance of term "IR Active."
- b) What is TMS?
- c) Which is best analytical tool to confirm the presence of bromine in a given organic sample?
- d) The IR spectrum of ethylene does not show double bond stretching absorption. Justify the statement.
- e) Addition of alkali to nitrophenol will cause \_\_\_\_\_ shift.



Write the structures of both the compounds (A or B). Which amongst them will have higher  $\lambda_{max}$  value?

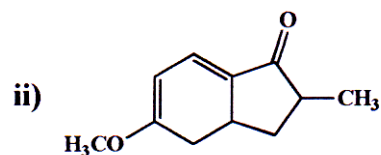
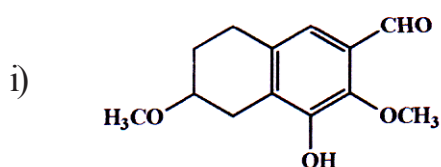
- g) In 100 MHz NMR,  $1\delta =$  \_\_\_\_\_ Hz.

**P.T.O.**

- h) Which electromagnetic radiation used in  $^{13}\text{C}$ -NMR spectroscopy.
- i) In the  $\alpha$ -cleavage of acetone, the  $m/z$  ratio is \_\_\_\_\_.
- j) The compound  $\text{CH}_3\text{-OCH}_2\text{-CH}_2\text{-OCH}_3$  in its PMR spectrum how many signals will show.
- k) In  $^{13}\text{C}$ -NMR spectroscopy chemical shifts on the  $\delta$  scale have values between \_\_\_\_\_.
- l) In PMR spectrum, aldehydic proton appears in the far down field region because it is \_\_\_\_\_.
- m) Which amongst the following have higher carbonyl stretching frequency?  
 $\text{CH}_3\text{-CONH}_2$  and  $\text{CH}_3\text{COOCH}_3$
- n) Give any one illustration that contains chemically equivalent but magnetically non-equivalent protons.
- o) Give the structure of an organic compound ( $\text{C}_5\text{H}_{10}\text{O}$ ) which exhibits four signals in H-decoupled  $^{13}\text{C}$ NMR spectrum.
- p) Calculate  $m/z$  value of parent ion which produces daughter ion and metastable ion at  $m/z = 108$  and  $94.82$  respectively.

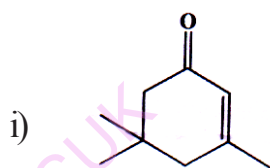
### SECTION - I

- Q2) a) Explain with suitable example genesis of metastable ions and its significance in interpretation of mass spectra. [8]
- b) Using Woodward-Fieser rules calculate  $\lambda_{\text{max}}$  for the following compound. [4]

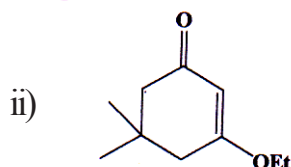


c) Match the following pairs.

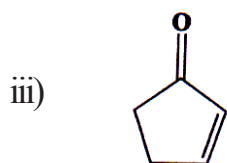
[4]



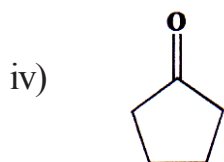
a) 1745



b) 1680



c) 1715



d) 1640

**Q3) a)** The organic compound having MF  $C_4H_9ON$  shows the spectrum at  $m/z$  87, 86, 72, 71, 59, 44 and 43. [6]

b) Explain the effect of purity on PMR spectrum of ethanol. [5]

c) Explain the use of isotope ion peaks (in MS) for the analysis of organohalo compounds. [5]

**Q4) a)** An organic compound with MF  $C_{12}H_{14}C_2$  shows the following spectral data.

Assign the structure and justify the spectral data. [8]

UV :  $\lambda_{max} = 272 \text{ nm}$

IR : 1720, 1628  $\text{cm}^{-1}$

$^1\text{H-NMR}$  :  $\delta$  7.8 (1H, d,  $J = 18 \text{ Hz}$ ), 7.5 (2H, d,  $J = 8 \text{ Hz}$ ), 7.1 (2H, d,  $J = 8 \text{ Hz}$ )  
6.8 (1H, d,  $J = 8 \text{ Hz}$ ), 4.1 (2H, q,  $J = 7 \text{ Hz}$ ), 2.4 (3h, s), 1.25 (3H, t,  $J = 7 \text{ Hz}$ ).

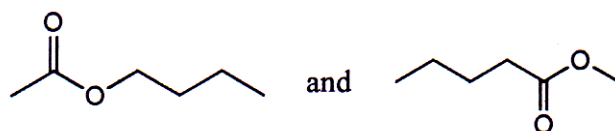
Mass :  $m/z = 190$

- b) Three isomers of  $C_3H_6Br_2$  display one, two, three signals at their respective PMR spectra. Assign structure to the isomers. [4]
- c) Absorption maximum of acetone is at  $279\text{ m}\mu$  in hexane as compared to  $264\text{ m}\mu$  in water. [4]

**SECTION - II**

- Q5)** a) What are the factors that increase complexity Of PMR. Give the techniques to resolve them. [8]
- b) Deduce the structure from the given data: [8]  
 M.F. :  $C_5H_7NO_2$   
 IR :  $1990, 2260, 1747, 1200\text{ cm}^{-1}$ .  
 PMR:  $\delta$  1.3 (t, 3H), 3.5 (s, 2H), 4.3 (q, 2H).  
 $^{13}C$ -NMR: 14 (q), 25 (t), 63 (t), 150 (s), 163 (s).  
 Justify the spectral data.

- Q6)** a) Give the brief account on McLafferty rearrangement and its use in differentiating following compounds. [4]



- b) The proton NMR data for a compound with the formula  $C_5H_{12}O_2$  is triplet  $\delta$ 1.25 (6H), quartet  $\delta$ 3.68 (4H), singlet  $\delta$ 4.43 (2H). The normal carbon-13 NMR and DEPT-135, DEPT-90 spectral results are tabulated. Draw the structure of compound. [8]

normal carbon-13	DEPT-135	DEPT-90
15 ppm	positive	No peak
63 ppm	negative	No peak
95 ppm	negative	No peak

- c) How many distinct absorptions will be observed in the  $^{13}C$ -NMR spectrum of hex-2-ene. [4]

- Q7)** Write notes on following.(Any four) [16]

- Nitrogen Rule
- Steric effect in biphenyls
- Off resonance decoupling technique
- Nuclear overhauser effect
- Solvent effect on vibrational frequencies

## SPECTROSCOPIC DATA

**Table I: Some characteristic IR frequencies (Only approximate values)**

$\equiv \text{CH}$ , 3300  $\text{cm}^{-1}$ ;  $\text{C}=\text{CH}$ , 3050;  $\text{O}=\text{C}-\text{H}$ , 2800;  $\text{NH}$ , 3300;  $\text{O}-\text{H}$ , 3600;  $\text{C}\equiv\text{N}$ , 2200;  $\text{C}=\text{C}$ , 1620 to 1680; Aromatic, 1600 – 1500;  $\text{C}=\text{N}$ , 1660; ketone, 1720; Ester, 1740; Saturated acids, 1720; Saturated aldehydes, 1730; Saturated amides, 1650;  $\text{CH}=\text{CH}_2$ , 900 and 910;  $\text{CH}=\text{CH}$  (trans); 960;  $\text{CH}=\text{CH}$  (CIS), 690;  $\text{C}=\text{CH}_2$ , 890;  $\text{C}=\text{CH}$ , 790-840;  $\text{NO}_2$ , 1530 and 1350; Monosubstituted aromatics 690-710 and 730 to 770; Disubstituted 735-770; trisubstituted 750-810; tetrasubstituted 770, 800-860;  $-\text{C}-\text{CH}_2\text{Cl}$ , 1745–1725.

$$\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{CH}_2\text{Cl} \end{array}$$
 Lactones. 1735  $\text{cm}^{-1}$ .

