

M.Sc. (FOURTH SEMESTER) EXAMINATION, 2013

CHEMISTRY

(SPECIALIZATION - ORGANIC CHEMISTRY)

(APPLICATION OF SPECTROSCOPY TO STRUCTURAL ANALYSIS)

TIME ALLOWED: THREE HOURS

MAXIMUM MARKS: 60

NOTE: SECTION-A IS COMPULSORY AND ANSWER ANY FIVE FROM SECTION-B

SECTION-A

10x2 = 20

(SHORT ANSWER TYPE QUESTIONS)

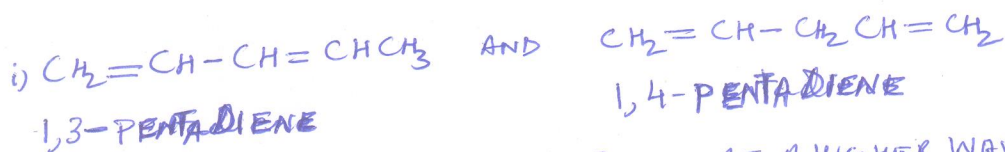
NOTE: ATTEMPT ALL QUESTIONS. ALL QUESTIONS CARRY 2 MARKS.

Q1 (a) THE POSITION OF ABSORPTION MAY BE INFLUENCED BY _____ IN PARTICULAR _____ AND CARBONYL COMPOUNDS. (WITH REFERENCE TO UV-VIS SPECTROSCOPY)

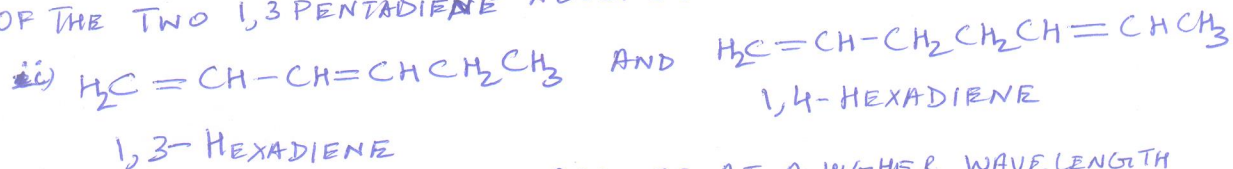
ANS 1 (a) SUBSTITUENTS; SUBSTITUTED DIENES

Q1 (b) LONGER THE CONJUGATION LONGER IS THE WAVELENGTH OF ABSORPTION IN UV-VIS SPECTROSCOPY; GIVE AT LEAST TWO EXAMPLES WITH STRUCTURES TO SUPPORT THE STATEMENT.

ANS 1 (b)



OF THE TWO 1,3-PENTADIENE ABSORBS AT A HIGHER WAVELENGTH



OF THE TWO 1,3-HEXADIENE ABSORBS AT A HIGHER WAVELENGTH

ANY SUCH STRUCTURAL EXAMPLE PAIRS WOULD BE ENOUGH.

Q1 (c) WHAT IS THE ESSENTIAL CRITERION FOR OBSERVING AN IR SIGNAL?

ANS 1 (c) ON PASSING INFRARED LIGHT THROUGH THE SAMPLE OF AN ORGANIC COMPOUND SOME OF THE FREQUENCIES GET ABSORBED AND SOME GET SINCE THE MOLECULES ARE MADE UP OF AN ASSEMBLAGE OF ATOMS THEY POSSESS VERY MANY VIBRATIONAL FREQUENCIES. IN ORDER TO SEE AN IR ABSORPTION BAND; THAT PARTICULAR VIBRATION SHOULD PRODUCE A FLUCTUATING DIPOLE (AND THUS A FLUCTUATING ELECTRIC FIELD) OTHERWISE IT CANNOT INTERACT WITH THE FLUCTUATING ELECTRIC FIELD OF THE INFRARED LIGHT.

SHORT ANSWER TYPE QUESTIONS
CONTINUED

Q1 (d) DIFFERENTIATE BETWEEN STRETCHING FREQUENCY AND BENDING FREQUENCY. (COMMENT ON THEIR RESPECTIVE POSITION IN AN IR SPECTRA). HOW DOES THE POSITION CHANGE WITH RESPECT TO BOND STRENGTH?

ANS1 (d) AT ORDINARY TEMPERATURES (OF MEASUREMENT) ORGANIC MOLECULES ARE IN CONSTANT STATE OF VIBRATION. STRETCHING ABSORPTIONS OF A BOND APPEAR AT HIGHER FREQUENCIES IN THE INFRARED SPECTRUM THAN THE BENDING ABSORPTIONS OF THE SAME BOND.

CONSIDERING A BOND TO SIMILAR TO A BALL ATTACHED TO A SPRING

$$\nu \propto \sqrt{\frac{\text{BOND STRENGTH}}{\text{MASS}}} \quad \text{i.e., } \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \text{where } \mu = \frac{m_1 m_2}{m_1 + m_2}$$

μ = REDUCED MASS m_1, m_2 = THE MASSES OF TWO BALLS (ATOMS)

k = FORCE CONSTANT

ν = FREQUENCY

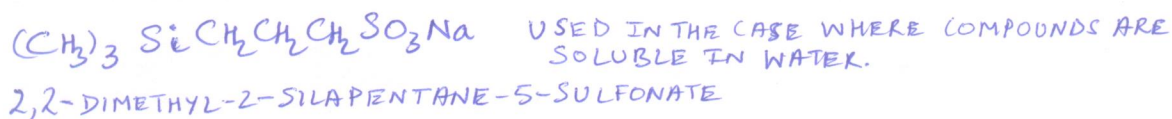
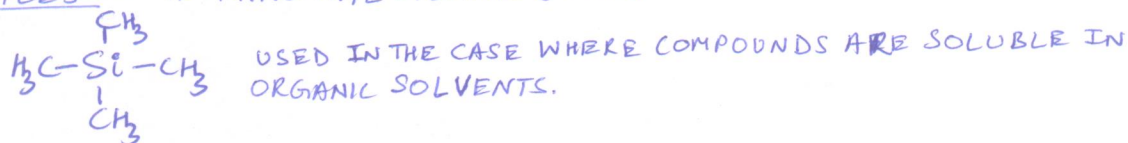
THEREFORE THE VIBRATIONAL FREQUENCY OF A BOND IS EXPECTED TO INCREASE WHEN THE BOND STRENGTH INCREASES AND ALSO WHEN THE REDUCED MASS OF THE SYSTEM DECREASES

★ FORMULA IS ESSENTIAL FOR THE EXPLANATION OF THE SECOND PART OF THE ABOVE QUESTION.

