Chhatrapati Shahu Ji Maharaj
University, Kanpur

Answer Script Details
Barcode 5620199

Roll No. 24063001034
Total Mark 58/75.00

Exam M.SC-III_ODD_EXAM_NOV_2025
Subject B020902T - Application of Spectroscopy

Question wise Mark Summary

Q.No	Mark	Q.No	Mark	Q.No	Mark	Q.No	Mark
1A	4/5						
1B	4/5						
1C	4/5						
1D	4/5						
1E	3/5						
1F	4/5						
1G	4/5						
1H	4/5						
1I	5/5						
2	0/15						
3	0/15						
4	0/15						
5	13/15						
6	0/15						
7	9/15						
8	0/15						
9	0/15						

Chhatrapati Shahu Ji Maharaj University
Kanpur, Uttar Pradesh

Date of Exam: 05/12/25 Shift: 3rd Room No.: 20
Paper Code: B020902T Subject: Chemistry Year/Sem: 3rd
Name of Candidate: Priya Kumari Gupta
Roll No.: 2 4 0 6 3 0 0 1 0 3 4

COE Facsimile

Signature of Invigilator

Signature of Candidate: Priya Kumari Gupta

PART-II

MARKS OBTAINED										
Q.	1	2	3	4	5	6	7	8	9	10
(a)										
(b)										
(c)										
(d)										
(e)										
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(i)										
(j)										
Total										

Total Marks in Figures: Max. Marks:
Total Marks in Words:

B 0 2 0 9 0 2 T
Paper Code

Signature of Evaluator

Course: Application of Spectroscopy.
Session: 2024-26 Year/Semester: 3rd
Subject Name: Chemistry
Medium: English ● Hindi ○

Paper Code
B 0 2 0 9 0 2 T

Exam Date
0 5 1 2 2 0 2 5

Name of Candidate
PRIYA KUMARI GUPTA

Father's Name
SAMBHUNATHPRASAD

College Code
U N 0 1

Exam Centre Code
U N 0 1

Type of Exam
Regular ● Ex-Student ○
Private ○ Back Paper Exam ○

ANSWER BOOKLET NO.
5620199

B 0 2 0 9 0 2 T
Paper Code

Enrollement Number: C S J M A 2 4 0 0 0 0 6 3 1 7 1

Candidate's Roll Number
2 4 0 6 3 0 0 1 0 3 4

Paper Code
B 0 2 0 9 0 2 T

Signature of Candidate

Signature of Invigilator

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INSTRUCTION TO THE CANDIDATE FOR FILLING PART-I

1. Read the instructions carefully given on the answer script and admit card.
2. Write Date of Exam, Shift, Paper Code & Name of Subject Correctly.
3. Write Name & Roll No. Correctly.
4. Write Semester & Branch Correctly.

INSTRUCTION TO THE CANDIDATE FOR FILLING PART-II

1. Use blue or black ball point pen for writing alphabets & numerals in ☐ boxes.
2. Carefully study the example before you start marking.
3. As shown in the example below, blacken thecircles completely.

Correct Method ① ● ② ④

Incorrect Method ✓ ✗ ◉ ◎

4. Make no Stray marks o n this sheet.

5. DO NOT WRITE OR MARK ON THE BAR CODE.

IN ORDER TO AVOD UFM (UNFAIR MEANS) :

1. The Roll No. and Answer Book no. found elsewhere or any other symbol found in the answer book will be treated as unfair means.
2. Any tempering of Bar Code and Booklet no shall be treated as Unfair Means.
3. Do Not bring the materials like slip of paper/mobile/digital diaries/ study material/ revision notes in examination hall. Possession of the mobiles/ digital diaries/electronic/digital/ watch and any other electronic gadget except memory less scientific calculator shall be considered as UFM case.
4. Do not keep or paste currency note in answer script it shall be consider as UFM.