**Table II: Approximate chemical shifts of  $-\text{CH}_3$ ,  $-\text{CH}_2$  and  $-\text{CH}$  protons in  $\delta$  (ppm):**

$\text{C}-\text{CH}_3$ , 0.9;  $\text{O}-\text{CH}_3$ , 1.4;  $\text{C}=\text{C}-\text{CH}_3$ , 1.6;  $\text{ArCH}_3$ , 2.2;  $\text{O}=\text{C}-\text{CH}_3$ , 2.3;  $\text{N}-\text{CH}_3$ , 2.3;  $\text{O}-\text{CH}_2$ , 3.3;  $\text{C}=\text{CH}_2$ , 4.6 to 5.3;  $\text{C}=\text{CH}:\text{Ar}-\text{H}$  7 to 9;  $-\text{C}-\text{C}=\text{CH}$ , 6.2;  $\text{C}-\text{CH}-\text{C}$ , 5.7

**Table III: Approximate  $^{13}\text{C}$  chemical shifts**

$\text{R}-\text{CH}_3$ , 5–30;  $\text{R}-\text{CH}_2-\text{R}$ , 25–25;  $\text{R}_3\text{CH}$ , 35 to 70;  $\text{R}_4\text{C}$ , 30–50;  $\text{R}_3\text{C}-\text{O}$ , 57-80;  $\text{R}_3\text{C}-\text{N}$ , 60 to 75;  $\text{C}\equiv\text{C}$ , 75 to 105;  $\text{C}\equiv\text{N}$  110 to 125;  $\text{C}=\text{C}$ , 100 to 140; Aromatic's 115 to 145;  $\text{R}-\text{COOR}$ /  
 $\text{R}-\text{COHN}_2$ , 155–180;  $\text{R}-\text{COOH}$ , 155–185;  $\text{R}-\text{CHO}$ , 185 – 205;  $\text{R}-\text{COR}$ , 190 – 225.



Seat No.	
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**M.Sc. (Part-II) (Semester-III) (CBCS)**  
**Examination, April-2019**  
**ORGANIC CHEMISTRY**  
**Advanced Spectroscopic Methods (Paper-OCH-X)**  
**Sub. Code : 60841**

Day and Date : Thursday, 4 - 04 - 2019

Total Marks : 80

Time : 3.00 p.m. to 6.00 p.m.

- Instructions :**
- 1) Question No.1 is compulsory.
  - 2) Answer any two questions from each section.
  - 3) Answers to the all the questions should written in the same answer book.
  - 4) Figure to the right indicate full marks.

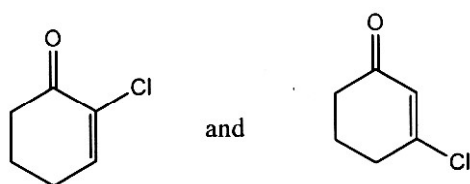
**Q1) Answer the following: [16]**

- a) Define bathochromic shift.
- b) Amongst 4-methoxyacetophenone and 4-aminoacetophenone, which will have higher carbonyl stretching frequency?
- c) Write the structure of an ion ( $m/z = 66$ ) resulted in MS of phenol.
- d) How would you differentiate between cis-butadiene and trans butadiene using UV spectroscopy?
- e) What is the relative area of each peak in a quartet spin-spin splitting pattern?
- f) Give region of characteristics of infrared stretching absorption frequency of alkynes.
- g) Electromagnetic radiation used in  $^{13}\text{C}$ -NMR spectroscopy are \_\_\_\_\_.
- h) A nucleus with an \_\_\_\_\_ atomic number or an \_\_\_\_\_ mass number has a nuclear spin that can be observed by the NMR spectrometer.

**P.T.O.**

## SD-198

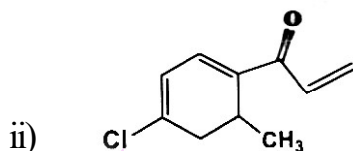
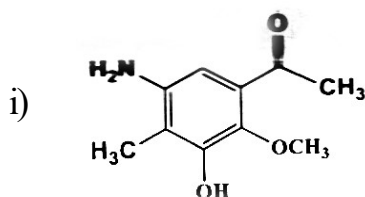
- i) If a signal is observed in the 170 to 200 ppm range in a  $^{13}\text{C}$ -NMR spectrum, what is the most likely type of functional group associated with that carbon atom?
- j) Mention any two ionization techniques used in mass spectroscopy.
- k) In  $^{13}\text{C}$ -NMR spectroscopy, chemical shifts on the  $\delta$  scale have values between \_\_\_\_\_.
- l) The molecular ion in the mass spectrum of  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-Br}$  is \_\_\_\_\_.
- m) Which amongst the following will have higher  $\lambda_{\text{max}}$  value.



- n) State whether true or false: Base peak and molecular ion peak in mass spectrum are same.
- o) A nuclear magnetic resonance transition is shifted from the reference in a 400 MHz NMR spectrometer by 529 Hz. Calculate the chemical shift.
- p) How many nuclear spin states are allowed for the  $^1\text{H}$  nucleus?

