M.Sc. 1st Semester Examination, 2018

CHEMISTRY

(Organic Chemistry)

Paper : CHEM-102C

Course ID : 11452

Time: 2 Hours

Full Marks: 40

The figures in the margin indicate full marks. Candidates are required to give their answers in their own words as far as practicable.

1. Answer *any five*:

2×5=10

(a) Draw a qualitative MO diagram for the following wave function indicating the nodal plane and also predict whether C_2 and σ are symmetric or antisymmetric:

 $\Psi = 0.37 \ \varphi + 0.6 \ \varphi_2 - 0.6 \ \varphi_3 - 0.37 \ \varphi_4.$

(b) Calculate λ_{max} value for the following compounds :



- (c) Mention the point group of BCl_3 and CCl_4 .
- (d) What is Larmor frequency?
- (e) Define the term with suitable example: 'Conformationally biased system'.
- (f) Explain why the IR spectrum of glucose shows no significant absorption on the stretching vibration region.
- (g) Draw the stereo-chemical structure in Fischer form of (R)–1-Bromo-1-phenyl ethane and (R)-Alanine.
- **2.** Answer *any four*:
 - (a) (i) Assign R,S-designations of the following compounds:



5×4=20

(2)

- (ii) 'Gauche form of butane is chiral but butane itself is optically inactive'.— Explain.
- (iii) Calculate expected apparent mass of the metastable ion produced when m/z 77 decompose by loss of CH \equiv CH to m/z 51. 2+1+2=5
- (b) (i) Write down the interaction matrix allylcation.
 - (ii) Calculate the approximate energy values of the MO.
 - (iii) Assign the MOs as bonding and antibonding. 1+2+2=5
- (c) Predict the products with mechanism and explanation:

(i)
$$\begin{array}{c} CH_{3} \\ Ph \end{array} \xrightarrow{M} C \xrightarrow{M} Ph \end{array} \xrightarrow{(i) LAH/Et_{2}O, 20 \text{ min}} ? \\ \hline (ii) LAH/Et_{2}O, 20 \text$$

- (iii) What do you mean by conformational energy? 2+2+1=5
- (d) (i) Explain with suitable example McLafferty rearrangement cleavage in mass spectroscopy.
 - (ii) Write the Winstein-Holness principle and derive this equation of any feasible reaction. 2+3=5
- (e) (i) Compare the stability of *cis* and *trans* 1, 3 Dimethylcyclohexane.
 - (ii) Explain the peaks appearing at m/z 69,67 & 93 in the mass spectrum of β -myrcene.

2+3=5

(f)



State the major product with explanation.

(ii) Predict whether the following compounds are aromatic, non-aromatic or anti-aromatic:



(iii) Predict the chemical shift position for the carbon in 3-Heptanone. 2+2+1=5

 $10 \times 1 = 10$

- 3. Answer *any one* question:
 - (a) (i) An Organic compound which is pale yellow colour, is slightly acidic in nature having MF-C₆ H₅ NO₃ and gives the following spectral results:
 - UV: $\lambda_{max} 280nm$, $\epsilon_{max} 6600$
 - IR (cm⁻¹): 3460 (broad, sharp), 3035 (m), 1608 (m), 1505 (m), 1510 (s), 1360 (s), 1320 (s) & 740 (s). The band at 3460 cm⁻¹ does not shift even on diluting the sample.
 - ¹HNMR: $\delta_{6.9}$ 1H(s), $\delta_{6.21}$ 4H(s) unsymmetrical pattern. Deduce the structure of the compound on the basis of the spectroscopic and spectrometric results.
 - (ii) Writes note on "off resonance".
 - (iii) Why is solvent choosen important for NMR spectroscopy? 5+3+2=10
 - (b) (i) How will you account for the appearance of prominant peak at m/z 31,42 and 70 in the mass spectrum of *n*-Pentanol?
 - (ii) How would you distinguish between the following pairs of compounds by NMR-spectroscopy?

- (iii) 'The unsaturated aldehydes CH_3 -(CH = CH)_n-CHO have UV absorption spectra that depends on the value of *n*, the λ_{max} being 220, 270, 312 and 343 nm as '*n*' changes from 1 to 4.'— Explain.
- (iv) Write down the two advantages of electron ionization process. 5+2+2+1=10