Indian Institute of Engineering Science and Technology, Shibpur

B.Tech. (Gr V-VIII) 1st Semester End-Semester Examination, November 2024

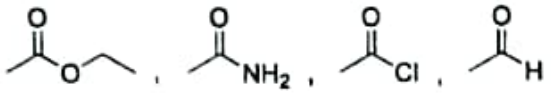
Chemistry (CH1101)

Full Marks: 50 **Time: 3 Hours**

Use separate answer scripts for each half

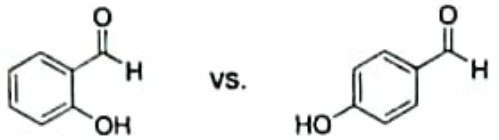
1st Half (Unit-I)

1. (a) Write the carbonyl stretching frequency of the following compounds:



(b) Distinguish the following pairs of compounds with the help of IR spectroscopy (***any one***):

(i) 

(ii) 

(c) Give a clear pictorial representation of various modes of bending and stretching vibration in the methylene (CH_2) group.

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

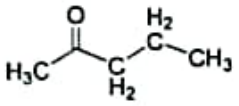
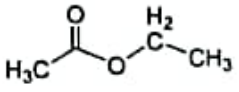
(e) Distinguish between the thermoplastics and thermosetting plastics with examples.

(f) For which of the following isotopes NMR spectroscopy is possible and why?

^{12}C, ^{13}C, ^{19}F, ^{16}O, ^{31}P and ^{10}B

(g) Calculate the Chemical Shift (δ) in ppm for a proton that has resonance 1800 Hz downfield from TMS on a spectrometer that operates at 400 MHz.

(h) Predict the number of signals and multiplicities in the ^{1}H-NMR spectra of the following compounds (***any one***).

(i)  (ii) 

[2+2+2+3+3+2+1+2]

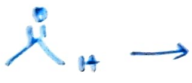
• CHEM1 Nov. 2024

1 (a)


→ Ester → 1735 cm^{-1}


→ Amide → 1690 cm^{-1}


→ Acid chloride → 1800 cm^{-1}


→ Aldehyde → 1725 cm^{-1}

Aldehyde → H group gives not additional effects.

Max → Acid chloride

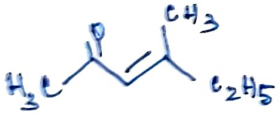
Strong pull by Cl atom to pull $e^{\ominus}$ density away from C, thereby ↑ C=O bond strength and freq ↑

Ester

The OR group provides some +R effect, donating $e^{\ominus}$ density to C=O, not as strong as $Cl^{\ominus}$

Amide → N lone pair participates in resonance reducing double bond character. better +I group. $e^{\ominus}$ shifts, bond strength ↓.

(b) (i)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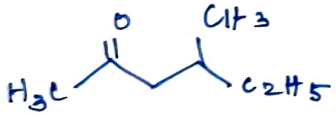
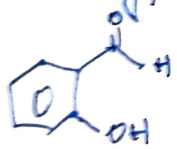


Clearly the first compound has a conjugation of double bond and carbonyl group, but the second compound does.

Therefore for the first compound, the C=O stretching is found at reduced peak than the C=O for second compound, due to presence of conjugation.

Now, the first compound has an additional C=C stretching, which is absent in second compound

(ii)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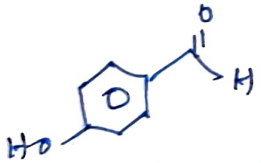


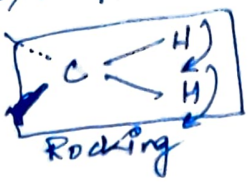
For the first compound, clearly there is the presence of intra molecular H-bonding, which causes no apparent change in O-H bond stretching. (Salicylic acid)

For the second compound, their is clear inter-molecular H-bonding, which causes lower frequency spectrum (p-hydroxy benzoic acid)

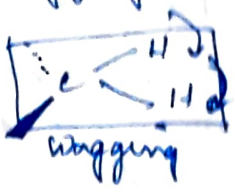
(c) CH_2 → 2 stretching vibrations
→ 4 bending vibrations.

Bending vibrations
1) in plane → Scissoring and Rocking
2) out plane → Wagging and Twisting

Scissoring



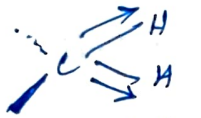
Rocking



Wagging

Twisting

Stretching vibrations
1) Symmetric stretch.
2) Asymmetric Stretch.