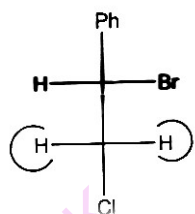
### SECTION - I

- Q2) a)** Using Woodward-Fieser rules calculate  $\lambda_{\text{max}}$  for the following compound. [6]

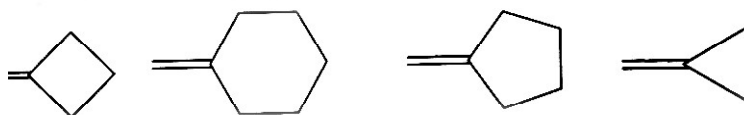


- b) The benzene proton appears 2181 Hz downfield from the TMS in 300 MHz NMR spectrophotometer instrument and 436 Hz downfield from TMS in 60 MHz NMR spectrophotometer instrument. Prove that the chemical shift ( $\delta$ ) expressed in  $\delta$  ppm is same at both 60 MHz and 300 MHz NMR spectrophotometer. [6]
- c) Determine the structure with the help of following spectral data. [4]
- FM =  $C_7H_8O$
- $^{13}C$ -NMR: 54, 114, 120.8, 129.5, 159.5

- Q3) a)** Define enantiotopic, homotopic, distereotopic atoms or groups. In the given following structure protons marked with semi circle are enantiotopic, homotopic, distereotopic. As a result how will be the splitting pattern of the marked protons. [8]

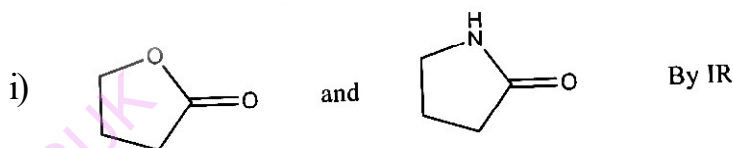


- b) Arrange the following compound in order of their increasing wave number of absorption due to  $C=C$  stretching. [4]

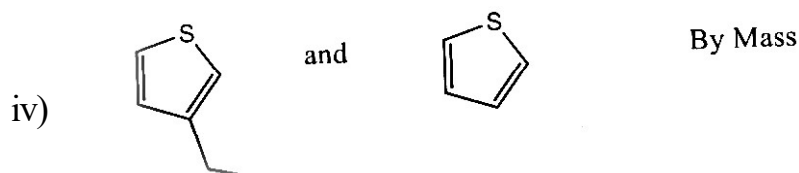
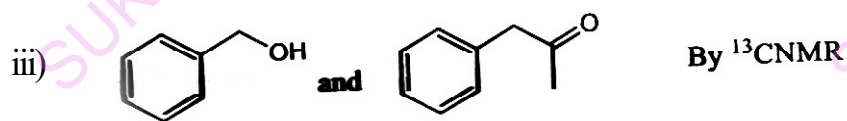
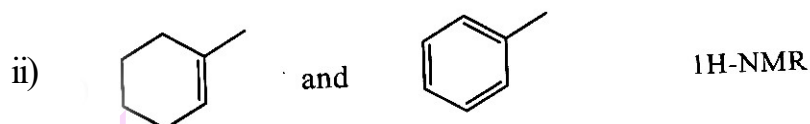


- c) Explain the use of McLafferty rearrangement in mass spectral analysis of ketons. [4]

- Q4) a)** Differentiate following pairs. [8]





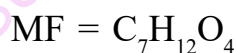


- b) What is a metastable ion? Explain Ethyl butyrate in mass spectrum shows two characteristic peaks at  $m/z$  88 and 60 abundant ion at  $m/z$  71. [8]

### SECTION - II

- Q5) a) Explain the broad band decoupling and off resonance decoupling technique. [8]

- b) Determine the structure with the help of following spectral data. [8]



$$\text{UV} = 212 \text{ nm } \epsilon_{\text{max}} = 60$$

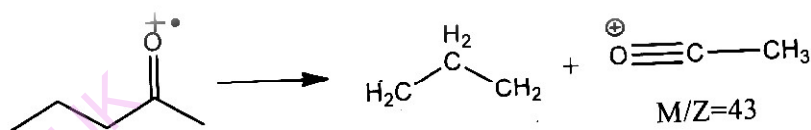
IR Spectral data:  $2941\text{-}2857\text{cm}^{-1}$ ,  $1742\text{cm}^{-1}$ ,  $1460\text{cm}^{-1}$ ,  $1056\text{cm}^{-1}$ ,

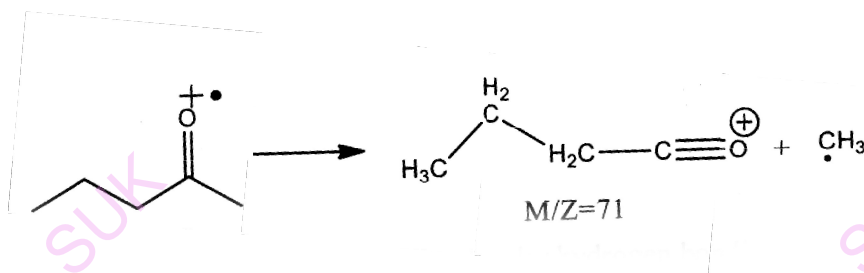
$^1\text{H-NMR}$  data: singlet  $7.5 \tau$  (5.3 squares), triplet  $8.71 \tau$  (16.5 squares)

( $J=7.2\text{Hz}$ ), quartet  $5.84 \tau$  (10.8 squares)  $J=7.2\text{Hz}$

Broad band decoupled  $^{13}\text{C-NMR}$  data:  $177 \delta$ ,  $60\delta$ ,  $20 \delta$ ,  $18 \delta$ .

- Q6) a) Explain why  $m/z=43$  peak is more intense than  $m/z=71$  peak in the following fragmentation. [4]





- b) Explain the effect of intra and intermolecular hydrogen bonding on carbonyl stretching frequency. [4]
- c) Using the given data, deduce the structure of an unknown organic compound and explain the genesis of listed ions from the MS of the derived compound. [8]

MF :  $\text{C}_{10}\text{H}_{12}\text{O}_3$

IR :  $1750\text{ cm}^{-1}$

PMR :  $\delta 3.4(3\text{H}, \text{S}), 3.7(3\text{H}, \text{S}), 4.8(1\text{H}, \text{S}), 7.3-7.6(5\text{H}, \text{m})$ .

CMR :  $\delta 52, 58, 82, 127(2\text{C}), 128(2\text{C}), 138(2\text{C}), 171$ .

MS : 180, 121, 107, 91, 77.

**Q7)** Write a note (Any four).

- NOE
- Nitrogen Rule
- Fermi resonance
- Karplus Equation
- Solvent polarity effect on  $n \rightarrow \pi^*$  transition.

[16]

## SPECTROSCOPIC DATA

Table: I Some characteristic IR frequencies (only approximate values)

$\equiv \text{CH}$ , 3300;  $= \text{CH}$ , 3050;  $\text{O} = \text{C} - \text{H}$ , 2800;  $\text{NH}$ , 3300;  $\text{O} - \text{H}$ , 3600;  
 $\text{C} \equiv \text{N}$ , 2200;  $\text{C} = \text{C}$ , 1620 to 1680; Aromatic, 1600 - 1500;  $\text{C} = \text{N}$ ,  
 1660; ketone, 1720; Ester, 1740; Saturated acids, 1720; Saturated  
 aldehydes, 1730; Saturated amides, 1650;  $\text{CH} = \text{CH}_2$ , 900 and 910;  
 **$\text{CH} = \text{CH}$  (trans); 960;  $\text{CH} = \text{CH}$  (cis), 690;  $\text{C} = \text{CH}_2$ , 890;  $\text{C} = \text{CH}$ ,  
 790-840;  $\text{NO}_2$ , 1530 and 1350; Monosubstituted aromatics 690-710  
 and 730 to 770; Disubstituted 735-770; trisubstituted 750-810;  
 tetrasubstituted 770. 800-860:  $-\text{C} - \text{CH}_2 \text{Cl}$ , 1745 - 1725;**



lactones, 1735  $\text{cm}^{-1}$ .