अनुचित साधन से बचने हेतु :

1. [illegible]
2. [illegible]
3. [illegible]
4. [illegible]

परीक्षार्थियों के लिए निर्देश

1. [illegible]
2. [illegible]
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4. [illegible]
5. [illegible] ID [illegible]
6. [illegible]
7. [illegible] (1-24) [illegible]
8. [illegible]
9. [illegible]
10. [illegible]

INSTRUCTION TO THE CANDIDATE

1. Read the instructions carefully given on the Question Paper, Admit Card & Answer Script.
2. Do not write anything on back side of the cover page.
3. Write on both sides of pages of answer book.
4. Do not write anything on question paper except Roll Number.
5. Write Paper Code & Question Paper Id carefully.
6. CHECK the number of pages (1-24) or any other kind of damage in your answer script, if found than change the answer script immediately before the commencement of examination.
7. CHECK the Question Paper for any kind of discrepancy e.g. Subject Code, S Name, and Question of the Question Paper during first THIRTY MINUTES of commencement of the exam, so that it can be corrected in TIME. After that no corrections shall be entertained by the university.
8. Do not use pencil for answering the question.
9. Write status correctly e.g. those appearing in carry over papers should fill in sta as Carry Over. Those appearing as Ex- Students should fill in status as ex.
10. No supplementary answer book & graph paper will be provided.

INSTRUCTION TO THE CANDIDATE FOR FILLING PART-IV

1. Use blue or black ball point pen for writing alphabets & numerals in ☐ Boxes
2. Use blue or black ball point pen for filling the circles

	1	8	1	5	4	3	2	1	6	9
0	0	0	0	0	0	0	0	0	0	0
1	●	1	●	1	1	1	1	●	1	1
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3	3	3	3	3	3	●	3	3	3	3
4	4	4	4	4	●	4	4	4	4	4
5	5	5	5	●	5	5	5	5	5	5
6	6	6	6	6	6	6	6	6	●	6
7	7	7	7	7	7	7	7	7	7	7
8	8	●	8	8	8	8	8	8	8	8
9	9	9	9	9	9	9	9	9	9	●

Note- If your Roll No. is of 10 digits. Please leave first three columns .

Paper Code

B 0 2 0 9 0 2 T

Section - A

1(A). Amines absorb at higher wavelength than alcohol because of :-

- Electronegativity difference : Oxygen is more electronegative than nitrogen that means in alcohol, the lone-pair on O are being held more tightly lower in energy compared to the lone pair on N atom in amines.

- Because of n- electrons in amines are higher energy than those in alcohols, the energy gap between that non-bonding orbital and anti-bonding (σ^*) orbital is smaller in amines than in alcohols.

- Smaller energy gap less energy required for the $n \rightarrow \sigma^*$ transition and hence absorption of light of longer wavelength from amines compared to alcohols.

(B) The stretching bands of X-H bonds shift to lower frequency when hydrogen bonding is present compared to free "X-H" vibrations.

The absorption bands also tend to broaden when hydrogen bonding exist.

In many cases the intensity of the band increases when hydrogen bonding is strong.

Thus, hydrogen-bonded O-H or N-H bands typically appear at lower wavelength and often stronger compared to free ones.

The key idea hinges on the IR band behaviour changes when we dilute the sample.

Types of H-bonding	What happens on dilution
• Intermolecular H-bonding	On dilution (or using non-H-bonding solvent) the molecules move apart as a result intermolecular H-bonds break the bonded X-H bands decrease disappear and free X-H band reappear (shift) back to high wavenumber.
• Intramolecular H-bonding	Because the donor and accepto are part of the same molecule dilution (or concentration change doesn't change their spatial proximity → the H-bond remains the IR absorption band remain unchanged in position and shape.

(c)

Spin-spin attraction, more commonly called spin-spin coupling, is a quantum mechanical interaction between the magnetic fields of neighbouring atomic nuclei, transmitted through bonding electrons in molecules, which causes the Nuclear magnetic Resonance (NMR) signals to split into 'multiplets' revealing molecular structure and connectivity; the working is as follows:-

- Tiny magnets :- Nuclei with spin act as tiny bar magnets creating their own magnetic field.
- Magnetic influence :- A nucleus's magnetic field influence the effective field experienced by its neighbours, affecting their resonance frequency.
- Coupling Constant (J) :- The distance between these split peaks (in Hertz) is the coupling constant indicating the strength of the interaction and closeness of the nuclei.

