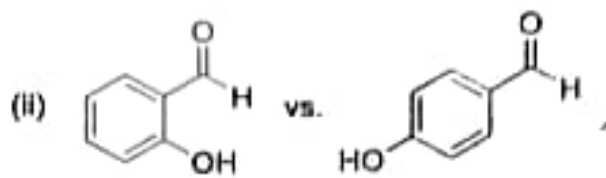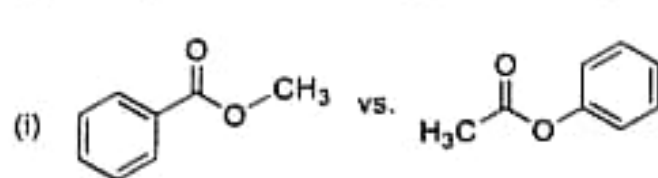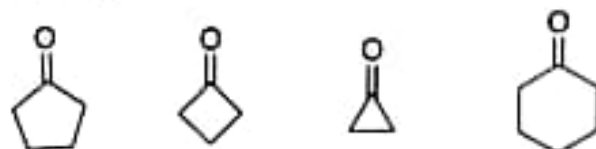1. (a) Distinguish the following pairs of compounds by IR spectroscopy:

(i) vs.

(ii) vs.

(b) Arrange the following compounds in decreasing order of their C=O stretching frequencies of IR spectra with appropriate explanation.

(c) For which of the following isotopes NMR spectroscopy is possible and why?
^{13}C, ^{16}O, ^{19}F, and ^{12}C

(d) Calculate the Chemical Shift (δ) in ppm for a proton that has resonance 2208 Hz downfield from TMS on a spectrometer that operates at 400 MHz.

(e) Draw and predict the number of signals and their relative intensities in the ^{1}H-NMR spectra of the following compounds.

(i)

(ii)

(iii)
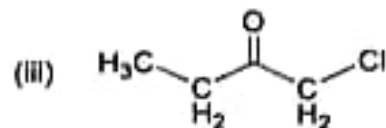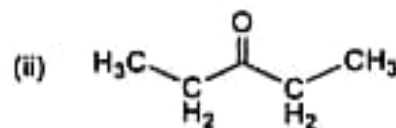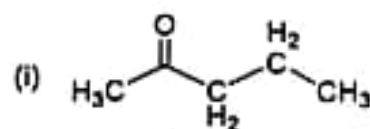
(f) Classify the polymers on the basis of *Tacticity*.

(g) Write down the difference between the addition polymerization and condensation polymerization with proper examples.

2(a) (i)
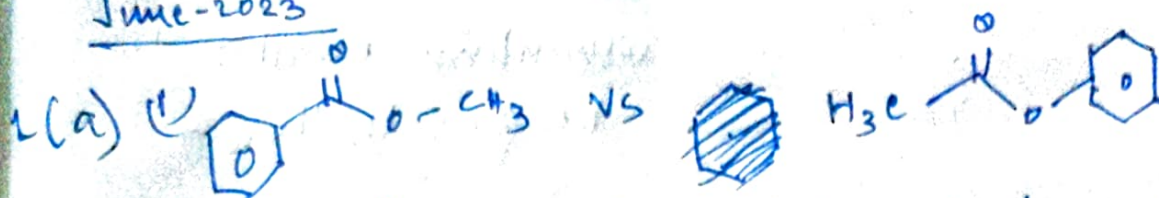
clearly 2 kinds of stretching is observed in both $c=0$, and $c-0$ bond: The first compound methyl benzoate has conjugation, whereas the ester $c=0$ stretch is not in conjugation with the aromatic ring. Thus the first compound shows a lower stretching value for $c=0$ group than the second mainly due to conjugation.

(ii)

and

Intra H bond

Inter H bond, lower of OH stretch freq.