Table: II Approximate chemical shifts of  $-\text{CH}_3$ ,  $-\text{CH}_2$  and  $-\text{CH}$  protons in  $\delta$  (ppm):

$\text{C} - \text{CH}_3$ , 0.9;  $\text{O} - \text{CH}_3$ , 1.4;  $\text{C} = \text{C} - \text{CH}_3$ , 1.6;  $\text{ArCH}_3$ , 2.2;  $\text{O} = \text{C} - \text{CH}_3$ ,  
 2.3;  $\text{N} - \text{CH}_3$ , 2.3;  $\text{O} - \text{CH}_3$ , 3.3;  $\text{C} = \text{CH}_2$ , 4.6 to 5.3;  $\text{C} = \text{CH} : \text{Ar} - \text{H}$  7 to 9;  
 $-\text{C} - \text{C} = \text{CH}$ , 6.2;  $\text{C} - \text{CH} - \text{C}$ , 5.7

Table: III Approximate  $^{13}\text{C}$  chemical shifts

$\text{R} - \text{CH}_3$ , 5-30;  $\text{R} - \text{CH}_2 - \text{R}$ , 25-55;  $\text{R}_3\text{CH}$  - 35 to 70;  
 $\text{R}_3\text{C}$ , 30-50;  $\text{R}_3\text{C} - \text{O}$ , 57-80;  $\text{R}_3\text{C} - \text{N}$ , 60 to 75;  $\text{C} \equiv \text{C}$ , 75 to 105;  $\text{C} \equiv \text{N}$   
 110 to 125;  $\text{C} = \text{C}$ , 100 to 140; Aromatic c's 115 to 145;  $\text{R} - \text{COOR}$  /  $\text{R} - \text{CONH}_2$ ,  
 155-180;  $\text{R} - \text{COOH}$ , 165-185;  $\text{R} - \text{CHO}$ , 185-205;  $\text{R} - \text{COR}$ , 190-225.



Seat No.	
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**M.Sc. (Part - II) (Semester - III) (CBCS)**  
**Examination, March - 2023**  
**ORGANIC CHEMISTRY**  
**Organic Reaction Mechanism (Paper - IX)**  
**Sub. Code : 80474/85415**

Day and Date : Wednesday, 21 - 06 - 2023

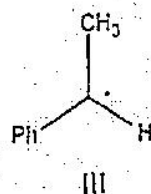
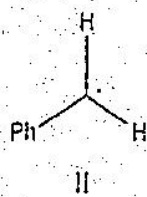
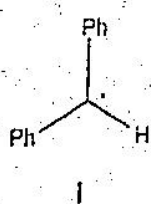
Total Marks : 80

Time : 10.30 a.m. to 01.30 p.m.

- Instructions :
- 1) All questions carries equal marks.
  - 2) Attempt in all five questions.
  - 3) Question No. 1 is compulsory.
  - 4) Select any two questions from each section I and section II.
  - 5) Figures to the right indicate full marks.
  - 6) Use of log table and calculator is allowed.

Q1) a) Answer the following (One Mark Each): [16]

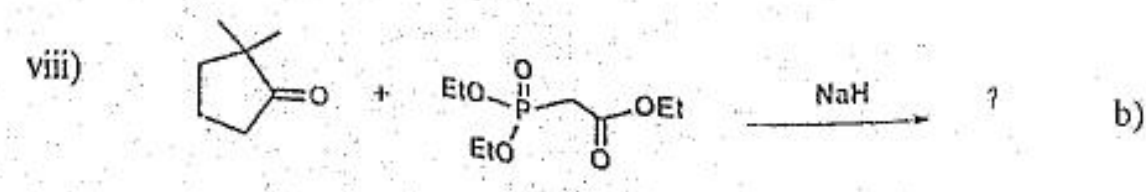
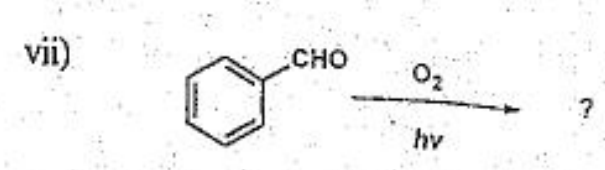
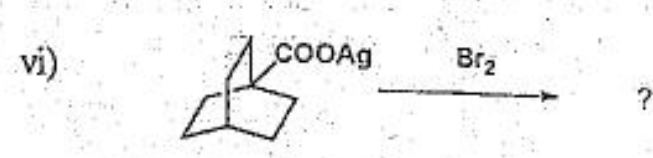
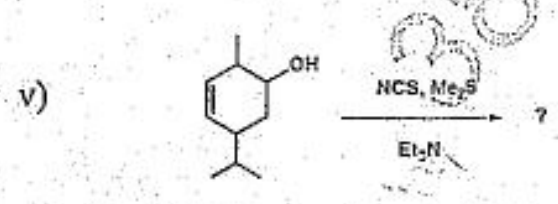
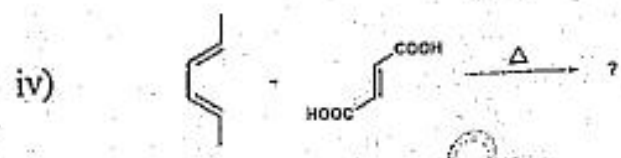
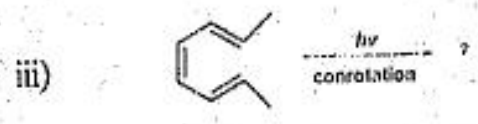
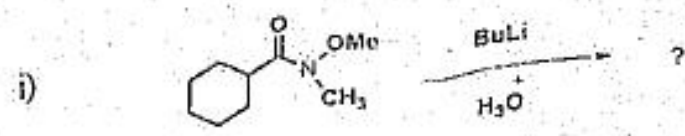
- i) What is kinetic isotope effect?
- ii) Define ENE reaction.
- iii) What is ylide?
- iv) Arrange the following free radicals according to their increase in stability.



- v) Name the reaction that is used to convert an alcohol into aldehyde or ketone using N - Chlorosuccinimide (NCS), dimethyl sulfide (DMS) and triethylamine (TEA).
- vi) Draw the HOMO and LUMO of 1,3 - butadiene in ground state.
- vii) Give any two radical initiators.
- viii) Give the catalysts most commonly used in the alkyne metathesis reaction.