<u>Significance :-</u>

- Structural Clues :- It reveals which atoms are near each other in a molecule, helping map out structure.
- Connectivity :- It helps determine the number of protons on adjacent carbons (e.g. CH_3-CH_2- shows splitting patterns for both groups).

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(b) Resonance decoupling in NMR is a powerful technique to simplify complex spectra by removing spin-spin interactions (coupling) between nuclei, typically protons and carbons using continuous radiofrequency irradiations at specific frequencies, causing nuclei to rapidly flip states, averaging their magnetic effects, and collapsing multiplets into singlets, which reveal the number of attached protons and simplifies structure determination.

Working of Decoupling :-

- The Problem :- In ^{13}C NMR carbons bonded to protons show splitting due to proton spin states, making spectra complex.
- The Solution : A strong, continuous RF field is applied at the proton's resonance frequency.
- The Effect :- Protons flip rapidly between their spin states preventing them from influencing the ^{13}C signals.
- The Result :- All ^{13}C signals collapse into simple singlets simplifying interpretations.

Benefits :-

- Simplifies Spectra :- Eliminates complex multiplets, making assignment easier

- Improves Sensitivity :- Can enhance signal intensity for rare nuclei like ^{13}C.

(E) NOESY (Nuclear Overhauser Effect Spectroscopy) applications in spectroscopy focus on mapping through space-distance between nuclei to determine molecular structure, stereochemistry and conformation and so on.

Key applications of NOESY are:-

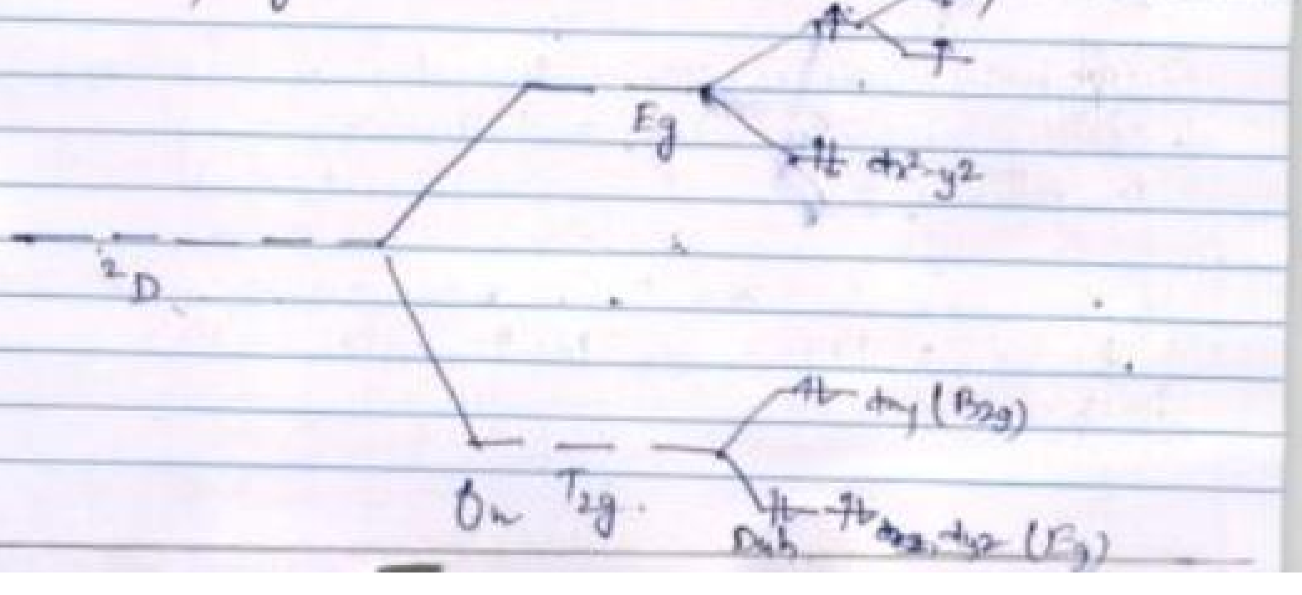
- Structural Elucidation:- Determining 3-D molecular geometry, stereochemistry, and relative orientation of groups in organic molecules and biomolecules.
- Biomolecular structure :- Essential for protein structure determination confirming protein folding and assigning resonances.
- Conformational Analysis :- Studying flexible molecules, identifying preferred conformations and mapping intra-molecular distances.
- Polymer Characteristics :- Assigning monomer ~~tre~~ sequences, studying chain packing, and investigating hydrogen bonding in polymers.
- Intermolecular interaction :- ~~Stating~~ Detecting interactions between molecules and identifying binding sites.