Q1 (e) WHAT ARE THE ESSENTIAL QUALITIES OF A NMR STANDARD/REFERENCE COMPOUND? GIVE TWO STRUCTURES OF NMR STANDARDS?

ANS1 (e) THE ESSENTIAL QUALITIES ARE a) VOLATILITY (VOLATILE STANDARD ALLOWS RECOVERY OF THE ANALYZED COMPOUND) b) THE PEAKS SHOULD NOT INTERFERE WITH THE SPECTRA OF THE COMPOUNDS BEING ANALYZED. c) IT SHOULD NOT REACT WITH THE COMPOUNDS BEING ANALYZED.

EXAMPLES - TETRAMETHYL SILANE (TMS)

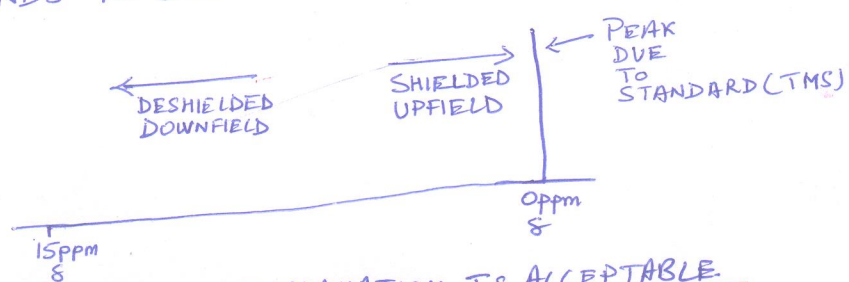


SHORT ANSWER TYPE QUESTIONS

CONTINUED

Q1 (g) IN A GIVEN NMR SPECTRUM, WHAT CONCLUSIONS CAN BE DRAWN FROM PEAK POSITION WITH RESPECT TO THE PEAK OBTAINED BY THE STANDARD?

ANS (g) THE PEAK POSITIONS RELATIVE TO THAT OF THE STANDARD IN NMR CONSTITUTE THE CHEMICAL SHIFT OF THE GIVEN NUCLEI. REGION CLOSER TO THE STANDARD CORRESPONDS TO AN SHIELDED REGION (UPFIELD SHIFT), REGION AWAY FROM THAT OF THE STANDARD CORRESPONDS TO DOWNFIELD SHIFT OR DESHIELDED REGION.



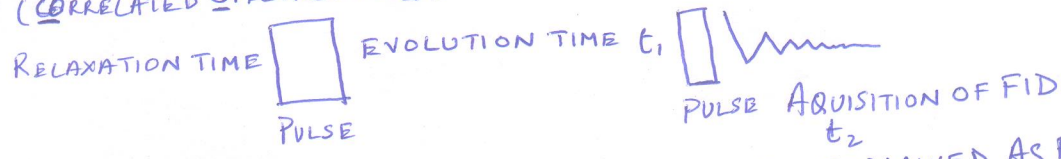
A DIAGRAM OR THE WRITTEN EXPLANATION IS ACCEPTABLE.

Q1 (g) WHAT ARE THE FACTORS THAT INFLUENCE THE CHEMICAL SHIFT OF ¹³C NUCLEI?

ANS (g) FACTORS THAT INFLUENCE THE CHEMICAL SHIFT OF ¹³C NUCLEI ARE
 a) ELECTRONEGATIVITIES OF THE SUBSTITUENTS ATTACHED TO THE CARBON
 b) HYBRIDIZATION OF THE CARBON
 c) ANISOTROPIC EFFECTS IN THE MOLECULE
 d) VAN DER WAALS DESHIELDING

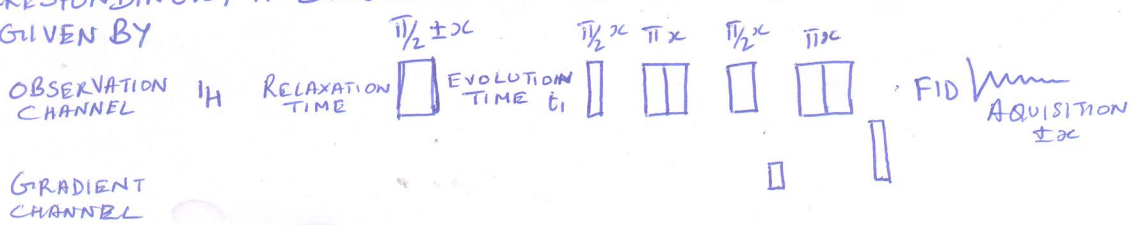
Q1 (h) WHAT IS THE PULSE SEQUENCE USED IN ¹H-¹H COSY EXPERIMENT? WHAT IS THE CONSEQUENCE OF THE PULSE?

ANS (h) GENERAL 2D NMR PULSE SEQUENCE CONSISTS OF THE FOLLOWING: COSY (CORRELATED SPECTROSCOPY)



BASED ON THE ABOVE PULSE SEQUENCE A 2D NMR CAN BE EXPLAINED AS FOLLOWS THE ACQUISITION STAGE IS SEPARATED FROM THE EXCITATION STAGE BY AN INTERMEDIATE STAGES CALLED EVOLUTION AND MIXING. WHERE t_1 IS INCREMENTED BY Δt AND SPECTRA IS ACQUIRED FOLLOWED BY ANALYSIS BY A 2D FOURIER TRANSFORM.