*P.T.O.*

b) Predict the products in the following reactions



Q2) Ex  
re:  
a)  
b)  
c)  
d)

Q3) a)

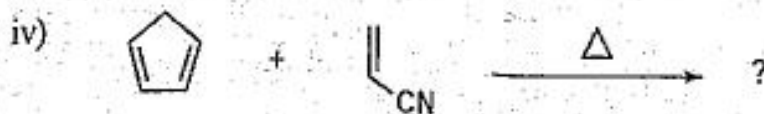
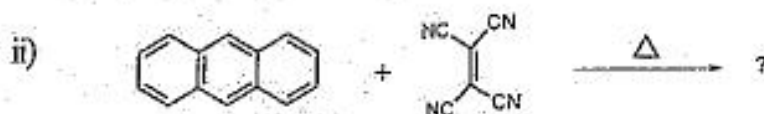
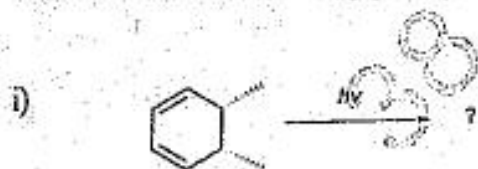
b)

Q4) a)

b)

SECTION - I

- Q2) Explain the use of the following methods in determining the mechanism of reaction. [16]
- Trapping of the intermediates
  - Reaction catalysis
  - Cross-over experiments
  - Stereochemical studies
- Q3) a) Explain the characteristics of pericyclic reactions. Derive Woodward-Hoffmann rules for conversion of butadiene into cyclobutene using FMO approach. [8]
- b) Explain the correlation diagram for [4+2] cycloaddition reaction. [8]
- Q4) a) Write the necessary selection rule and give stereochemistry of the product for each of the following pericyclic reactions. [8]



- b) State and explain Hammett equation and explain the significance of substituent constant ( $\sigma$ ) and reaction constant ( $\rho$ ) [8]



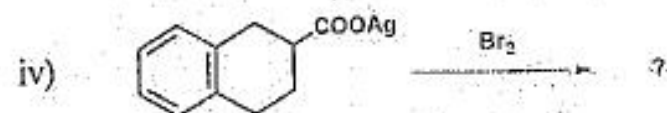
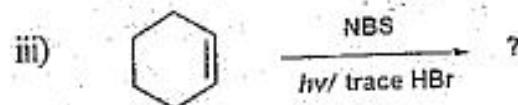
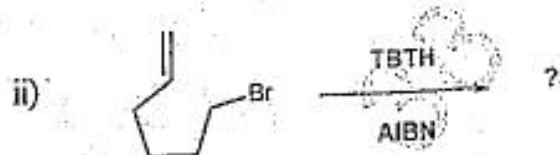
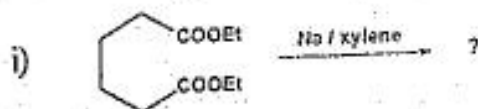
SECTION - II

Q5) a) Give an account of the methods of preparation and synthetic utility of sulfur ylides. [8]

b) Explain the following reactions with mechanism [8]  
i) Petasis reaction  
ii) Henry reaction

Q6) a) Explain the following reactions giving mechanism [8]  
i) Abstraction reactions  
ii) Hunsdiecker reaction

b) Write the products of the following reactions giving mechanism. [8]



Q7) Write notes on (any four): [16]

- Sandmeyer's reaction
- Cope rearrangement
- Weinreb ketone synthesis
- Isotopic labelling
- Phosphorus ylides

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Seat No.	Back QP.
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M.Sc. (Part - II) (Semester - III) (CBCS) Examination,  
November - 2023

ORGANIC CHEMISTRY  
OCH 3:1 : Organic Reaction Mechanism (Paper - IX)  
Sub. Code : 80474/85415

Day and Date : Wednesday, 29-11-2023  
Time : 2.30 a.m. to 5.30 p.m.

Total Marks : 80

- Instructions:
- 1) Question No. 1 is compulsory.
  - 2) Select any two questions from each section.
  - 3) Answer to the all questions must be written in the same answer book.
  - 4) All questions carry equal marks.
  - 5) Figures to the right indicate full marks.

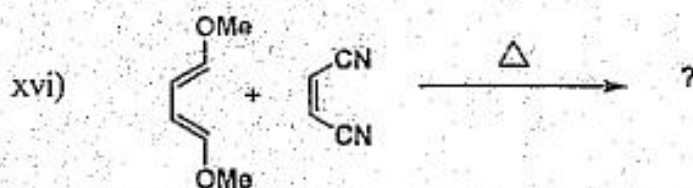
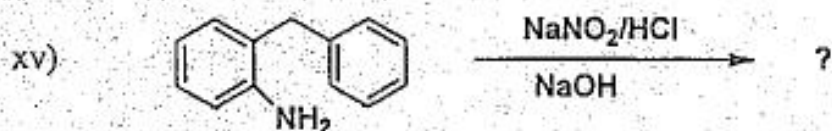
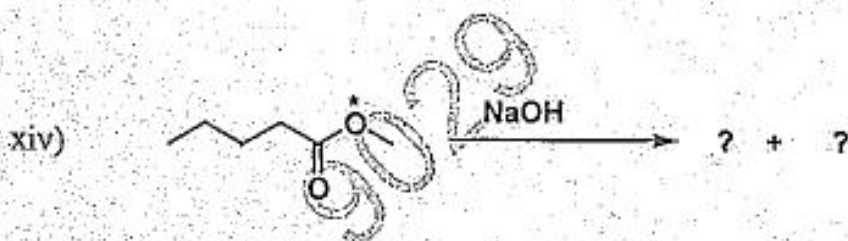
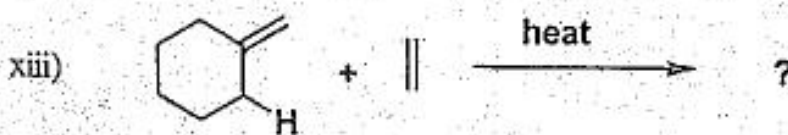
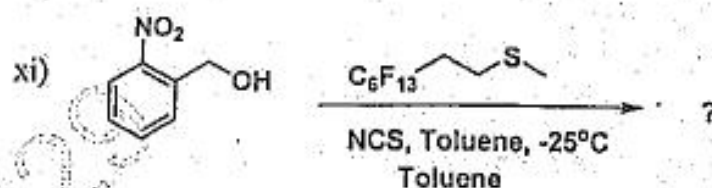
Q1) a) Answer the following questions: [16]

- i) Why is trimethylsilyl chloride added during acyloin condensation?
- ii) Draw the HOMO of 1, 3, 5 - hexatriene under photochemical conditions?
- iii) What is auto-oxidation?
- iv) Which ylides are used for preparation of compounds with exocyclic double bonds?
- v) Mention any two methods for generation of free radicals.
- vi) Mention two factors that decide the stereochemical outcome of cycloaddition reactions.
- vii) What is kinetic isotope effect?
- viii) What is labelling technique?
- ix) State True or False : Cross-over experiments help to confirm whether reaction is intramolecular or intermolecular.
- x) What is ENE reaction?

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b) Write the products of the following reactions.