Symmetric

Asymmetric

(d) Addition Polymer:- Repeated addition of monomers usually having double bonds. Involves free radical, cationic or anionic polymerization. No By products released.
Eg:- Polythene, Polystyrene.

condensation Polymer :- Repeatd ~~addition of~~ condensation reactions b/w bi-functional monomers. Involves step-growth polymerization. By products like water and HCl.
Eg:- Nylon 6,6, Bakelite.

(e)

Thermoplastic	Thermosetting
Soften up when heated, can be reshaped and reused several times	Do not soften up when heated, cannot be moulded once shaped.
Formed by addition polymerization, long chain linear polymers	Formed by condensation polymerization, cross-linked structure
Weak, soft, and less brittle	hard, strong and brittle
Eg:- Polyethene, Polystyrene	Eg:- Bakelite

f) ^{12}C, ^{13}C, ^{19}F, ^{1}H, ^{31}P and ^{10}B.

Only ^{13}C, ^{19}F and ^{31}P are possible NMR spectroscopy active.

These compounds have their mass number odd and atomic number odd as well.

Thus their spin quantum number is always greater than zero, thus NMR active.

g) Operation freq = 400 MHz $\Rightarrow$ 400×10^6 Hz

Resonance freq (ν_x) = 1800 Hz $\nu_{TMS} = 0$ (standard)

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

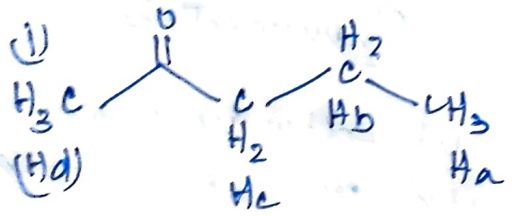
$$= \frac{1800 - 0}{400 \times 10^6} \times 10^6 \text{ ppm}$$

$$= 4.5 \text{ ppm}$$

NMR, if downfield is considered in -ve dirn

$$\delta = -4.5 \text{ ppm}$$

h)



only asked number of signals and multiplicities

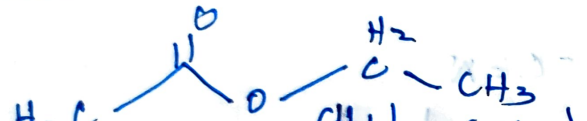
Ha → (2+1) = triplet — (1:2:1) (Area of 3 protons)

Hb → (5+1) = sextet — (1:5:10:10:5:1) (Area of 2 protons)

Hc → (2+1) = triplet — (1:2:1) (Area of 2 protons)

Hd → (0+1) = singlet — (1) (Area of 3 protons)

(ii)



Ha → (2+1) = triplet  (1:2:1)

Hb → (3+1) = ~~Quinte~~ Quartet  (1:3:3:1)

Hc → (0+1) = singlet  (1).

Chemistry (CH1201)

Full Marks: 50 **Time: 3 Hours**

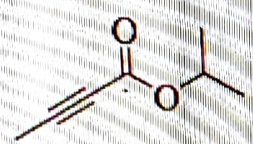
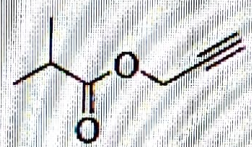
Use separate answer script for each half

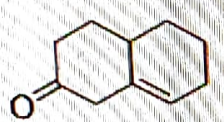
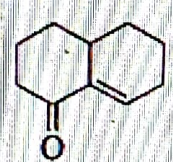
1st Half (Unit-I)

Answer all questions

1. (a) The C–H stretching vibrations in dimethyl sulfoxides occur at 2997 and 2909 cm^{-1}. Using Hooke's law, and assuming that the C–H bond is the same strength as the C–D bond (same force constant, k), calculate any one of the stretching frequencies of the C–D bonds in dimethyl sulfoxides-d_6.

(b) How could you distinguish the following pairs of compounds with the help of IR spectroscopy (***any two***)?

(i)  and 

(ii)  and 

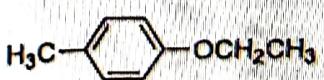
(iii) $CH_3–CH_2–C{\equiv}CH$ and $CH_3–CH_2–C{\equiv}N$

(c) How Nylon 6,6 is prepared? Give reactions involved.

(d) What are Copolymers? Write the structure of SBR or any other co-polymer.

(e) Show all steps of radical polymerization of ethylene by using AIBN initiator.

(f) Predict the multiplicities and approximate chemical shift for the absorption in the proton NMR spectra of the following compounds:

(i) $CH_3COCH_2OCH_3$ and (ii) 

(g) Write the chemical shift values of the methyl proton of the following compounds and explain their variation with reason: CH_3F, CH_3Cl, CH_3Br, CH_3I

OR

In the proton NMR, acetylene proton gives peak at 2.0 ppm, whereas benzene protons appear at 7.2 ppm. Explain.

