This question paper contains **7** printed pages]

NY—10—2023

FACULTY OF SCIENCE

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

NOVEMBER/DECEMBER, 2023

CHEMISTRY

(CH-511/CH-531)

(Advanced Spectroscopic Methods)

(Tuesday, 5-12-2023) **Time : 2.00 p.m. to 5.00 p.m.**

Time—3 *Hours* *Maximum Marks*—75

N.B. :— (1) *All* questions are compulsory.

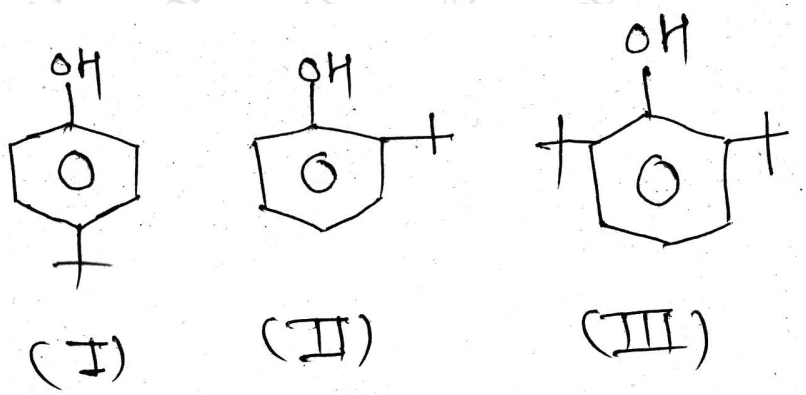
(2) Figures to the right indicate full marks.

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

(*a*) *n*-Butyl methyl ketone exhibits McLafferty rearrangement in mass fragmentation but acetone does not exhibit the same.

(*b*) Explain why trans-isomer absorbs UV at higher wavelength than cis-isomer.

(*c*) In substituted phenols the O—H stretching is at 3608 cm^{-1} in I at 3605 cm^{-1} in II and at 3643 cm^{-1} in III. Explain :



(I) (II) (III)

P.T.O.

(*d*) An organic compound with MF $C_7H_{14}O$ displays the following ^{13}C-NMR spectral data

^{13}C-NMR : δ 13.4(*q*), 17.6(*t*), 44.8(*t*) and 210.2(*s*).

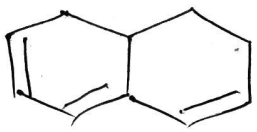
(*e*) How one can use PMR spectral data to differentiate between the followng isomeric compounds :

$CH_3—CH_2—OH$ and $CH_3—O—CH_3$

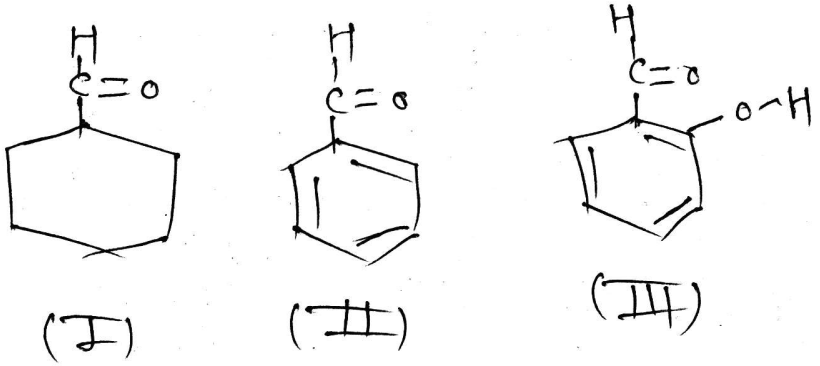
$CH_3—CH_2—COOH$ and $CH_3—COOCH_3$

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

(*a*) Partial hydrogenation of the triene shown below results in two compounds, D and E, both of molecular formula $C_{10}H_{14}$. Compound D shows λ_{max} = 235 nm and E, 275 nm. Assign the structure :



(*b*) Predict the frequency shift of the carbonyl absorption in the aldehyde :



(*c*) Deduce the structure of a compound using C^{13} NMR spectroscopy.

Molecular formula : $C_7H_{14}O$.

13.4(*q*), 17.6(*t*), 44.8(*t*), 210.2(*s*).

(*d*) How can one do distinction between 3-methyl cyclohexene and 4-methyl cyclohexene on the basis of mass spectroscopy ?

(*e*) An organic compound with M.F. $C_7H_{14}O$, displays the following H^1-NMR data :

δ : 1.05 (d, 12H, J = 7Hz)

δ : 2.7 (septet, 2H, J = 7Hz).

3. Solve the following : 8

(*a*) Deduce the structure from given data :

PMR (δ) : 1.3 (*t*, 3H, 8Hz),

: 3.4 (*s*, 2H, exchange with D_2O),

: 3.9 (*q*, 2H, 8Hz)

: 7-7.3 (*m*, 4H).

P.T.O.