(b)
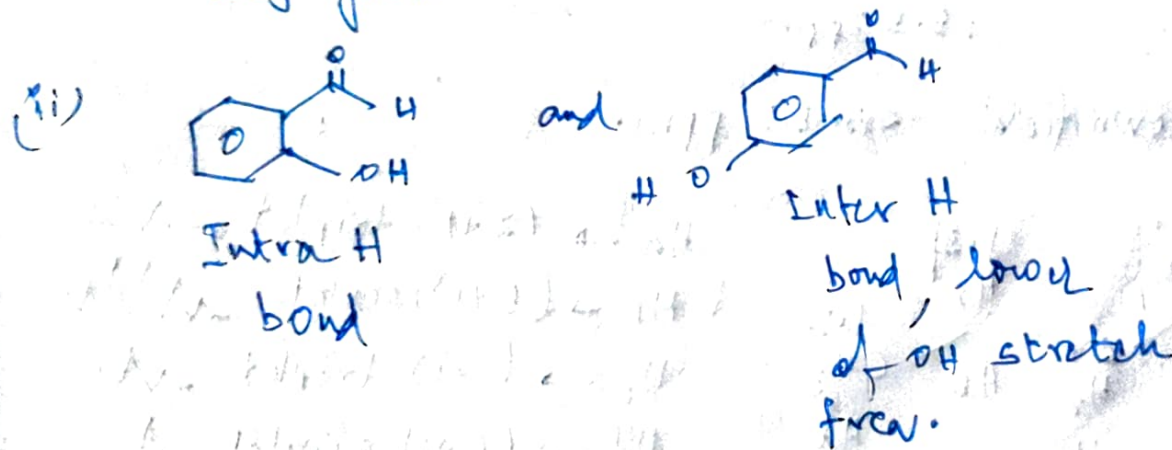
Ring strain is the main point of difference among these compounds. Rings with more C-atoms have lots of confrontations, thus ring strain is relieved where as less C-atoms have high ring strain.

Also the /s-character is higher for db (external) in smaller ring, which causes inc in absorption freq. as ring size decreases. This causes overall decrease in λ when ring size decreases.
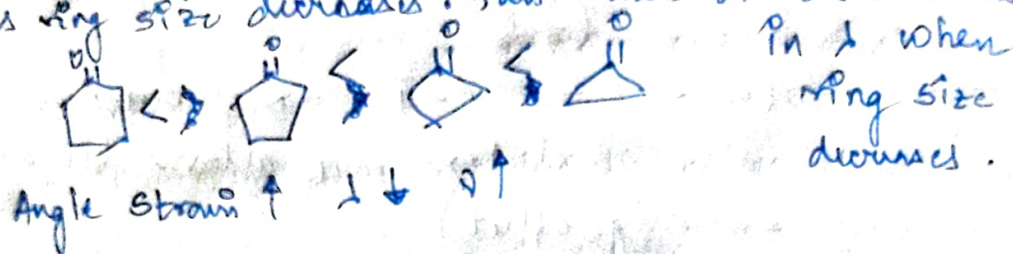

Angle Strain ↑   λ ↓   ν̃ ↑

(c) ^{13}C, ^{1}H, ^{19}F and ^{12}C

^{13}C and ^{19}F, due to odd number of protons/neutrons which cause the spin quantum number to be greater than 0.

(d) $\nu_R = 2208\ Hz$ $\nu_{TMS} = 0$ (standard)

$\nu_0 = 400\ MHz$

$\delta_H \cdot \nu_{TMS}$ / ν_0 × 10^6

δ in ppm : $\dfrac{2208 - 0}{400 \times 10^6} \times 10^6$

$= 5.52\ ppm$

δ in down field : ~5.52 ppm.

(e) (i)
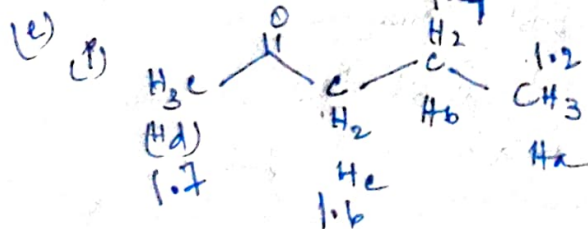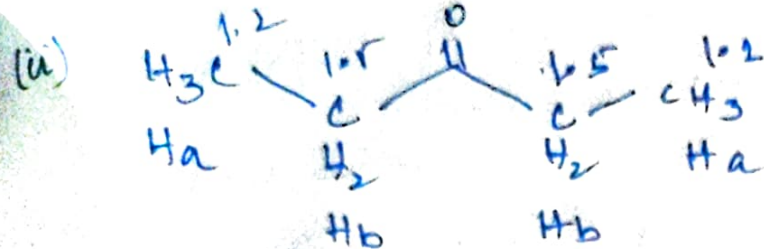

$H_a \rightarrow (2+1)$ triplet

$H_b \rightarrow (5+1)$ sextet

$H_c \rightarrow (2+1)$ triplet

$H_d \rightarrow (0+1)$ singlet

(ii)

H_3C — $\overset{1.2}{}$ — $\overset{1.r}{C}$ — $\overset{O}{\overset{||}{C}}$ — $\overset{1.5}{\underset{}{C}}$ — CH_3 — $\overset{1.2}{}$