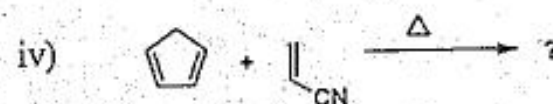
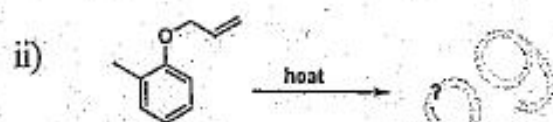
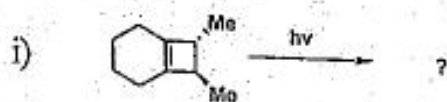
SECTION - I

Q2) Elaborate various non-kinetic methods of determining reaction mechanism. [16]

Q3) a) Explain the correlation diagram for electrocyclic reaction with suitable example. [8]

b) Explain Woodward-Hoffmann rules by taking Diels-Alder reaction as an example. [8]

Q4) a) Write the products of following pericyclic reactions giving necessary selection rule. [8]



b) Give an account on Hammett equation? Explain the significance of sigma and rho values. [8]

SECTION - II

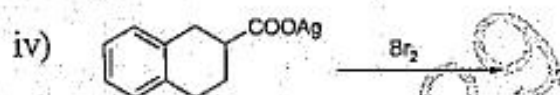
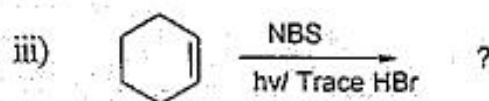
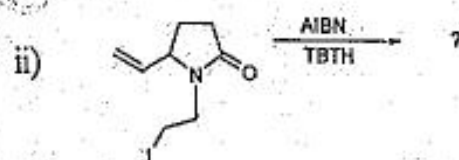
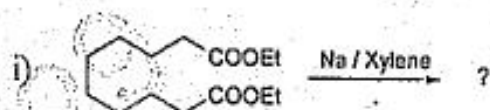
Q5) a) What are sulfur ylides? Give an account on the preparation and synthetic utility of sulfur ylides. [8]

b) Explain the following reactions. [8]

i) Alkyne metathesis

ii) Corey-kim oxidation

- Q6) a) Explain the mechanism of the Hunsdiecker reaction and autooxidation reaction. [8]
- b) Write the products giving mechanism: [8]



- Q7) Write notes on (any four) [16]

- Phosphorus ylides
- Petasis reactions
- Sandmeyer reaction
- Energy of activation
- Sigmatropic rearrangements

33 33

Seat No.	
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M.Sc. (Part-II) (Semester-III) (CBCS) Examination, November-2023

OCH 3.1 : ORGANIC CHEMISTRY  
Organic Reaction Mechanism (Paper-IX)

Sub. Code : 92065

Day and Date : Wednesday, 29-11-2023

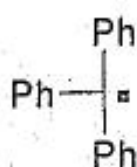
Total Marks : 80

Time : 2.30 p.m. to 05.30 p.m.

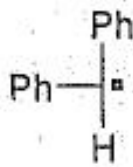
- Instructions :
- 1) Question No. 1 is compulsory.
  - 2) Select any two questions from each section.
  - 3) Answer to the all questions must be written in the same answer book.
  - 4) Figure to the right indicate marks.

Q1) A) Answer the following: [16]

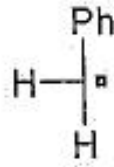
- i) Enlist the types of pericyclic reactions.
- ii) Why are cross-over experiments used in determining reaction mechanism?
- iii) Cite an example indicating Diels-Alder reaction is stereospecific.
- iv) Which method can be used to know the exact bond cleavage during hydrolysis of esters?
- v) Which metal is the most commonly used for alkyne metathesis reactions?
- vi) What is sign of sigma value for electron donating substituents?
- vii) What is kinetic isotope effect?
- viii) Draw the HOMO of 1, 3, 5- hexatriene under photochemical conditions?
- ix) What is Weinred amide?
- x) Arrange the following free radicals in order of increasing stability.



I



II

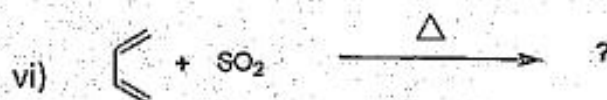
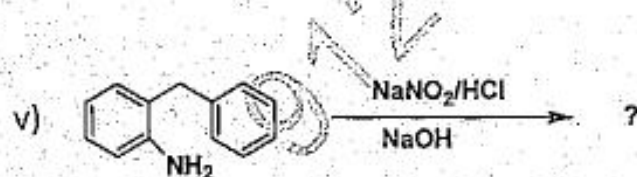
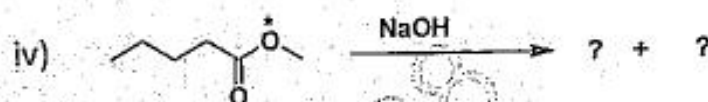
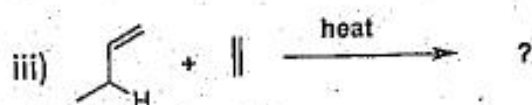
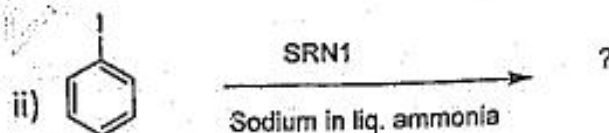
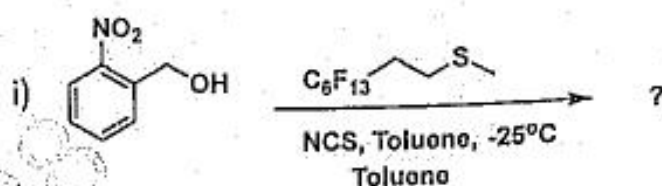


III

P.T.O.



B) Write the products of the following reactions.



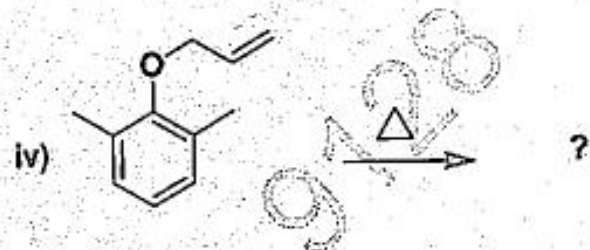
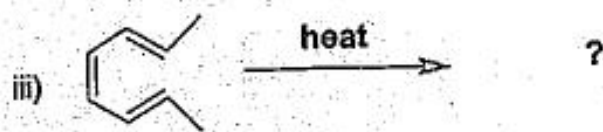
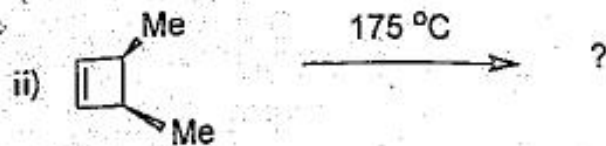
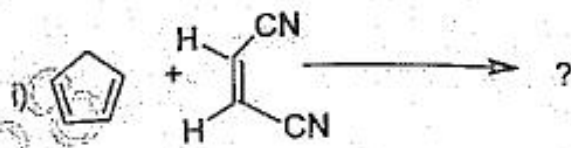
### SECTION-I

Q2) Describe various kinetic methods of determining reaction mechanism. [16]