CORRESPONDINGLY A DOUBLE QUANTUM COHERENCE COSY - DQF-COSY PULSE SEQUENCE IS GIVEN BY



A ANY PULSE SEQUENCE WITH CORRECT EXPLANATION IS ACCEPTABLE.

SHORT ANSWER TYPE QUESTIONS
CONTINUED

Q1 (i) ILLUSTRATE THE RELATIONSHIP BETWEEN MOLECULAR FORMULA AND INDEX OF HYDROGEN DEFICIENCY?

ANS (i) IN ADDITION TO THE KINDS AND NUMBERS OF ATOMS, THE MOLECULAR FORMULA GIVES THE INDEX OF HYDROGEN DEFICIENCY

$$\text{INDEX} = \frac{\text{CARBONS} - \frac{\text{HYDROGEN}}{2} - \frac{\text{HALOGENS}}{2} + \frac{\text{NITROGENS}}{2} + 1}{2}$$

IT ALLOWS A CHEMIST TO CONCLUDE OR ASCERTAIN THE PRESENCE OF A UNSATURATION OR RINGED STRUCTURE.

EXAMPLE: A BENZENE RING ITSELF ACCOUNTS FOR FOUR SITES OF UNSATURATION

★ FORMULA AND AN EXAMPLE ARE ESSENTIAL.

Q1 (ii) WHAT IS FRAGMENTATION? AND WHAT IS ITS ROLE IN STRUCTURAL ELUCIDATION? (ANSWER VERY BRIEFLY)

ANS (ii) FRAGMENTATION IS INITIATED BY ELECTRON IMPACT. RESULTING IN A CATION-RADICAL SPECIES FORMS THE BASIS OF UNAMBIGUOUS ASSIGNMENT OF STRUCTURE IN CONJUNCTION OTHER SPECTROSCOPIC TECHNIQUE.

FOR EXAMPLE (ODD ELECTRON)



ALLOWS FOR INTERPRETATION OF THE STRUCTURE 'EI-MS ANALYSIS AS THE INTENSITY OF THE MOLECULAR ION (MI) PEAK IS OFTEN OF LOW INTENSITY.

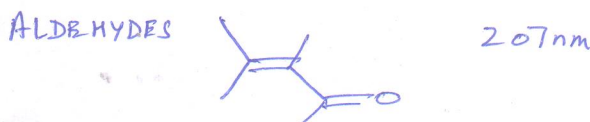
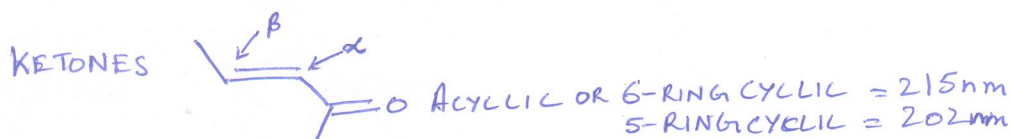
SECTION B

5x8=40

(LONG ANSWER TYPE QUESTION)

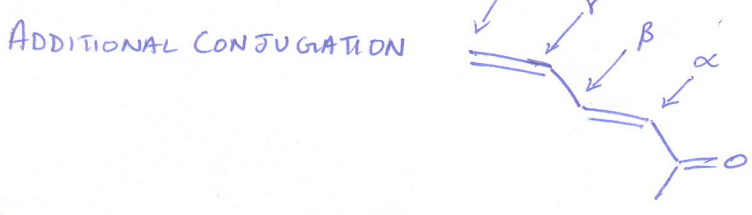
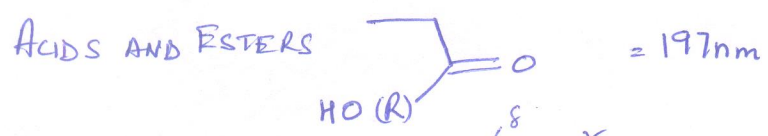
NOTE: ATTEMPT ANY FIVE QUESTIONS. EACH QUESTION CARRIES 8 MARKS

Q2 CONSIDERING THE FOLLOWING BASE VALUES AND THE VALUES FOR THE CONTRIBUTION BY EACH SUBSTITUENT (BASED ON WOODWARD RULE), CALCULATE THE POSITION OF THE MOST INTENSE BAND FOR THE FOLLOWING STRUCTURES. (IDENTIFY EACH VALUE ADDITION WITH THE SUBSTITUENTS CLEARLY)



SECTION B
LONG ANSWER TYPE QUESTIONS
CONTINUED

Q2 CONTINUED:



30nm (IF THE SECOND DOUBLE BOND IS HOMOANNULAR WITH THE FIRST ADD 39nm)

ADDITION FOR EACH SUBSTITUENT

-R ALKYL (INCLUDING PART OF CARBOCYCLIC RING)

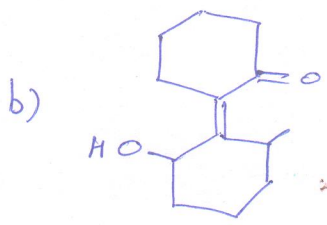
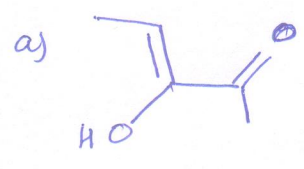
$\alpha = 10\text{nm}$ $\beta = 12\text{nm}$, $\gamma = 17\text{nm}$; $\delta = 17\text{nm}$

-OR

$\alpha = 35\text{nm}$, $\beta = 30\text{nm}$, $\gamma = 17\text{nm}$, $\delta = 31\text{nm}$

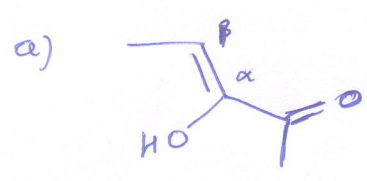
-OH

$\alpha = 35\text{nm}$, $\beta = 30\text{nm}$, $\gamma = 30\text{nm}$, $\delta = 50\text{nm}$



WHAT WILL BE THE EFFECT OF CHANGING THE SOLVENT ON THE λ VALUE (WATER, METHANOL AND CYCLOHEXANE)

