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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.

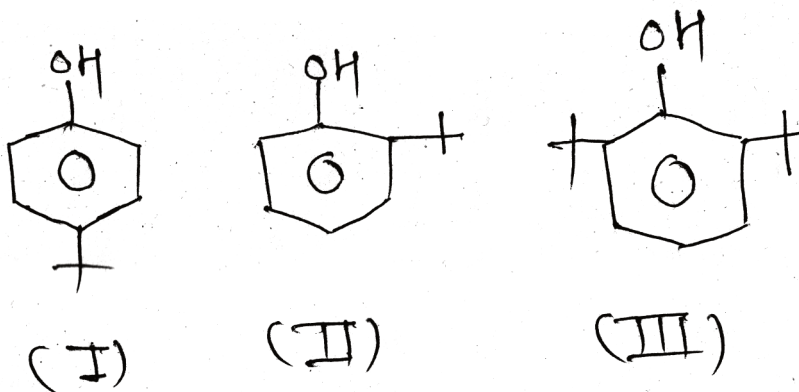
(2) Figures to the right indicate full marks.

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 :



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(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 following isomeric compounds :

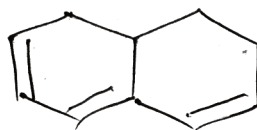
CH_3-CH_2-OH and CH_3-O-CH_3

CH_3-CH_2-COOH and $CH_3-COOCH_3$

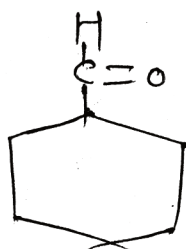
2. Attempt any *three* of the following :

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(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 $\lambda_{max} = 235$ nm and E, 275 nm. Assign the structure :



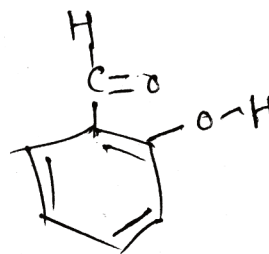
(b) Predict the frequency shift of the carbonyl absorption in the aldehyde :



(I)



(II)



(III)

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(3)

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- (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, $J = 7\text{Hz}$)

δ : 2.7 (septet, 2H, $J = 7\text{Hz}$).

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).

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Or

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

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

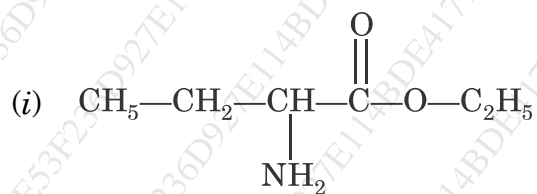
UV : 272 nm (ϵ 18000)

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*, $J = 16$ Hz).

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

7

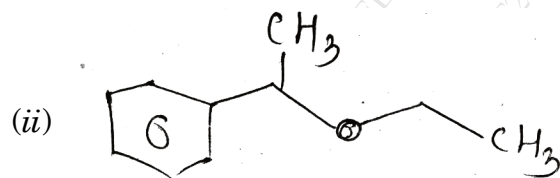


M/z : 30, 3d, 58, 74, 102

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(5)

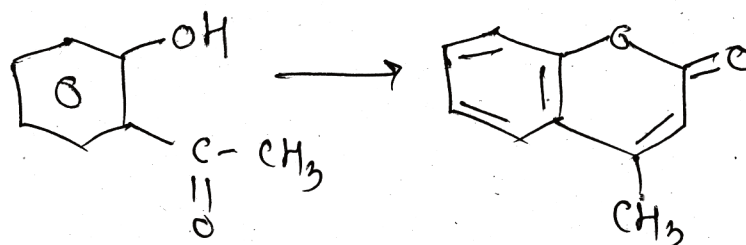
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M/z : 77, 79, 105, 106, 135, 150

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.

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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^+), 55, 45, 41.

PMR (δ) : 2.52 (m , 20 mm)

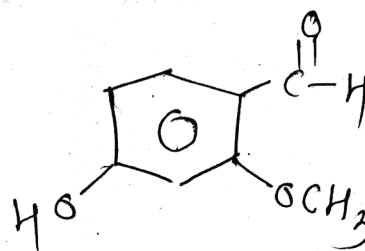
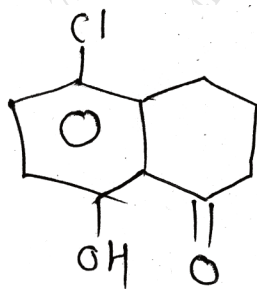
: 5.15 (dd , $J = 10$ and 1.5 Hz, 5 mm)

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

: 5.86 (m , 5 mm)

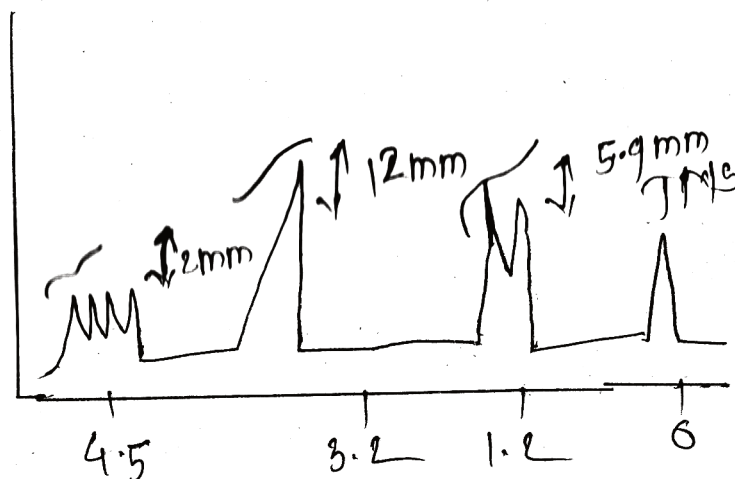
: 11.50 (bs , 5 mm, exchangeable with D_2O)

(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

- Spin-spin coupling in PMR
- McLafferty rearrangement
- Electronic transition in UV spectroscopy
- Fermi resonance and overtone band.