Or

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

Molecular formula : $C_{11}H_{11}N$

UV : 272 nm (r 18000)

IR : 2712, 1604, 845, 814 cm^{-1}

PMR (δ) : 1.03 (3H, d, J = 7 Hz)

: 2.60 (2H, q, J = 7 Hz)

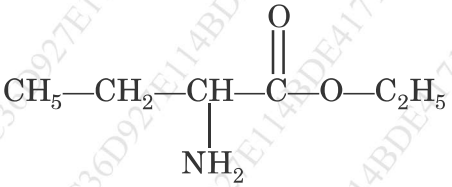
: 5.60 (1H, d, J = 16 Hz)

: 7.21 (2H, d, J = 8.5 Hz)

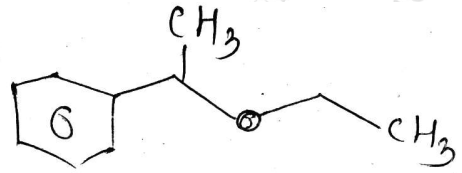
: 7.43 (2H, d, J = 8.5 Hz)

: 7.72 (1H, d, J = 16Hz).

(*b*) Explain the genesis of ions of the following : 7

(*i*) 

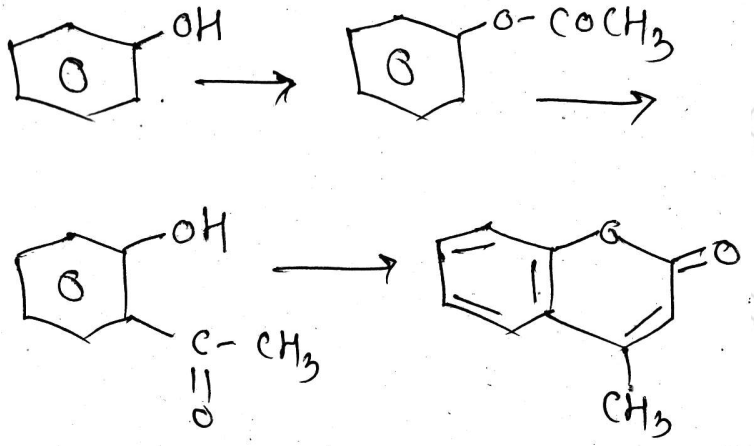
M/z : 30, 3d, 58, 74, 102

(*ii*) 

M/z : 77, 79, 105, 106, 135, 150

Or

How will you follow the course of the following reactions by IR spectroscopy ?



4. Solve the following : 8

(*a*) Deduce the structure of the compound based on the following spectral data :

M.F. : $C_9H_{10}O_2$

UV : λ_{max} 214 nm; (Σ max 2050)

IR : 3031, 2941, 1700(*s*), 1608, 1504, 1060, 830 cm^{-1}

^1H–NMR : (δ-scale, ppm); δ 2.38 (*s*, 9 mm)

3.82 (*s*, 9 mm) 7.21-7.85 (*m*, 12mm).

P.T.O.

Or

Assign structure to the compound based on the following data :

Molecular formula : $C_5H_8O_2$

IR : 3300-2700 (broad), 1715, 1638 cm^{-1}

MS : 100 (M^t), 55, 45, 41.

PMR (δ) : 2.52 (m_1 20 mm)

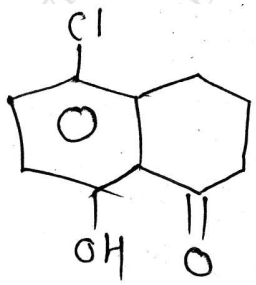
: 5.15 (*dd*, J = 10 and 1.5 Hz, 5 mm)

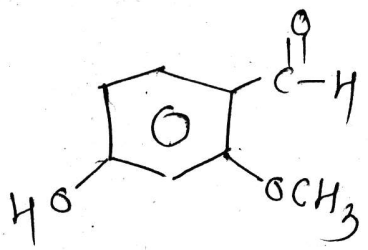
: 5.25 (*dd*, J = 16 and 1.5 Hz, 5 mm)

: 5.86 (*m*, 5 mm)

: 11.50 (*bs*, 5 mm, exchangeable with D_2O)

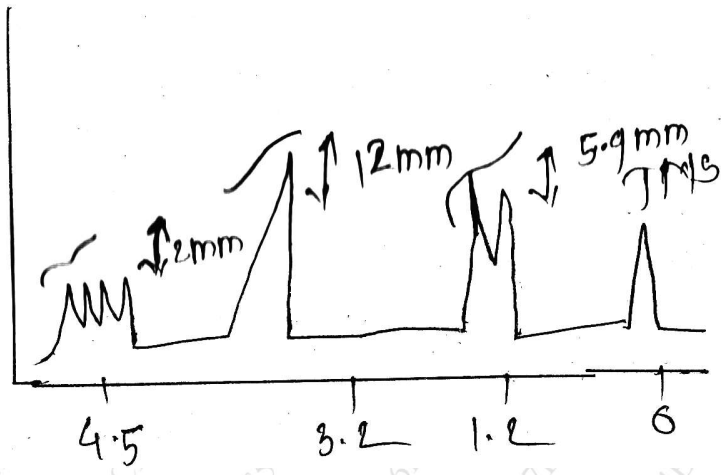
(*b*) Calculate λ_{max} for the following compounds by A.I. Scott rules : 7





Or

A compound $C_4H_{10}O_2$ shows the following NMR spectrum. Deduce the structure :



5. Write short notes on (any *three*) : 15

(*a*) Spin-spin coupling in PMR

(*b*) McLafferty rearrangement

(*c*) Electronic transition in UV spectroscopy

(*d*) Fermi resonance and overtone band.