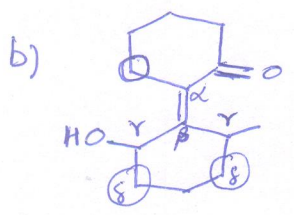
ANS 2



KETONE α, β UNSATURATED ACYCLIC
∴ BASE VALUE = 215nm

R = CH₃ SUBSTITUENT AT $\beta = 12\text{nm}$
-OH SUBSTITUENT AT $\alpha = 35\text{nm}$

∴ BASED ON WOODWARD RULE THE $\lambda_{\text{max}} = 215 + 12 + 35 \text{ nm} = 262 \text{ nm}$



KETONE α, β UNSATURATED PART OF SIX MEMBERED CARBOCYCLIC

∴ BASE VALUE = 215nm

R = -CH₂ (OF CARBOCYCLIC RING) SUBSTITUENT AT $\alpha = 10\text{nm}$
-OH SUBSTITUENT AT $\gamma = 30\text{nm}$
R = -CH₃ SUBSTITUENT AT $\gamma = 17\text{nm}$
2X-CH₂ (OF CARBOCYCLIC RING) AT $\gamma = 34\text{nm}$

LONG ANSWER TYPE QUESTIONSCONTINUEDANS 2 CONTINUED:

∴ BASED ON WOODWARD RULE THE $\lambda_{MAX} = 215 + 10 + 30 + 17 + 34 \text{ nm}$
 $= 306 \text{ nm}$

THE CONTRIBUTION TO λ_{MAX} BASED ON SOLVENT USED IS AS FOLLOWS

WATER = +8 nm

METHANOL = 0

CYCLOHEXANE = -11 nm

	WATER	METHANOL	CYCLOHEXANE
a)	262 nm	270 nm	262 nm
b)	306 nm	314 nm	306 nm

SUCH THAT THE UV ABSORPTIONS SHIFTS TO SHORTER WAVELENGTHS AS SOLVENT POLARITY DROPS.

★ THE LABELLING OF THE DIFFERENT CONTRIBUTIONS DUE TO SUBSTITUENTS ESSENTIAL. EFFECT OF SOLVENT SHOULD BE CLEARLY DEFINED.

Q3 EXPLAIN EFFECT OF HYDROGEN BONDING (IN IR SPECTROSCOPY), WITH REFERENCE TO THE FOLLOWING FUNCTIONAL GROUPS O-H AND N-H; IN ASSOCIATING SOLVENT / NON ASSOCIATING SOLVENTS; C=O & AROMATIC RINGS IN THE SAME COMPOUND CARRYING O-H AND N-H GROUPS

- i) IN ENOLS AND CHELATES
- ii) IN CARBONYL COMPOUND
- iii) π CLOUD INTERACTION
- iv) AMINES (STRUCTURES ARE ESSENTIAL)

ANS 3

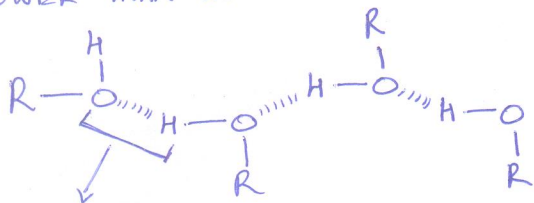
IN THE CASE OF NON ASSOCIATING SOLVENTS SUCH AS CCl_4 , CS_2 , CHCl_3 DO NOT AFFECT THE IR SPECTRA BUT POLAR SOLVENTS ACETONE OR BENZENE ASSOCIATING SOLVENTS SHOW MARKED EFFECT C=O AND AROMATIC RINGS IN THE SAME COMPOUND CARRYING O-H OR N-H ALSO CAUSE A SIMILAR SHIFT

EXAMPLE BUTANOL 1% IN $\text{CCl}_4 \rightarrow 3650 \text{ cm}^{-1}$ (OH)_{STR} SHARP
 3350 cm^{-1} BROADBAND (OH)_{STR}
 IN A HYDROGEN BONDED ALCOHOL

PURE BUTANOL - 3500 cm^{-1}

LONG ANSWER TYPE QUESTIONSCONTINUEDANS 3 CONTINUED:

AS INDICATED IN THE EXAMPLE BROADENING OF SIGNAL DUE TO HYDROGEN BONDING TAKES PLACE AT THE SAME TIME O-H_{STR} APPEARS LOWER THAN THAT OF FREE O-H_{STR}



LEADS TO LENGTHENING OF

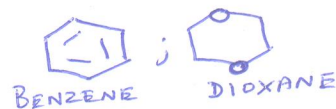
BOND

LEADS TO LOWER FORCE CONSTANT CONSEQUENTLY LOWER FREQUENCY

i) IN THE CASE OF ENOLS AND CHELATES THE HYDROGEN BONDING IS STRONG
FREQUENCIES ARE LOWER FOR (O-H)_{STR}

ii) IN THE CASE OF CARBONYL COMPOUNDS THE BASICITY OF THE CARBONYL IS THE MAIN REASON FOR IT TO BE MORE HYDROGEN BONDED
C=O HAS MORE SINGLE BOND CHARACTER ABSORBS AT LOWER FREQUENCY

iii) CARBOXYLIC ACIDS FOR EXAMPLE BENZOIC ACID - ITS IR SPECTRA SHOWS BROAD BAND SIGNAL 2500-3500 cm⁻¹ CORRESPONDING TO O-H_{STR}
IN BENZENE AS SOLVENT LEADS TO OR PROMOTES DIMER FORMATION
HOWEVER IN DIOXANE NO DIMER FORMATION IS OBSERVED SINCE THE ACIDIC HYDROGEN BONDS PREFERENTIALLY TO THE SOLVENTS.