(F) Spin-orbit coupling in ESR is an interaction between an electron's spin and its orbital angular momentum that affects the g-factor and can split spectral lines, especially in transition metal ions. This coupling is stronger for atoms with higher atomic numbers and leads to a departure from the ideal g-value of 2.00, resulting in an anisotropic or modified g-value that provides information about the electron's environment.

Working :-

• Basic ESR :- In standard ESR, the energy levels of an unpaired electron's spin are split by an external magnetic field. A transition between these spin states absorb microwave radiation and absorption is detected.

• Spin-orbit interaction :- The electron's motion around the nucleus creates a magnetic field that interacts with its intrinsic spin magnetic moment. This spin-orbit coupling introduces a term to the spin transition



(2) Raman spectroscopy provides biochemical fingerprints of cells, tissues and fluids by detecting molecular vibrations, enabling label-free, non-invasive analysis for disease diagnosis, drug detection in forensics, food safety, etc.

Key Applicati [illegible]

- Cancer Diagnosis :- Differentiating cancerous from healthy tissues and identifying positive surgical margins in real-life.

- Neurodegenerative Diseases:- Evaluating changes in neurons and tissues for conditions like Alzheimer's.

- Metabolic & Infectious Diseases:- Analyzing blood, urine and other fluids for metabolic shifts & microbial identification

- Drug Detection and Forensics:- Identifying drugs in biological fluids like urine and tracing biological samples.

- Tissue Analysis :- Characterizing bone, teeth and pathological mineral deposits

- Cellular Studies :- Monitoring intracellular components, protein/lipid interactions and red blood cell membrane disorders.

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(4) The Nuclear Overhauser Effect (NOE) is a phenomenon in NMR where irradiating one nucleus affects the intensity of a nearby nucleus's signal through dipole-dipole interactions. It occurs through space, not chemical bonds and is used to determine 3-D structure by indicating proximity between nuclei. The magnitude of effects is inversely proportional to the 6th power of the distance between the nuclei. $\left(\frac{1}{r^6}\right)$.

- **Mechanism** :- NOE relies on the transfer of spin polarization between nuclei that are close in space, typically within 2-4 Å.

- **Irradiation** :- A specific nucleus's resonance frequency is saturated with radiofrequency pulses.

- **Signal change** - This perturbation alters the signal intensity of another nucleus located nearby.