Ha $\underset{Hb}{H_2}$ $\underset{Hb}{H_2}$ Ha

$Ha \rightarrow (2+1)$ triplet

$\underset{\sim\!\!\wedge\!\!\wedge\!\!\sim}{}$

$Hb \rightarrow (3+1)$ Quartet

$\underset{\sim\!\!\wedge\!\!\wedge\!\!\wedge\!\!\sim}{}$

$1:3:3:1$

(iii)

$H_3\overset{1.3}{C}$ — $\overset{1.7}{\underset{H_2}{C}}$ — $\overset{O}{\overset{||}{C}}$ — $\overset{1.6}{\underset{H_2}{C}}$ — cl

$H c$ $\underset{Hb}{}$ $\underset{Ha}{}$
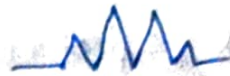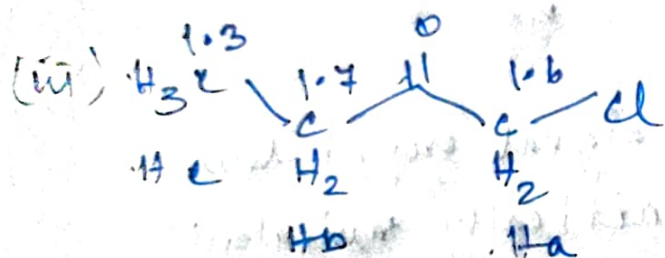
$Ha \rightarrow (0+1)$ singlet $\underline{\wedge}$

$Hb \rightarrow (3+1)$ quartet $\underset{\sim\!\!\wedge\!\!\wedge\!\!\sim}{}$

$H_c \rightarrow (2+1)$ triplet $\underset{\sim\!\!\wedge\!\!\sim}{}$

(f) According to tacticity there are three kinds of polymers

(1) Isotactic polymer :- Stereo centres in the chain have same configuration. High quality

(b) Syndiotactic Polymer :- Stereochemistry for their stereocentre alternates b/w R and S

(c) Atactic polymer :- Stereocentre have random configuration. Poor quality

(g) Refer Nov. 2024 Q(4).

1ᵗ Half (Unit I)

1. (a) (i) Write down normal C=O stretching frequency values of the following transformation:

$$RCOCl \rightarrow RCHO \rightarrow RCOR \rightarrow RCONH_2$$

(ii) How can you distinguish the following pair of compounds by IR spectroscopy?

4-Hydroxybenzaldehyde   Salicyladehyde

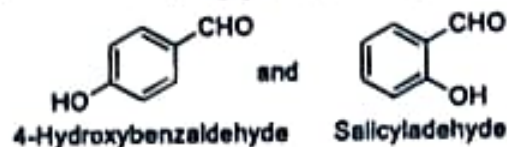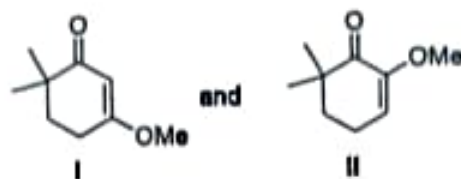(iii) How IR spectroscopy can be used to differentiate the following pair of compounds?

I   II

(b) (i) In NMR spectroscopy which compound is used as internal standard and explain why?

(ii) Calculate the Chemical Shift (δ) in ppm for a proton that has resonance at 640 Hz downfield from TMS on a NMR spectrometer that operates at 300 MHz.

(iii) Which NMR solvents do you prefer to use for a substance which is soluble in water and in chloroform?

(iv) Write down the intensity ratio of a septet signal using Pascal's triangle.

(v) Draw and predict the number of signals and their relative intensities in the ¹H-NMR spectra of the following compounds.

I   II
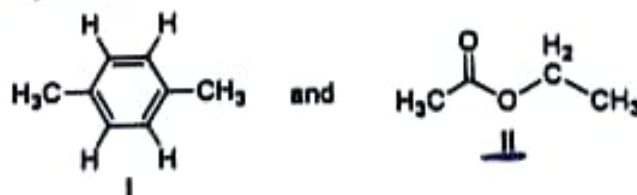
(c) (i) In a polystyrene polymer, there are 100 molecules of molecular weight 10^5, 200 molecules of molecular weight 10^3 and 300 molecules of molecular weight 10^4. Find out $\bar{M}_n$, $\bar{M}_w$ and $\overline{DP}_n$.

(ii) What is the difference between Isotactic and Atactic polymeric conformation with neat diagram.

(iii) How can you synthesize Nylon 6,6 from readily available starting materials.