FURTHERMORE FINE STRUCTURES ARE OBSERVED DUE TO VIBRATIONAL COUPLINGS WITH OVERTONES OF LOWER FREQUENCIES (IN BENZOIC ACID IR SPECTRA)

iv) π CLOUD INTERACTION: SINCE ALKENE AND AROMATIC π CLOUDS CAN BEHAVE AS LEWIS BASES THEY TEND TO FORM HYDROGEN BONDS TO ACIDIC HYDROGENS
FOR EXAMPLE O-H FREQUENCY OF PHENOLS CAN BE FURTHER LOWERED BY 40-100 cm⁻¹ IN BENZENE AS A SOLVENT IN COMPARISON TO CCl₄.

v) AMINES: OWING TO LOWER ELECTRONEGATIVITY IN COMPARISON TO OXYGEN THE N-H_{STR} FREQUENCIES ARE LOWER THAN THAT OF OH_{STR} AND THE SHIFTS DUE TO HYDROGEN BONDING LESS DRAMATIC THAN O-H_{STR} SHIFTS FOR EXAMPLE N-H_{STR} IN CONCENTRATED SOLUTION IS AT 3300 cm⁻¹ HOWEVER IN DILUTE SOLUTIONS IT SHIFTS TO 3600 cm⁻¹

LONG ANSWER TYPE QUESTIONSCONTINUED

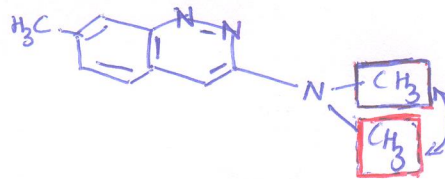
Q4. EXPLAIN THE FOLLOWING TERMS ASSOCIATED WITH ROUTINE NMR SPECTROSCOPY

- CHEMICAL EXCHANGE
- SOLVENT SHIFTS
- INTEGRALS IN PROTON NMR
- CONCENTRATION, TEMPERATURE EFFECT AND HYDROGEN BONDING.
[EXPLAIN WITH EXAMPLES AND STRUCTURES WHEREVER POSSIBLE]

ANS 4 ONE OF THE MAJOR CONTRIBUTING FACTORS INFLUENCING CHEMICAL SHIFTS IN NMR IS DUE TO THE CHEMICAL ENVIRONMENT OF THE NUCLEI

- a) CHEMICAL EXCHANGE
CONFORMATIONAL CHANGES MAY ALSO RESULT IN CHANGE IN CHEMICAL ENVIRONMENT

FOR EXAMPLE A ZAPROPAZONE DERIVATIVE



THE TWO METHYL GROUPS HIGHLIGHTED ABOVE UNDERGO RAPID EXCHANGE AT ROOM TEMPERATURE DUE TO ROTATION ACROSS —N—. THE SIGNALS APPEAR AS A BROAD SINGLET. AS THE TEMPERATURE IS LOWERED

THE INTERCONVERSIONS ARE NON-EXISTENT

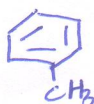
°° N,N-DIMETHYL GROUPS APPEAR AS TWO SHARP PEAKS CLEARLY INDICATING THEY WERE EXCHANGING BETWEEN DIFFERENT CHEMICAL ENVIRONMENT.

- b) SOLVENT SHIFTS : SINCE THE SOLVENTS USED FOR NMR ANALYSIS VARY IN THEIR POLARITY AND MAGNETIC SUSCEPTIBILITY, THE NMR SPECTRUM OF A COMPOUND DISSOLVED IN ONE SOLVENT MAY BE SLIGHTLY DIFFERENT FROM THAT MEASURED IN A MORE POLAR SOLVENT.

FOR EXAMPLE NMR SIGNAL OF CHLOROFORM DISSOLVED IN CYCLOHEXANE APPEARS AT δ 7.3, BUT IN BENZENE IT APPEARS AT δ 5.74
 (BENZENE IS BEHAVING AS A LEWIS BASE)

- c) AREA UNDER EACH NMR SIGNAL IN THE SPECTRUM IS PROPORTIONAL TO THE NUMBER OF HYDROGEN ATOMS IN THAT ENVIRONMENT.

FOR EXAMPLE TOLUENE



RELATIVE RATIO OF THE PEAKS

5:3

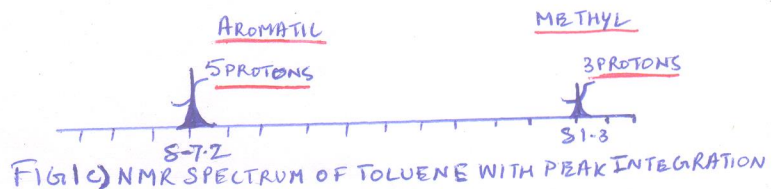


FIG 1) NMR SPECTRUM OF TOLUENE WITH PEAK INTEGRATION

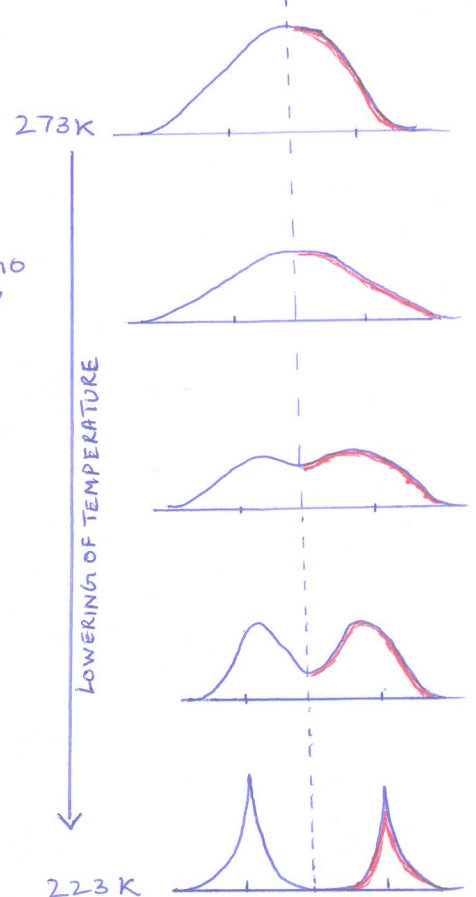


FIG 1a) DESCRIPTION OF CHEMICAL EXCHANGE PHENOMENA.