Applications :-

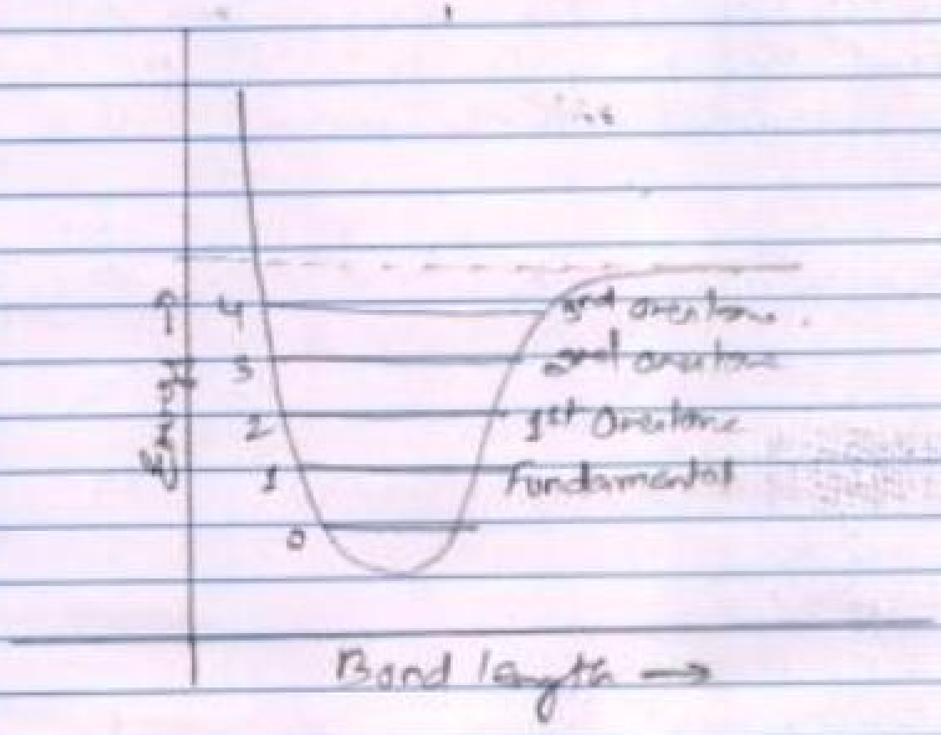
- Peak assignment :- It helps assign NMR signals, as a proton-proton NOE will link carbons close to its gem.

- Structure determination :- NOE is crucial for determining the 3-D and stereochemistry of molecules, particularly biomolecules.

(5) Overtones and combination bands are vibrational absorptiond bands in spectroscopy that appear at frequencies other than the fundamental transitions

Overtones are result from an excitation from the ground state to higher vibrational levels appearing at approximately a multiple of the fundamental frequency like 3v, 4v, ...

Combinational bands result from simultaneous excitation from two or more fundamental vibrations, with the observed frequency being the sum of fundamental frequencies, $v_1 + v_2$...



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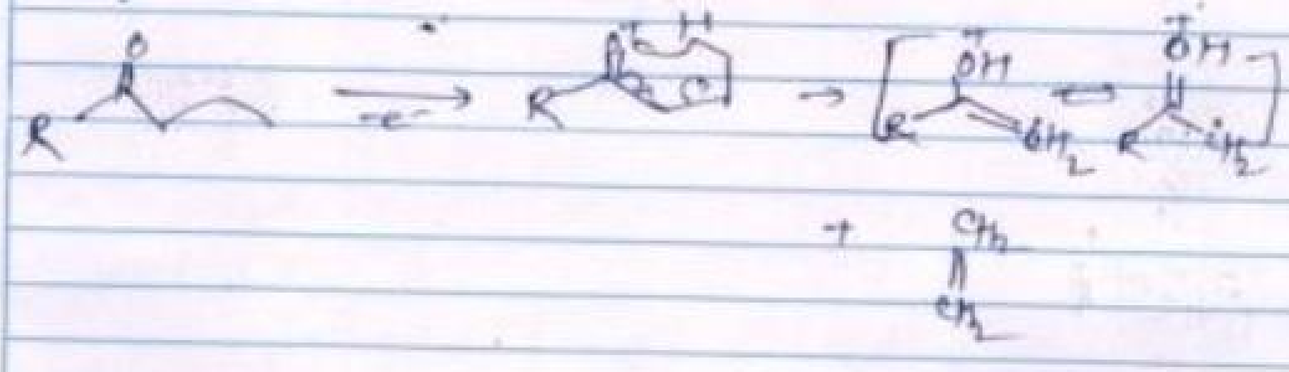
Section-B

5. The McLafferty rearrangement is a fragmentation reaction observed in mass spectroscopy of organic molecules in which the parent radical cation splits into daughter radical action cation and neutral spin-paired molecule.

It is sometimes found that a molecule containing a keto group undergoes β-cleavage, with the gain of the γ-hydrogen atom, as first reported by Anthony Nicholson working. This rearrangement is a retro-ene-reaction and a member of the sigmatropic family of reactions.

A description of the reaction was later published by Fred McLafferty in 1959 leading to his name being associated with the process.