[(2+2+1)+(1+1+1+1+2)+(2+2+2)]

August 2022

1(a) (i) $RCOCl \longrightarrow RCHO \longrightarrow RCOR \longrightarrow RCONH_2$

$1800 \, cm^{-1}$ $1725 \, cm^{-1}$ $1735 \, cm^{-1}$ $1690 \, cm^{-1}$
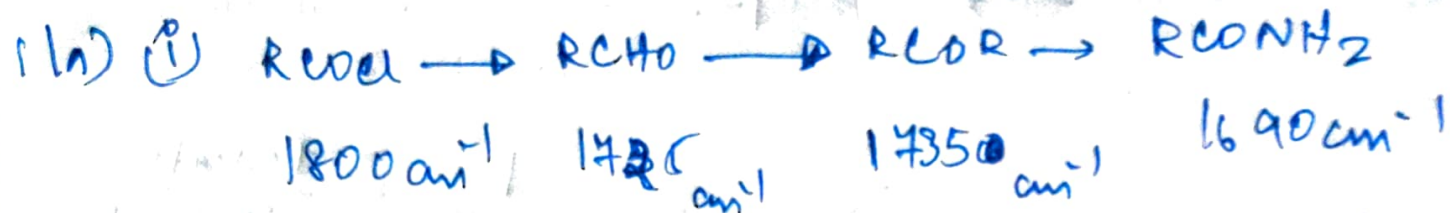
(ii) Refer to Nov. 2024 Q1 (b)(ii)

(iii)

vs

(b) (i) In NMR spectroscopy tetramethyl silane (TMS) is used as an internal standard.

$$Me - \underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}} - Me$$

The reasons being

- → Can provide intense sharp signal even at low temp. 12 protons in magnetically equivalent positions
- → chemically inert   → low boiling point
- → soluble in most organic solvents.

(ii) $\vartheta_x = 640$ Hz $\vartheta_{TMS} = 0$ $\nu_0 = 300$ MHz
$$= 300 \times 10^6 \text{ Hz}$$

$$\delta \text{ in ppm} = \frac{\vartheta_x - \vartheta_{TMS}}{\nu_0} \times 10^6$$

$$= \frac{640 - 0}{300 \times 10^6} \times 10^6 = 2.133 \text{ ppm}$$

(iii) for water → 3-(methyl ethyl)-propane sulfonic acid

for chloroform → 19 F.

(iv) Septet intensity ratio

1 : 6 : 15 : 20 : 15 : 6 : 1

					Pascal's		
			1		Triangle		
		1		1			
	1		2		1		
1		3		3		1	
1		4	6		4		1
1	5		10		10	5	
1	6	15		20		15	6

(v)

H_3C —(ring with H, H at top, Hb, H, H at bottom)— CH_3 and H_3C —(—O—)—$\overset{O}{\overset{\|}{C}}$—$\overset{H_2}{C}$—$CH_3$

H_b (H_A) (H_c) Ab H_a

(H_A) ↓

$H_a \rightarrow (4+1) = 5$ quintet ～～～

$H_b \rightarrow (2+1) = 3$ Triplet ～～

$H_A \rightarrow (2+1) = 3$ triplet ～～

$H_b \rightarrow (3+1) = 4$ quartet ～～

$H_c \rightarrow (0+1) = 1$ Singlet ∧

(↓) (i) $\overline{M_n} = \dfrac{\Sigma N_i M_i}{\Sigma N_i} = \dfrac{N_1 M_1 + N_2 M_2 + N_3 M_3}{N_1 + N_2 + N_3}$

$= \dfrac{100 \times 10^5 + 200 \times 10^3 + 300 \times 10^4}{100 + 200 + 300}$

$= 22 \times 10^3$

$\overline{M_w} = \dfrac{\Sigma N_i M_i^2}{\Sigma N_i} = \dfrac{100 \times 10^{10} + 200 \times 10^6 + 300 \times 10^8}{600}$

$= 1717 \times 10^6 = \cdot$

$\overline{DP_n} = \dfrac{M_n}{M_0} = \dfrac{22 \times 10^3}{\text{Mol. wt of Styrene}} = \dfrac{22 \times 10^3}{104} = \underline{211.54}$

(ii) Isotactic :- Stereocentres in the chain have same configuration (R R R R R R) fine quality polymer

Atactic :- Stereocentres have random configuration poor quality polymer.

(iii) Nylon 6,6 - preparation

combined

$$\left(HN - \overset{O}{\underset{}{C}} - (CH_2)_4 - \overset{P}{\underset{14}{C}} - N - (CH_2)_6 - \underset{14}{N} \right)_n$$

Nylon 6,6