**MASTER OF SCIENCE (CHEMISTRY) (CBCS - 2018 COURSE)**
**M.Sc. (Chemistry) Sem-III OC : WINTER- 2022**
**SUBJECT : SPECTROSCOPIC METHODS IN STRUCTURE DETERMINATION**

Day : Thursday | Time : 02:00 PM-05:00 PM

Date : 29-12-2022 | **W-20151-2022** | Max. Marks : 60

**N.B.**

1) All questions are **COMPULSORY.**
2) Figures to the right indicate **FULL** marks.

## SECTION – I

**Q.1** Explain **ANY THREE** of the following: **(15)**

**a)** Intensities of methyl, methylene and methine carbons differ in $^{13}C$ NMR.

**b)** *Ter.* Butyl fluoride in CMR shows a doublet at 1.5δ with J = 2OHz while, on adding $SBF_5$ it shows a singlet at 4.6δ.

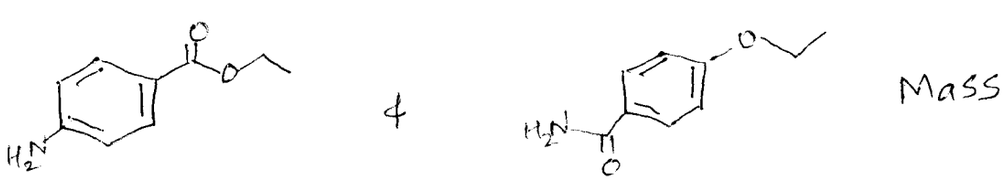
**c)** The mass spectrum of 3-butyn-2-ol shows base peak at m/z = 55. Why the fragment is strong?

**d)** How will you distinguish the following isomeric esters by $^1$HNMR $PhCH_2OCOCH_3$ and $PhCOOCH_3$?

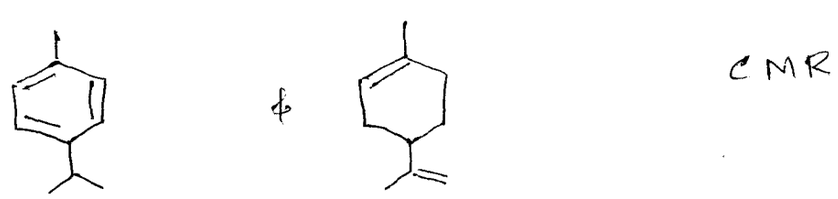
**e)** The –OH proton usually appears at a lower field in DMSO than $CDCl_3$.

**Q.2** Distinguish between **ANY THREE** of the following by given spectral methods. **(15)**

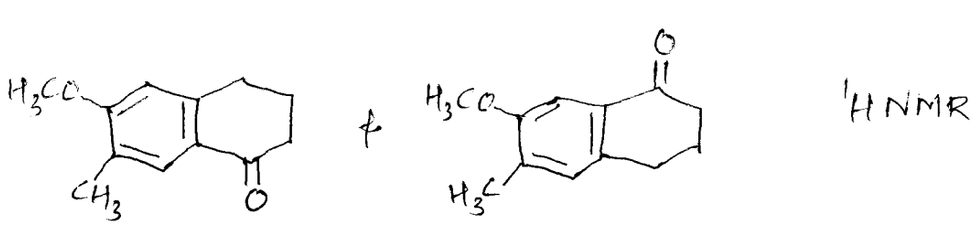
**a)**



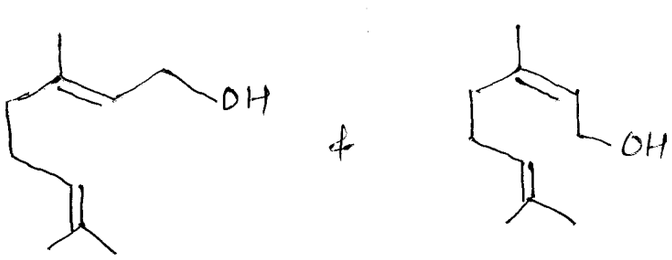

**b)**



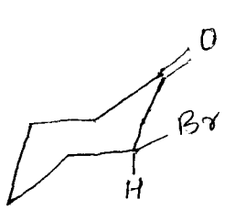
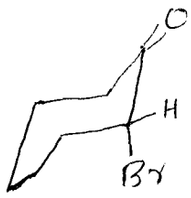

