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**LB—10—2023**

**FACULTY OF SCIENCE**

**M.Sc. (Second Year) (Third Semester) EXAMINATION**

**APRIL/MAY 2023**

**(New/CBCS Pattern)**

**CHEMISTRY**

**Paper-XV (CH-511/531)**

**(Advanced Spectroscopic Methods)**

**(Wednesday, 3-5-2023)**

**Time : 2.00 p.m. to 5.00 p.m.**

*Time— Three Hours*

*Maximum Marks—75*

*N.B. :—* (i) All questions are compulsory.

(ii) Figures to the right indicate full marks.

1. Attempt any *three* of the following : 15

(a) When *p*-aminophenol is dissolved in water,  $\lambda_{\max}$  is at longer wavelength than in acid solution.

(b) The  $> C = O$  stretching frequency in *p*-nitroacetophenone is higher than in *p*-methoxyacetophenone.

(c) In PMR spectroscopy a proton on hetero atom can be detected by the use of  $D_2O$ .

(d) Off resonance  $^{13}C$  spectrum is useful in the interpretation.

(e) Pentanoic acid gives  $m/2$  60 in mass spectrum. Explain.

P.T.O.

2. Attempt any *three* of the following :

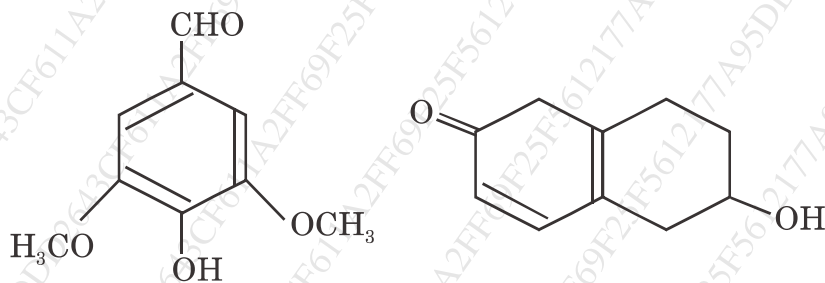
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(a) Assign the structure of the compound using PMR data :

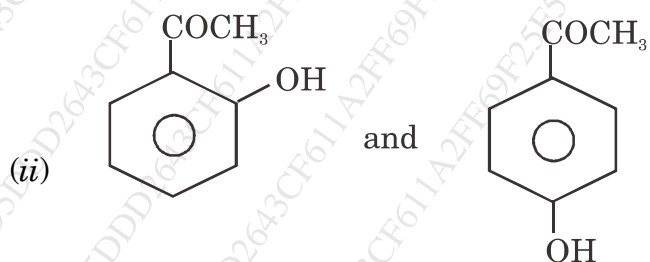
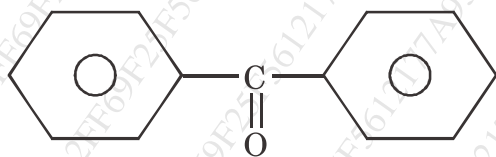
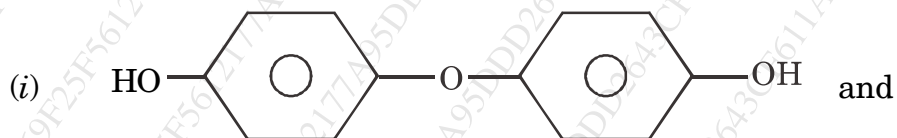
M.F. :  $C_8H_9Br$

$\delta(\text{ppm})$  : 2.7(2H), 3.4(2H), 7.22(5H)

(b) Calculate  $\lambda_{\text{max}}$  for the following compounds :



(c) The following pairs of compounds can be distinguished by IR spectroscopy :



- (d) What do you understand by metastable ion ? Explain the importance of these ions in mass spectroscopy.
- (e) An organic compound with MF  $C_5H_{10}O$  displays the following  $^{13}C$ -NMR spectral data :
- $^{13}C$ -NMR :  $\delta$  18(*q*), 27.3(*q*), 42(*d*), 211(*s*).
- Assign the structure of the compound.

3. Solve the following :

- (a) Partial hydrogenation of triene shown results into two compounds A and B, having molecular formula  $C_{10}H_{14}$ . Compound A shows absorption maximum at 235 nm and B shows at 275 nm. Assign the structures to the A and B compounds. 7

Or

What is McLafferty rearrangement ? Illustrate possible mass fragmentation pathways including McLafferty rearrangement of an aliphatic aldehyde.