Mechanism :

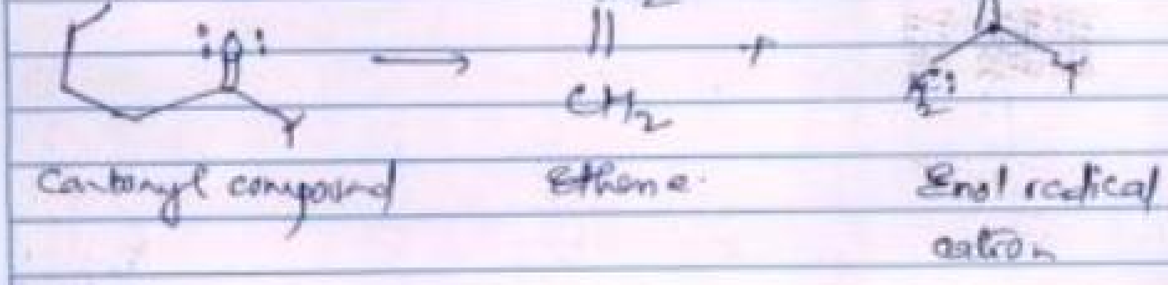
The rearrangement involves a six-membered ring transition state in which the carbonyl group splits the molecule into two pieces. These pieces consist of an enol radical cation and a neutral alkene fragment.

The enol radical cation is observed in the mass spectrum, while the neutral alkene fragment is not observed.

Any carbonyl compound with hydrogen in the gamma position will likely have a peak in the mass spectrum corresponding to enol radical cation formed by the Lafferty rearrangement.

Both ketones and aldehydes give prominent molecular ion peaks though the $[M^{+}]$ peak is more prominent in Ketones.
Only ketones and aldehydes that do not undergo this rearrangement are those which lack a side chain that can donate a hydrogen atom to the pi system.

MacLafferty Rearrangement :-



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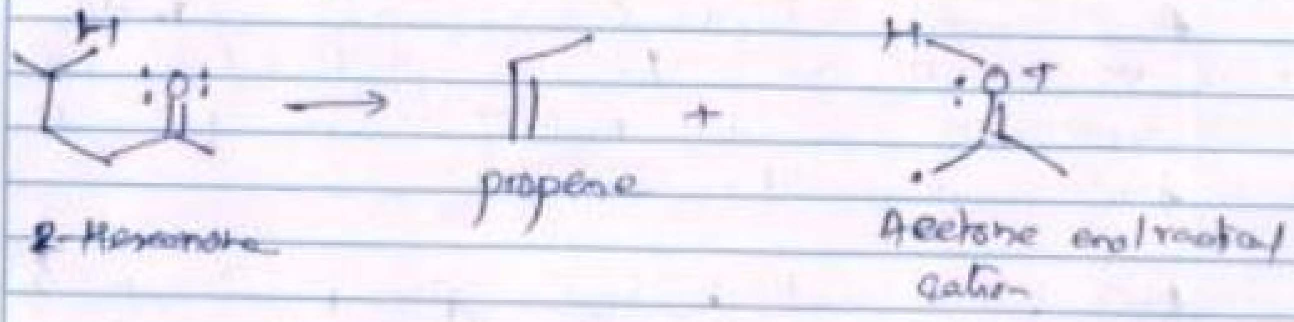
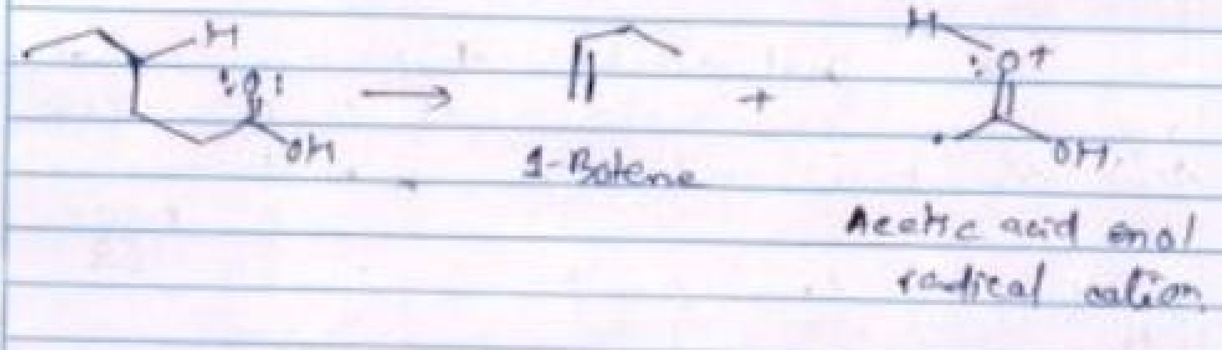
Examples :-