LONG ANSWER TYPE QUESTIONS
CONTINUED

ANS 4. CONTINUED:

d) CONCENTRATION, TEMPERATURE EFFECT AND HYDROGEN BONDING.

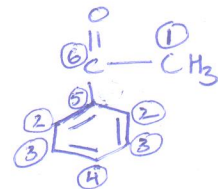
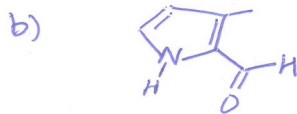
THE EFFECT OF THE ABOVE MENTIONED PARAMETERS IS MOST PRONOUNCED IN THE CASE OF -NH -SH AND -OH PROTONS, SINCE THESE PROTONS ALL HAVE THEIR NMR SIGNALS SUBSTANTIALLY MOVED ON CHANGING TO SOLVENTS OF DIFFERING POLARITY (DUE TO HYDROGEN BONDING) EVEN WHEN DIFFERENT CONCENTRATIONS ARE USED IN THE SAME SOLVENT. THE HYDROGEN INVOLVED IN HYDROGEN BONDING EXPERIENCES A NET DESHIELDING EFFECT WHEN HYDROGEN BONDING IS STRONG.

- ∞ HIGHER CONCENTRATION — STRONG DESHIELDING
- ∞ HIGHER TEMPERATURES — REDUCES INTERMOLECULAR HYDROGEN BONDING
- ∞ LOWER δ VALUES FOR THE INVOLVED HYDROGENS

HOWEVER INTRAMOLECULAR HYDROGEN BONDING IS UNAFFECTED BY VARYING CONCENTRATION

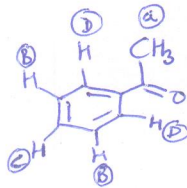
★ ANY ANSWER HIGHLIGHTING THE UNDERLINED PHENOMENA WITH STRUCTURE OR DIAGRAMATIC REPRESENTATION IS ACCEPTABLE

Q5. DRAW THE ¹H NMR AND THE BROADBAND DECOUPLED ¹³C NMR SPECTRUM FOR THE FOLLOWING COMPOUNDS [YOU NEED TO BE ABLE TO DRAW THE PEAK POSITIONS CLOSE TO THE REAL VALUES]



ANS 5.

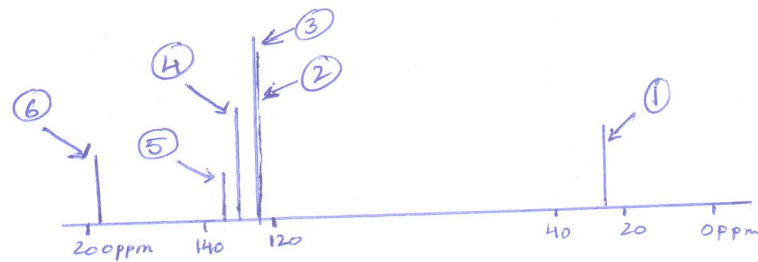
a)



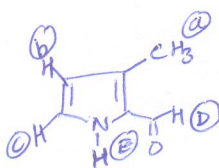
¹H NMR



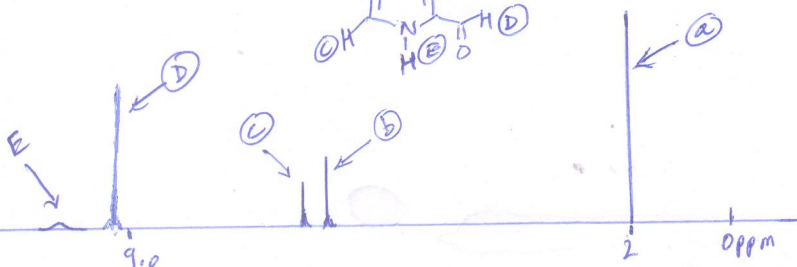
¹³C NMR



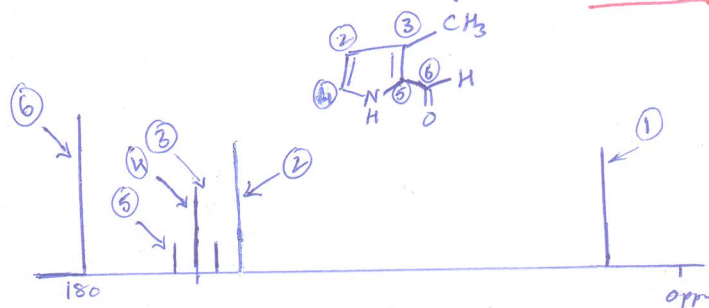
b)