Q3) a) Explain Woodward-Hoffman's rules of the conservation of orbital symmetry in conversion of 1,3,5-hexatriene into 1,3-cyclohexadiene. [8]

b) Describe [4+2] cycloaddition reaction by using FMO approach. [8]

Q4) a) Write the products of following pericyclic reactions giving necessary selection rule. [8]



b) Give an account on Hammett equation? Explain the significance of sigma and rho values. [8]

### SECTION-II

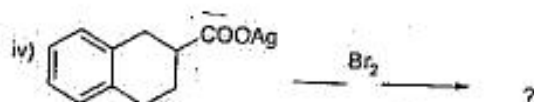
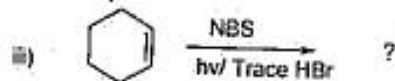
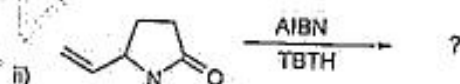
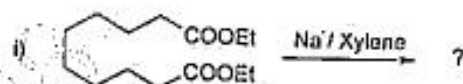
Q5) a) What are nitrogen ylides? Explain the reactivity of nitrogen ylides. [8]

b) Describe the mechanism and applications of following reactions. [8]

i) Petasis reactions

ii) Corey-Kim oxidation

- Q6) a) Explain the Acyloin condensation and Hurdiecker reaction. [8]  
 b) Write the products giving mechanism: [8]



- Q7) Write notes on (any four):

- a) Stereochemical studies in  $S_N1$  and  $S_N2$  reactions  
 b) Phosphorus ylides  
 c) Sigmatropic rearrangements  
 d) Auto-oxidation  
 e) Reactions of carboxylic acids

[16]

Seat No.	
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M.Sc. (Part - II) (Semester - III) (CBCS) Examination,  
March - 2023

ORGANIC CHEMISTRY (Paper - X)  
Advanced Spectroscopic Methods  
Sub. Code : 80475/85411

Day and Date : Thursday, 22 - 06 - 2023

Total Marks : 80

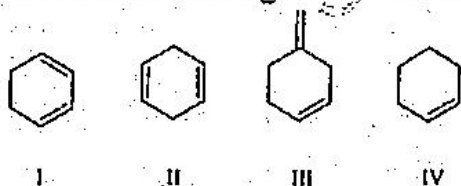
Time : 10.30 a.m. to 01.30 p.m.

- Instructions :
- 1) Question 1 is compulsory.
  - 2) Attempt any two questions from each section.
  - 3) Answers to the two sections must be written in the same answer book.
  - 4) All questions carry equal marks.
  - 5) Figure to the right indicates full marks.

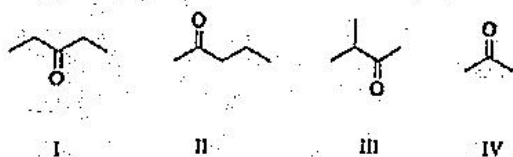
Q1) Answer the following : [16]

a) Why  $D_2O$  exchange technique is used in NMR analysis?

b) Which of the following molecule absorbs at the longest wavelength?



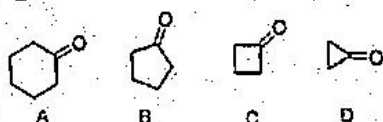
c) Identify the ketone which will show McLafferty rearrangement.



d) Write any two solvents used for scanning NMR.

e) Identify the shift which aniline shows in acidic medium.

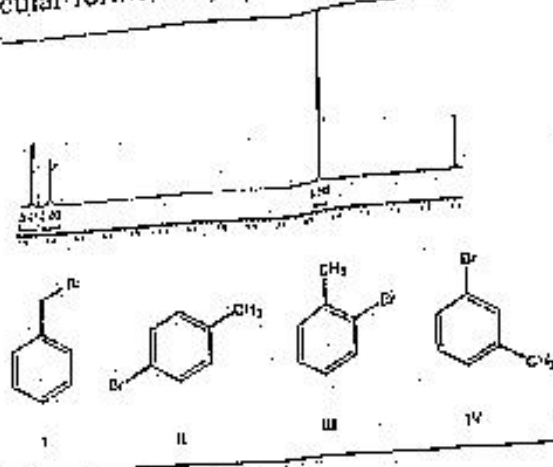
f) Arrange the following ketones in descending order of carbonyl stretching.



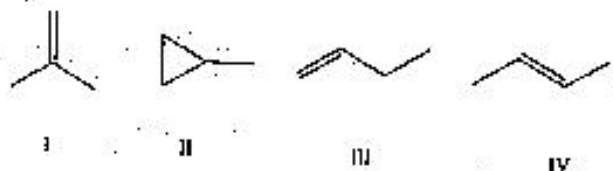
P.T.O.



- g) Choose the plausible structure from following for the compound with molecular formula  $C_7H_7Br$ , whose  $^1H$  NMR spectrum is shown below.



- h) Which is the common observation in DEPT-45, DEPT-90 and DEPT-135?
- i) How many signals does the aldehyde  $(CH_3)_3CCH_2CHO$  have in  $^1H$  NMR spectrum?
- j) Identify the fragment and calculate the  $m/z$  value of peak obtained in mass spectrum due to benzylic cleavage of n-butyl benzene.
- k) Give the mathematical expression of Hooke's law.
- l) Among the following four constitutional isomers which one would exhibit the most stable fragment ion at  $m/z$  41?



- m) Deduce the structure of the compound from the following spectral data  
 M.F.  $C_3H_7ON$   
 IR- 3500, 3400, 3370, 1670, 1800  $cm^{-1}$   
 PMR- $\delta$  2.25 (q, 2H); 6.40 (s, 2H); 1.20 (t, 3H)
- n) How will you distinguish between primary, secondary and tertiary amines by IR spectroscopy?

- o) How many signals are observed in  $^{13}\text{C}$ -NMR spectrum of acetone?
- p) Which monohalogeno compound shows M and M+2 peaks with equal intensity?

### SECTION - I

Q2) a) Explain factors affecting on carbonyl stretching frequencies with suitable examples. [8]

b) Explain Homotopic, enantiotopic and distereotopic protons with suitable examples. [8]

Q3) a) Explain McLafferty rearrangement with suitable examples. [10]

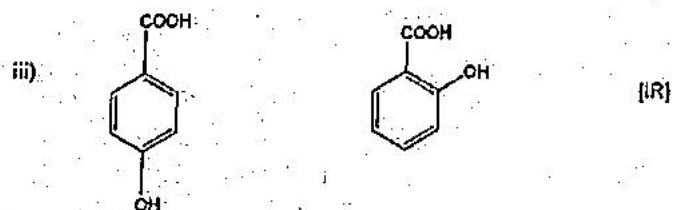
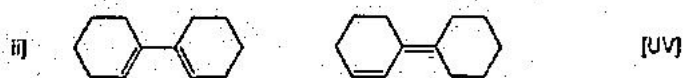
b) Predict the structure of an organic compound based upon following data. [6]

M.F. =  $\text{C}_7\text{H}_9\text{N}$

IR = 3480, 3395  $\text{cm}^{-1}$

$^1\text{H}$  NMR =  $\delta$  0.16 (3H, s), 3.24 (2H, s), 7.37 (2H, d,  $J = 7\text{Hz}$ ), 7.79 (2H, d,  $J = 7\text{Hz}$ ).