An example of Mclafferty rearrangement is the fragmentation of 2-hexanone, producing acetone and enol radical cation and a neutral molecule propene.





Section - C

7. In NMR spectroscopy, nuclei such as ^1H and ^{13}C behave like tiny magnets. When placed in an external magnetic field (B_0), they align either with or against the field.

However, the actual magnetic field experienced by the nucleus is not the same as the applied field.

Shielding (Electron Shielding)

Shielding occurs when electron density around a nucleus generate an induced magnetic field that oppose the applied field (B_0).
This reduces the effective magnetic field acting on the nucleus.
Effective field:-

$$B_{eff} = B_0 - B_{induced}.$$

Result in NMR:-

- A shielding nucleus requires more energy to flip its spin.
- It appears upfield (lower chemical shift)
- Typically – 0–3 ppm for protons in electron-rich environments.

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Causes of Shielding:-

- High electron density (alkyl groups)
- Aromatic rings currents (in certain regions).
- Nearby atoms with lone pairs.

Examples:-

- CH_3- protons are more shielded than $-CH_2$ or $-CH$.
- Protons attached to carbons near electron-donating groups (~~[illegible]~~ $-O^-$, $-NH_2$) are more shielded.

Deshielding (Electron Withdrawal).

Deshielding occurs when electron density around a nucleus decreases, so the nucleus feels a stronger external magnetic field.

$$B_{eff} = B_0 + \text{smaller opposing field.}$$

Results in NMR:-

- A deshielding nucleus requires less energy to flip its spin
- Appears downfield (higher chemical shift, larger δ value)
- Typical regions:- 4-12 ppm for strongly deshielded protons.

Causes of deshielding :-

- Electron withdrawing groups ($-NO_2$, $-CN$, $-COOH$)
- Nearby electronegative atoms (O, N, halogens).
- Hydrogen bonding.
- Aromatic ring current (deshielding above / below the ring plane).

Examples :-

- Proton near electronegative atoms: CH_3-Cl, CH_3-O-R.
- Aldehyde proton appears around 9–10 ppm.
- Carboxylic acid proton appears 10–13 ppm

Comparison.

Factors	Shielding Nucleus	Deshielding Nucleus.
• Electron density	High	Low
• Effective nuclear charge	Lower	Higher
• NMR position	Upfield	Downfield
• Chemical shift (δ)	Small	Large.

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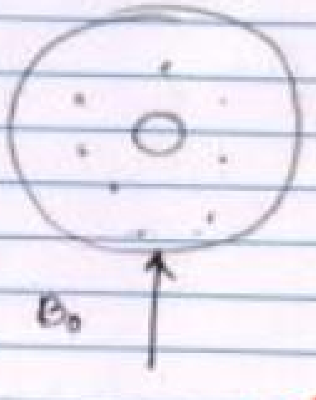
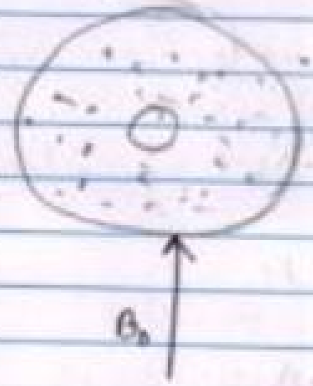
Low e^- density

High e^- density.



E^- cloud shields the nuclei from the magnetic field



This nucleus experiences stronger magnetic field because it is not shielded as much.

This nucleus is shielded and experiences weaker magnetic field which appear upfield.

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