¹H NMR

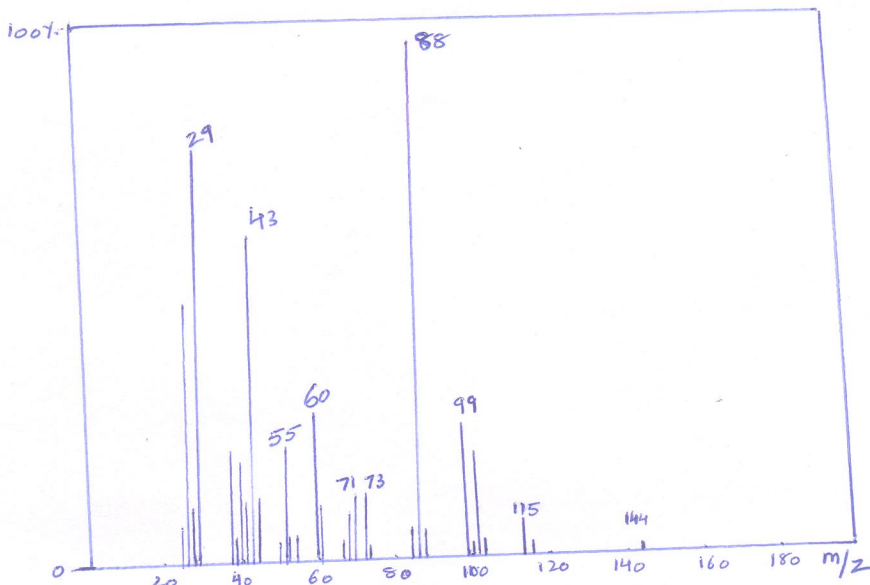


¹³C NMR



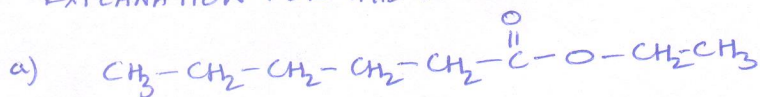
LONG ANSWER TYPE QUESTIONSCONTINUED

- Q6. FOR THE FOLLOWING EI MASS SPECTRUM OF ETHYL HEXANOATE, WRITE REASONABLE REACTION MECHANISMS AND STRUCTURES TO ACCOUNT FOR THE PEAKS AT THE FOLLOWING MASES: 144, 73, 99, 71, 129, 88, 101, 115.



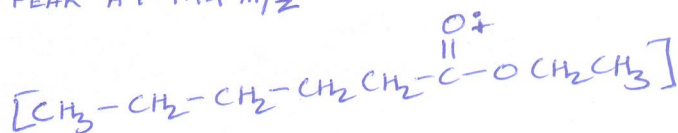
- ANS 6. BASED ON THE GIVEN MASS SPECTRA ABOVE PEAK AT m/z 88 FORMS THE BASE PEAK. THE HIGHEST MOLECULAR WEIGHT IS ATTRIBUTED TO THE LOWEST INTENSITY PEAK AT m/z 144 OR THE MOLECULAR ION PEAK $M^{+\cdot}$

EXPLANATION FOR THE PEAKS IS AS FOLLOWS.

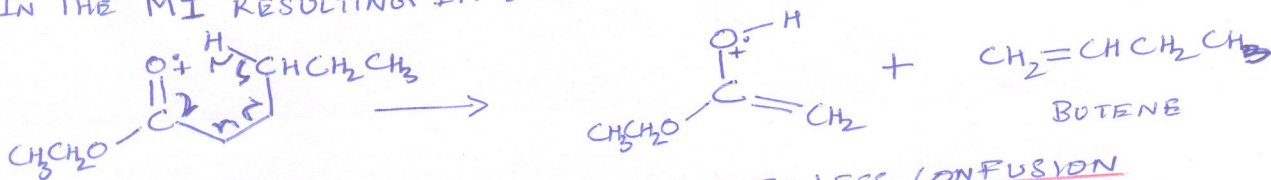


$$\begin{aligned} \text{TOTAL MASS} \Rightarrow & \text{C} - 8 \times 12 = 96 \\ & \text{H} - 16 \times 1 = 16 \\ & \text{O} - 2 \times 16 = 32 \\ & \hline & 144 \end{aligned}$$

MI PEAK AT 144 m/z



- b) BASE PEAK AT m/z 88 IS A RESULT OF Mc LAFFERTY REARRANGEMENT IN THE MI RESULTING IN LOSS OF 1-BUTENE



* A SINGLE HALF ARROW IS BETTER AS THEIR IS LESS CONFUSION

- c) m/z 101 OBTAINED VIA PROPYL LOSS (γ -CLEAVAGE)
- d) m/z 99 OBTAINED VIA ETHOXY LOSS (α -CLEAVAGE)
- e) m/z 115 OBTAINED VIA ETHENE LOSS
- f) m/z 73 $(\text{CH}_2)_2\text{COOH}^+$

LONG ANSWER TYPE QUESTIONS
CONTINUED

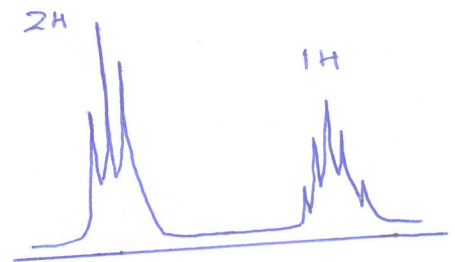
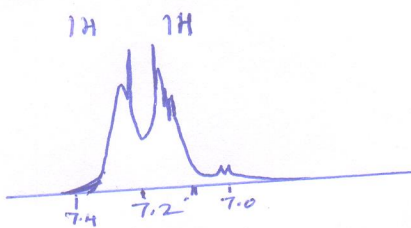
ANS 6. CONTINUED :

- (f) m/z 73 OBTAINED VIA LOSS OF PROPYL GROUP. $[(CH_2)_2COOH]^+$
SINCE FRAGMENTATION OF THE CARBOXYLIC ACID IS DOMINATED BY IONS $C_n H_{2n-1} O_2$
- (g) m/z 129 OBTAINED VIA LOSS OF METHYL
- (h) m/z 71 LOSS OF NEUTRAL SPECIES CO_2

★ THE COMPLETE DESCRIPTION OF EACH MASS ION WITH ANY TWO MECHANISMS IS ESSENTIAL.

Q7. FOR THE GIVEN MOLECULAR FORMULA C_9H_{10} IDENTIFY THE CORRECT STRUCTURE OF THE COMPOUND BASED ON THE FOLLOWING SPECTRAL DATA. IR BANDS ARE PRESENT IN THE REGIONS $3000-2850cm^{-1}$, $3060cm^{-1}$, $1600-1585cm^{-1}$, $1500-1400cm^{-1}$ AND $900-675cm^{-1}$. BASED ON THE STRUCTURE CORRELATE THE NMR TO THE CORRESPONDING PROTONS IN THE GIVEN STRUCTURE

