UNIVERSITY OF THE PUNJAB

B.S. 4 Years Program / Eighth Semester – Spring 2022

Paper: Organic Chemistry (Sp. Theory-I)   Course Code: CHEM-428

Time: 3 Hrs. Marks: 60

THE ANSWERS MUST BE ATTEMPTED ON THE ANSWER SHEET PROVIDED

Q.1.   Write short answers to the following questions.

(a)   (2.5 x 2 = 5)

I.   Why only a small quantity of the sample (in the vapour state) is used for analysis in the mass spectrometer?

II.   Explain why the deuterium-coupled 1H-spectrum of cyclohexane-d11 contains only a sharp singlet at room temperature but two singlet at 170 K.

(b).   (2.5 x 2 = 5)

I.   How will you distinguish between CH_3Cl, CH_3Br, and CH_3I by mass spectrometry?

II.   What are natural products?

(c).   (2.5 x 2 = 5)

I.   In benzaldehyde, two of the ring protons have resonance at 7.87 ppm, and the other three have resonance in the range from 7.5 to 7.6 ppm. Explain.

II.   Arrange the following protons in the decreasing order of their δ values in 1H-NMR and account for your order: Methyl, ethylenic, acetylenic, aryl and aldehydic.

(d). How would you distinguish between primary, secondary and tertiary butyl alcohols by mass spectrometry? **(5).**

(e).   How can you distinguish among the seven isomers of $C_4H_{10}O$ by the number of distinct signals and areas under them in their PMR spectra?   **(5)**

(f)   What fragments are expected as a result of McLafferty rearrangement in the following compounds? **(1x5 = 5)**

i)   5-Methyl hexanal,   ii)   4-Methyl-2-pentanone,   iii)   2-Butylcyclohexanone,

iv)   Butyl 2,2-dimethylpropanoate   v)   2-Ethylhexanoic acid.

Q.2.   Write detailed answers to the following questions.

(a)   Define ionization in mass spectroscopy. Briefly explain the different modes of ionization in mass spectrometry. **(10).**

(b)   Deduce the structure of each of the following compounds on the basis of their molecular formula and PMR data.   **(2.5x4=10)**

    i. $C_{10}H_{14}$: δ 1.3 (9H, singlet) and 7.0-7.5 (5H, multiplet)
    ii. C_6H_{14}: δ 0.9 (12H, doublet) and 1.4 (2H, heptet)
    iii. $C_4H_6Cl_4$ δ 3.9 (4H, doublet) and 4.6 (2H, triplet)
    iv. C_3H_7OCl: δ 2.0 (2H, quintet), 2.8 (1H, singlet), 3.7 (2H, triplet) and 3.8 (2H, triplet).

(c)   Write a short note on alkaloids. Briefly explain the isolation procedure of alkaloids.   **(10).**