Q4) a) How will you differentiate between following pairs using depicted spectroscopic technique. [10]



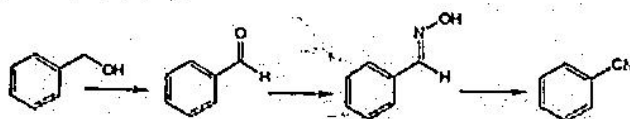
b) Explain DEPT technique in  $^{13}\text{C}$ CMR spectroscopy? [6]

SECTION - II

- Q5) a) Explain various factor affecting chemical shift. [10]
- b) Predict the structure of an organic compound based upon following data. [6]
- M.F.  $C_5H_7NO_2$   
 IR = 2200, 1747, 1200  $cm^{-1}$   
 $^1H$ NMR =  $\delta$  1.1 (3H, t), 3.8 (2H, q), 1.2 (2H, s)

Sea  
No  
M

- Q6) a) Explain various ionization techniques in mass spectroscopy. [10]
- b) Explain the use of IR spectroscopy in monitoring following transformations. [6]

D:  
Ti  
In

- Q7) Write notes on (any four) :

[16]

- Retro Diels Alder reaction in Mass spectroscopy.
- Sampling techniques in IR spectroscopy.
- Pascal triangle.
- Significance of coupling constant.
- Chromophore and auxochrome.



Seat No.	
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M.Sc. (Part - II) (Semester - III) (CBCS) Examination, December - 2023

**ORGANIC CHEMISTRY**

**OCH - X : Advanced Spectroscopic Methods**

Sub. Code : 80475/85411

Day and Date : Friday, 01 - 12 - 2023

Total Marks : 80

Time : 2.30 p.m. to 5.30 p.m.

- Instructions :
- 1) Question No. 1 is compulsory.
  - 2) Answer any two questions from each section.
  - 3) Answers to the all the questions should write in the same answer book.
  - 4) Figure to the right indicates full marks.

Q1) Answer the following:

[16]

- a) Give the reason for generation of metastable ions in recording MS.
- b) Define bathochromic shift.
- c) Why - C=O stretching frequency in IR of salicylaldehyde is observe at lower frequency.
- d) Write full form of MALDI.
- e) Which are D<sub>2</sub>O exchangeable protons?
- f) Write significance of nitrogen rule in mass spectroscopy.
- g) Write the significance of DBE = 3.
- h) What will be the structure of an organic compound with MF C<sub>3</sub>H<sub>6</sub>O which exhibit signal at  $\delta$  27 and 200 ppm in its <sup>13</sup>C NMR spectrum?
- i) Identify the acid derivative showing a strong carbonyl stretching near 1820 cm<sup>-1</sup>.
- j) Write the coupling constant of o<sup>r</sup>, m<sup>r</sup> and p<sup>r</sup> protons of disubstituted benzene in the <sup>1</sup>H NMR spectra.
- k) Which electromagnetic radiation used in <sup>13</sup>C-NMR spectroscopy.
- l) How would you differentiate between cis-butadiene and trans butadiene using UV spectroscopy?

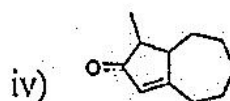
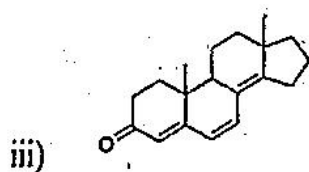
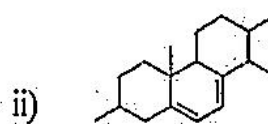
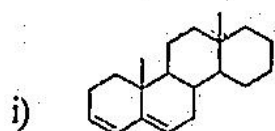
P.T.O.

- m) State the significance of term "IR Active."
- n) The compound  $\text{CH}_3\text{-OCH}_2\text{-CH}_2\text{-OCH}_3$  in its PMR spectrum how many signals will show?
- o) In  $^{13}\text{C-NMR}$ , the signal due to  $\text{DMSO-d}_6$  appears \_\_\_\_\_  $\delta$  value.
- p) UV spectrum of cyclohexane - 1, 3-dione was scanned in ethanol as well as in aqueous alkali. In which solvent absorption maximum will be more?

### SECTION - I

- Q2) a) Define the term coupling constant and write its significance in identifying stereochemical protons. [6]
- b) Butane-1, 4-diol on oxidation is expected to give dialdehyde. However, it gives unexpected product which shows 3-signals at  $\delta$  1.2(2H, m), 2.5(2H, t), 4(2H, t) with molecular ion peak at  $m/z$  84, 42. Illustrate the structure of the product. [6]
- c) Absorption maximum of acetone is at 279  $m\mu$  in hexane as compared to 264  $m\mu$  in water. [4]

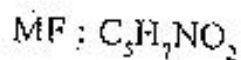
- Q3) a) With the help of Woodward-Fieser rules, calculate the absorption maxima of the following compounds. [10]



- b) The organic compound having MF  $\text{C}_4\text{H}_9\text{ON}$  shows the spectrum at  $m/z$  87, 86, 72, 71, 59, 44 and 43. [6]

Q4) a) Deduce the structure from the given data:

[8]



IR : 1990, 2260, 1747, 1200  $cm^{-1}$

PMR :  $\delta$  1.3 (t, 3H), 3.5 (s, 2H), 4.3 (q, 2H).

$^{13}C$ -NMR : 14 (q), 25 (t), 63 (t), 150 (s), 163 (s).

Justify the spectral data.

b) How many distinct absorptions will be observed in the  $^{13}C$ -NMR spectrum of hex-2-ene. [4]

c) Arrange the following compound in order of their increasing wave number of absorption due to  $C=O$  stretching. [4]

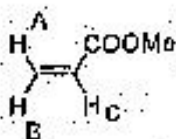


### SECTION - II

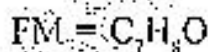
Q5) a) Explain the factors affecting on carbonyl stretching frequencies with suitable examples. [10]

b) Explain the effect of purity on PMR spectrum of ethanol. [6]

Q6) a) Draw the splitting diagrams for  $H_A$ ,  $H_B$  and  $H_C$  showing appropriate coupling constants and chemical shift for following molecule. [8]



- b) Explain the use of McLafferty rearrangement in mass spectral analysis of ketons. [4]
- c) Determine the structure with the help of following spectral data. [4]



$^{13}\text{C-NMR}$ : 54, 114, 120.8, 129.5, 159.5

Q7) Write a note (Any four):

[16]

- a) UV spectra of diketones
- b) NOE
- c) Lanthanide shift reagents
- d) Steric effect in biphenyls
- e) Fermi resonance and coupled vibrations

