22. i) Three isomeric dimethyl cyclopropanes give respectively two, three and four NMR signals. Draw a stereoisomeric formula for the isomer giving rise to each number of signals.

ii) Deduce the structure of the compound C_9H_8O which exhibited the following spectral data:

UV: λ_{max} 285 nm (ε 45000)

IR: 3090, 2820, 2750, 1685, 1630, 1610, 970, 745 cm^{-1}

NMR: δ 6.62 (1H, dd) J=16 and 7 Hz; 7.41 (1H, d), 7.4 (5H, m), 9.66 (1H, d)

MS: m/z 132, 131, 103, 91, 77 and 51.

31/10/25

TM253815X **Reg. No :.....**

Name :.....

MASTER'S DEGREE (C.S.S) EXAMINATION, OCTOBER 2025

2024 ADMISSIONS REGULAR

SEMESTER III - CORE COURSE

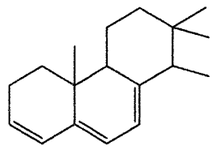
CH3C12TM20 - Spectroscopic Methods in Chemistry

Time : 3 Hours **Maximum Weight : 30**

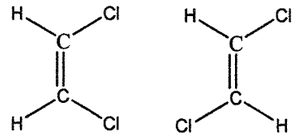
Part A

I. Answer any Eight questions. Each question carries 1 weight **(8x1=8)**

1. With the aid of Woodward Fieser rule calculate the λ_{max} for the following structure.

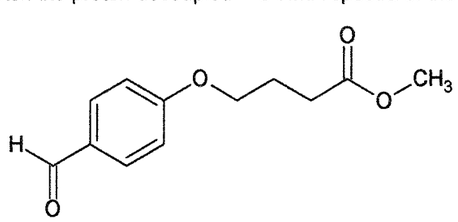


2. State Beer-Lambert Law.
3. Distinguish between the following compounds using IR spectroscopy.

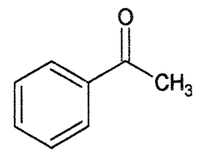


4. Explain briefly the functional group region and finger print region in IR spectroscopy.
5. Sketch the proton decoupled ^{13}C NMR spectra of the following compounds:

i)

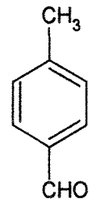


ii)

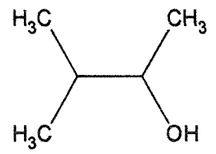


6. Draw the ^{1}H NMR spectrum for each of the following compounds:

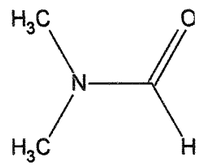
i)



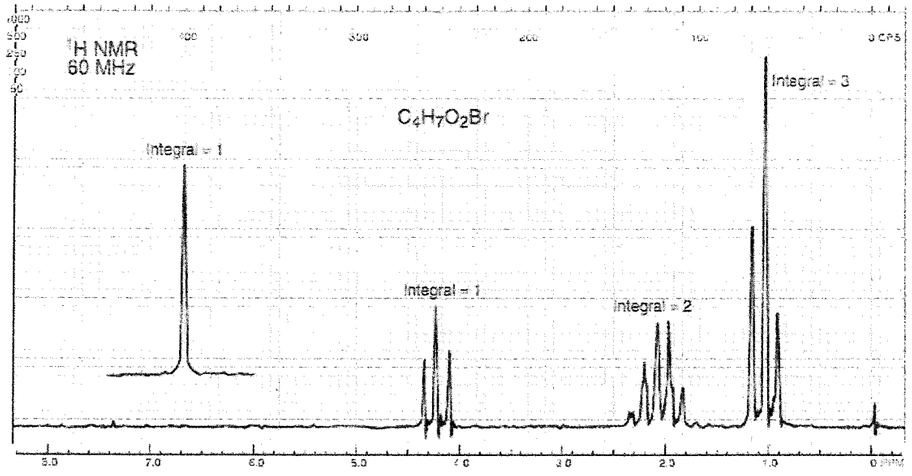
ii)



iii)