**c)**




**d)**




P.T.O.

e)  +  $^1$HNMR

## SECTIION – II

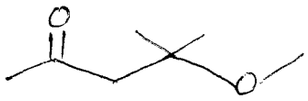
**Q.3** Write notes on **ANY THREE** of the following: **(15)**

**a)** Maldi technique in mass spectroscopy.
**b)** Methods for simplification of NMR. Explain one.
**c)** N, N dimethyl formamide shows two signals for two methyl groups.
**d)** AMX system
**e)** Homo and Hetro nuclear correlated spectroscopy.

**Q.4** Attempt **ANY THREE** of the following: **(15)**

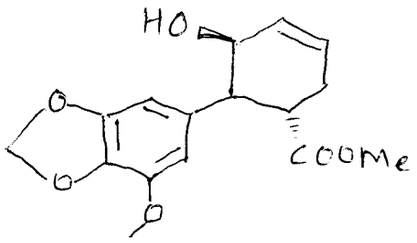
**a)** On a 60 MHz instrument, the AB quartet show $\sigma_A$ = 112 Hz, $\sigma_B$ = 120 Hz, and $J_{AB}$ = 15 Hz. Calculate the line positions of the four lines in Hz. Clearly write all the calculations.

**b)** Explain the genesis of the following:



m/z = 130, 115, 100, 73, 43

**c)** Assign chemical shifts to various carbons present in the following compound.



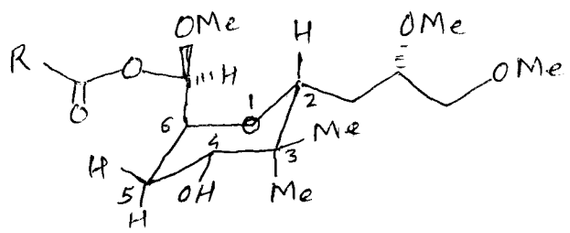
30(t), 39(d), 48(d), 51(q), 56(q), 66(d), 101(t), 103(d), 108(d), 127(d), 128(d), 34(s), 136(s), 144(s), 149(s), 175(s)

**d)** Deduce the structures using the following spectral data;

**i)** Mol for, $C_{10}H_{12}$ ; $^1$HNMR : 0.65 (m, 2H), 0.81 (m, 2H) 1.37(S, 3H); 7.17(m, 5H)

**ii)** Mol for, $C_6H_8O_2$ : CMR : 17(t), 21(t), 69(t), 120(s) 166(d), 191(d)

**e)** $^1$HNMR of the following compound exhibits the following signals. Assign the signals & justify. Use decoupling expt.
Note: give signals for only numbered protons



1.85 (ddd, J = 5, 10, 12 Hz, 1H); 2.10 (ddd, J = 3, 4, 12 Hz, 1H)
3.75(dd, J = 4, 10Hz, 1H); 3.85(ddd, 3, 5, 8 Hz, 1H)
4.0 (dd, J = 3 & 7 Hz, 1H)

Decoupling Expt.

**i)** Irradiation of 2.1 δ changes ddd at 1.85 to dd, J = 5 & 10 Hz
2.1 δ changes ddd at 3.85 to dd, J = 5 & 10 Hz
2.1 δ changes dd at 3.75 to d, J = 10 Hz

**ii)** Irradiation of 3.85 δ changes ddd at 2.10 to dd, J = 4 & 12 Hz
3.85 δ changes ddd at 1.85 to dd, J = 10 & 12 Hz

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