[2+(1½×2)+2+2+2+(2×2)+2]

(CH1201) April 2024

1(a) $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$ → k is same for both

$\mu_{C-H} = \frac{12 \times 1}{12+1} = 0.923$

$\mu_{C-D} = \frac{12 \times 2}{12+2} = \frac{24}{14} = 1.714$

μ → reduced mass = $\frac{m_1 m_2}{m_1 + m_2}$

$\frac{\nu_{C-D}}{\nu_{C-H}} = \sqrt{\frac{\mu_{C-H}}{\mu_{C-D}}}$

$\frac{\nu_{C-D}}{\nu_{C-H}} = \sqrt{\frac{0.923}{1.714}} = \sqrt{0.5386} \approx 0.7337$

$\nu_{C-D} = 0.7337 \times \nu_{C-H}$

$(\nu_{C-D})_1 = 0.7334 \times 2909 = 2134\ cm^{-1}$

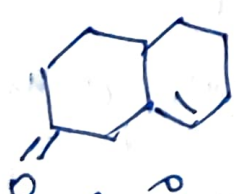
$(\nu_{C-D})_1 = 0.7334 \times 2994 = 2199\ cm^{-1}$ } Ans

(b) (i)

and

clearly the first compound is conjugated, thus the value of frequency is lowered a bit, also, it has presence of $C \equiv C-H$, whereas the second compound is not conjugated with the C=O which does not lowers the value, also it has a presence of $C \equiv C-H$ presence.

(ii)



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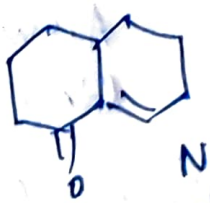


conjugation

Non-conjugation

(iii) $CH_3-CH_2-C\equiv CH$ and $CH_3-CH_2-C\equiv N$

The first compound has two triple bond one of $C\equiv C$ and another $\equiv C-H$, while the second compound only has $C\equiv N$, no $\equiv C-H$ stretch is present.

(c) Nylon 6,6 is prepared by condensation reaction b/w two monomers hexamethyl diamine and Adipic acid.

$H_2N-(CH_2)_6-NH-$ [H + HO] $-C-(CH_2)_4-COOH$

$\downarrow$

$(H_2N-(CH_2)_6-NH-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-OH)_n$

Nylon-6,6

(d) Polymers which comprise of two or more monomers are called co polymer. Eg:- Synthetic Rubber, made up of styrene and 1,3-butadiene.

Structure :- $-[CH_2-CH=CH-CH_2]-[CH_2-CH(Ph)]-$

$[CH_2-CH=CH-CH_2]-$

1,3-butadiene — styrene

(e) !!

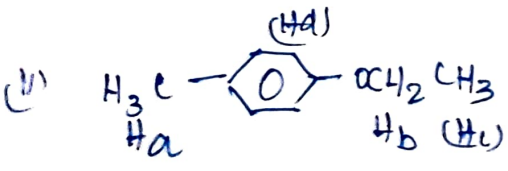
(f) (i)

$\overset{(H_c)}{CH_3}-\overset{}{CO}-\overset{(H_b)}{CH_2}-\overset{(H_a)}{OCH_3}$

$H_a \rightarrow (0+1) \rightarrow$ Singlet $\rightarrow$ 3.7 ppm

$H_b \rightarrow (0+1) \rightarrow$ Singlet $\rightarrow >3.7$ around 4.2 ppm

$H_c \rightarrow (0+1) \rightarrow$ Singlet $\rightarrow$ 2.1 ppm

(ii) 

Aromatic H's (6.0 - 8.0)

(Hd) (1+1) = doublet

$H_a \rightarrow -CH_3$ on ring (2.3 ppm)

NO adjacent (0+1) singlet

$H_b \rightarrow CH_2 \rightarrow$ beside O

(3+1) = quartet 4 ppm

$CH_3 \rightarrow (2+1) = 3$ triplet

(1.2) ppm.

(9) chemical shift

$CH_3-F \rightarrow 4.26$

$CH_3-Cl \rightarrow 3.10$

$CH_3Br \rightarrow 2.68$

$CH_3I \rightarrow 2.16$

Since the electronegativity value decreases down the group the shielding and deshielding effect of the F, Cl, Br, I group decreases their value decreases, hydrogen nuclei are surrounded by EN density.

OR

Acetylene proton → ($-C\equiv C-H$) → lower chemical shift value, π-electrons are aligned linearly inducing shielding effect).

Benzene proton → when placed in magn field, π delocalized electrons create a deshielding effect thus increasing the chemical shift value.