NMR



ANS 7. a) BASED ON THE MOLECULAR FORMULA ONE CAN IDENTIFY THE DEGREE/INDEX OF UNSATURATION

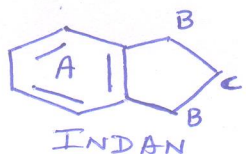
$$\text{INDEX} = \text{CARBON} - \frac{\text{HYDROGEN}}{2} - \frac{\text{HALOGENS} + \text{NITROGEN}}{2} + 1$$

$$\text{INDEX} = 9 - \frac{10}{2} - 0 + 0 + 1 = 5$$

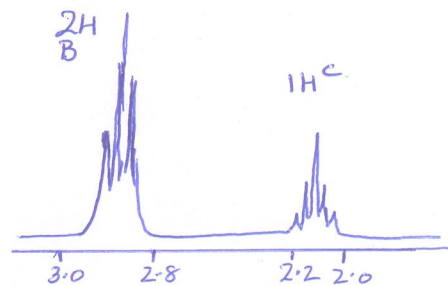
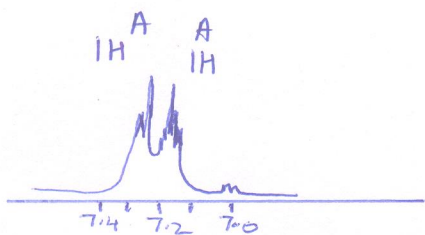
SUGGESTING AN AROMATIC RING + ANOTHER π /pi BOND OR ALIPHATIC RING.

- b) THE BANDS AT $3000-2850$ INDICATE C-H ALKANE STRETCHES. THE BAND AT 3060 INDICATES C-H AROMATIC STRETCH. AROMATICS ALSO SHOW BANDS IN THE REGIONS $1600-1585$ AND $1500-1400$ (C-C IN RING STRETCH) AND $900-675$ (C-H OUT OF PLANE).

LONG ANSWER TYPE QUESTIONS
CONTINUED

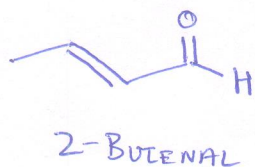
ANS 7CONTINUED:

POSSIBLE



SINCE THE RATIO OF PEAKS REMAINS THE SAME, ON MULTIPLYING THE INTEGRAL VALUES BY TWO GIVES THE RIGHT NUMBER OF HS.

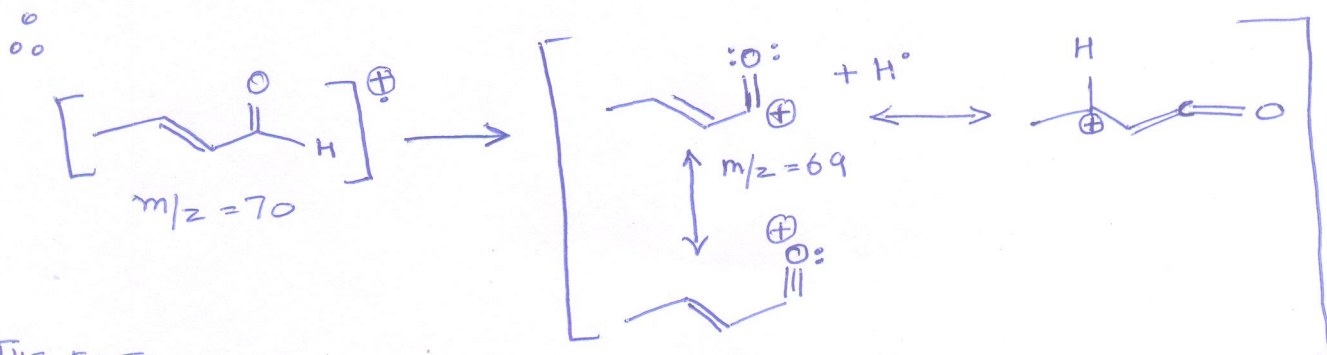
- Q8. a) THE MASS SPECTRUM OF 2-BUTENAL SHOWS A PEAK AT m/z 69 THAT IS 28.9% AS INTENSE OF THE BASE PEAK, PROPOSE AT LEAST ONE FRAGMENTATION ROUTE TO ACCOUNT FOR THIS PEAK AND EXPLAIN WHY THIS FRAGMENT WOULD BE REASONABLY STABLE?
- b) THE MASS SPECTRUM OF 3-BUTYN-2-OL SHOWS THE BASE PEAK AT m/z 55. EXPLAIN WHY THE FRAGMENT GIVING RISE TO THIS PEAK WOULD BE VERY STABLE?

ANS 8 a)

MOLECULAR ION PEAK WOULD BE OBSERVABLE

$$\begin{array}{r} \text{AT} \\ 4 \times 12 = 48 \\ 1 \times 16 = 16 \\ 6 \times 1 = 6 \\ \hline 70 \end{array}$$

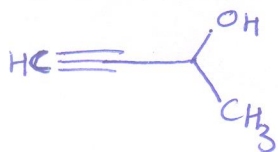
THE MOLECULAR ION PEAK OF ALIPHATIC ALDEHYDES IS USUALLY DISCERNIBLE. CLEAVAGE OF THE C-H AND C-C BONDS NEXT TO THE OXYGEN ATOM RESULTS IN AN M-1 PEAK



THE EXTRA STABILITY OF RADICAL CATION FOLLOWING LOSS OF HYDROGEN ATOM IS DUE TO THE RESONANCE STABILIZED POSITIVE CHARGE.

LONG ANSWER TYPE QUESTIONSCONTINUEDANS 8

b)



3-BUTYN-2-OL

MOLECULAR ION PEAK WOULD BE OBSERVABLE AT

$$\begin{array}{r}
 4 \times 12 = 48 \\
 1 \times 16 = 16 \\
 6 \times 1 = 6 \\
 \hline
 70
 \end{array}$$

LOSS OF METHYL $\text{CH}_3 = 15$ WOULD JUSTIFY THE APPEARANCE OF THE BASE PEAK AT m/z 55.

FOLLOWING THE FRAGMENTATION RULE WHICH STATES THAT THE C-C BOND NEXT TO A HETEROATOM ARE FREQUENTLY CLEAVED LEAVING THE CHARGE ON THE FRAGMENT CONTAINING THE HETEROATOM WHOSE NON BONDING ELECTRONS PROVIDE RESONANCE STABILIZATION