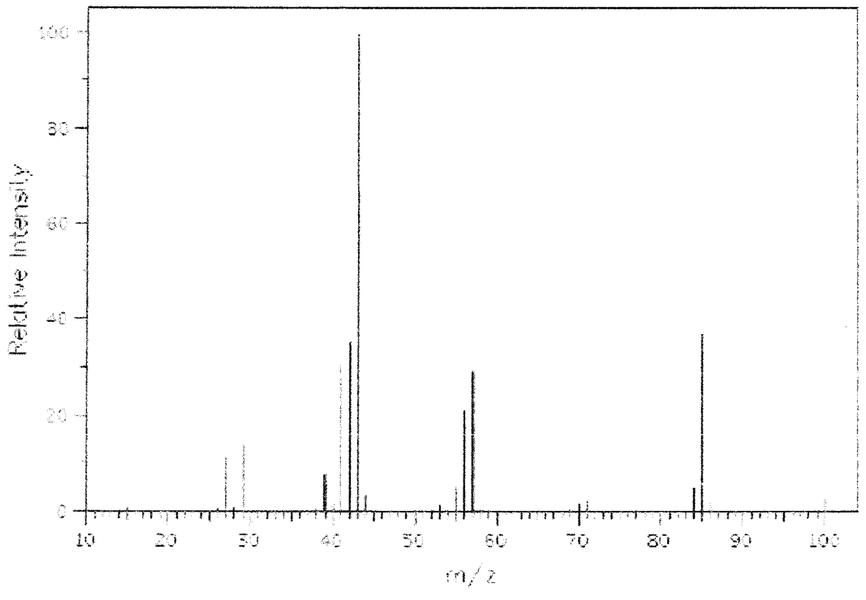
7. In the EI mass spectrum of 2-hexanone an intense peak at m/z 58 is observed. Identify the structure and justify.
8. Illustrate McLafferty rearrangement with suitable examples.
9. Draw the spectrum of an ultrapure sample of ethanol. Draw a tree diagram for the methylene groups in ethanol that takes into account the coupling to both the hydroxyl and methyl groups
10. The following compound is a carboxylic acid that contains a bromine atom: $C_4H_7O_2Br$. The peak at 10.97 ppm was moved onto the chart (which runs only from 0 to 8 ppm) for clarity. Deduce is the structure of the compound.



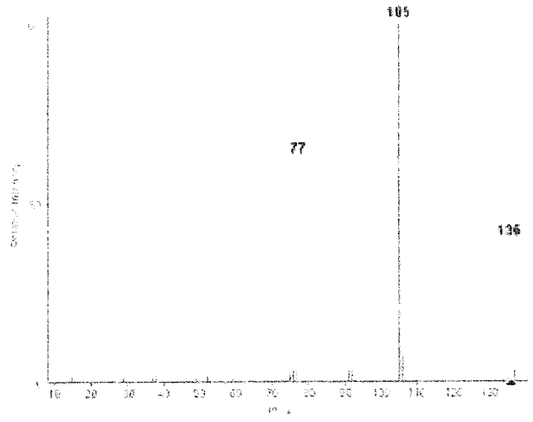
Part B

II. Answer any Six questions. Each question carries 2 weight **(6x2=12)**

11. Describe the effect of stereochemistry on UV- visible absorption spectra.
12. Explain Cotton effect and its application.
13. With the help of suitable examples explain the different factors that affect the vibrational frequency in IR spectroscopy.
14. Explain how coupled vibrations and Fermi resonance affect the vibrational frequency in IR spectra of a compound.
15. Discuss briefly MRI.
16. Below is the mass spectrum of 2-methylhexane. What is the m/z value of the M+ peak and of the base peak? Give possible structures of the fragments giving rise to the large peaks at m/z = 85, 57, and 43.



17. A compound is a volatile organic liquid with a fruity smell. Its mass spectrum is given below. Identify the fragments at m/z = 77 and 105, then propose a structure for this compound.



18. At room temperature, the NMR spectrum of cyclohexane shows only a single resonance peak. As the temperature of the sample is lowered, the sharp single peak broadens until at −66.7°C it begins to split into two peaks, both broad. As the temperature is lowered further to −100°C, each of the two broad bands begins to give a splitting pattern of its own. Explain the origin of these two families of bands

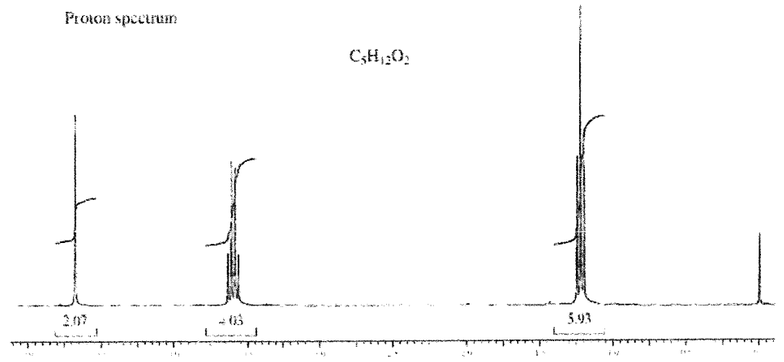
Part C

III. Answer any Two questions. Each question carries 5 weight **(2x5=10)**

19. Illustrate with examples the effect of a) Conjugation b) Hydrogen bonding on the UV spectrum of a compound.
20. (i) The proton NMR spectrum for a compound with formula C_8H_{18} shows only one peak at 0.86 ppm. The carbon-13 NMR spectrum has two peaks, a large one at 26 ppm and a small one at 35 ppm. Draw the structure of this compound.

(ii) The proton NMR spectrum for a compound with formula $C_5H_{12}O_2$ is shown below. The normal carbon-13 NMR spectrum has three peaks. The DEPT-135 and DEPT-90 spectral results are tabulated. Draw the structure of this compound.

Normal Carbon	DEPT-135	DEPT-90
15 ppm	Positive	No peak
63	Negative	No peak
95	Negative	No peak



21. Explain the fragmentation pattern of the following: i) Alcohols ii) carbonyl containing compounds.