- (b) An organic compound with MF  $C_5H_4O_2$  exhibits the following spectral data : 8

UV :  $\lambda_{max}$  274 nm

IR : 3070, 2840, 2755, 1704, 1670, 1170  $cm^{-1}$

PMR ( $\delta$  scale, ppm)  $\delta$  6.5 (*dd*, 1H), 7.2 (*dd*, 1H), 7.5 (*dd*, 1H), 9.5 (*s*, 1H).

Rationalize the spectral data and assign structure to the compound.

P.T.O.

Or

Assign the structure to the compound with MF  $C_9H_{10}O_2$  which exhibits the following spectral data :

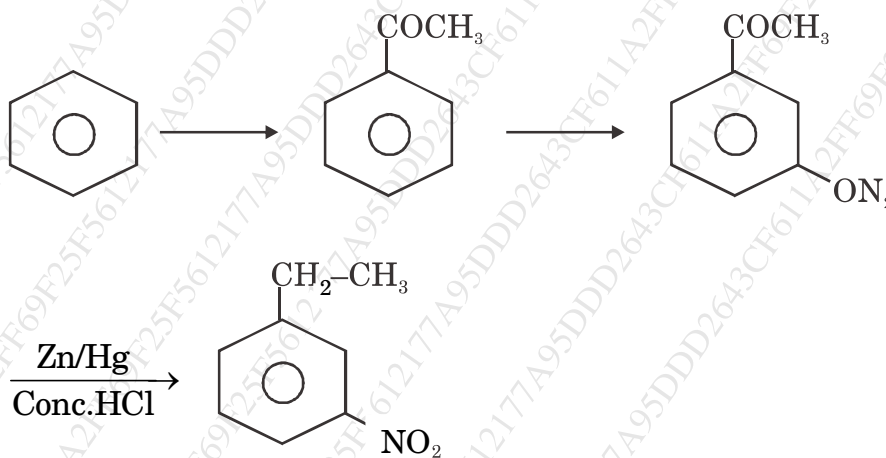
$^1H$ NMR :  $\delta$  2.15 (s, 3H), 3.6(s, 2H), 7.1 – 7.6 (m, 5H).

$^{13}C$  NMR :  $\delta$  28(q), 51(t), 126(d), 128(d), 129(d), 134(s), 205(s).

Rationalize the spectral data and assign the structure.

4. Solve the following :

(a) How will you follow the course of the following reactions by IR Spectroscopy ? 7



Or

Assign structures to the compounds which displays the following PMR data :

Compound A : MF  $C_2H_3F_3O$

PMR ( $\delta$  scale, ppm) :  $\delta$  3.2 (s, 1H, exchangeable with  $D_2O$ ), 3.8(q, 2H).

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Compound B : MF  $C_{11}H_{15}Br$

PMR :  $\delta$  1.5 (s, 6H),

3.1 (t, 2H),

3.6 (t, 2H),

7.5 (s, 5H).

Justify your answer.

- (b) Deduce the structure of the compound based on the following data :

MF :  $C_8H_{11}ON$

IR : 3450, 3390, 1600, 1580, 1500, 1140 and 840  $cm^{-1}$

PMR : ( $\delta$  ppm) :

$\delta$  1.3 (t, 3H, J = 8 Hz)

3.4 (s, exchange with  $D_2O$ )

3.9 (q, 2H, J = 8 Hz)

7-7.3 (m, 4 H)

Justify the spectral data.

Or

Deduce the structure of the compound based on the following data :

Molecular formula :  $C_{14}H_{10}O_2$

UV :  $\lambda_{max}$  260 nm ( $E_{max}$  21000)

IR : 1670, 1600, 1580, 1500  $cm^{-1}$

P.T.O.

WT

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PMR ( $\delta$  ppm) :  $\delta$  7.5 (*m*, 36 mm)

7.9 (*m*, 24 mm)

MS: *m/z* 210 (*m*<sup>+</sup>), 105, 77, 51.

Justify the spectral data.

5. Write short notes on any *three* of the following :

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- (a) Stretching and bending vibrations in IR Spectroscopy.
- (b) Shielding and deshielding effect in PMR.
- (c) Mass spectrum of 2-Hexanone.
- (d) Off resonance <sup>13</sup>C spectrum.