2022

M.Sc.

4th Semester Examination

CHEMISTRY

PAPER—CEM-401

ORGANIC, INORGANIC AND PHYSICAL SPECIAL

Full Marks : 40

Time : 2 Hours

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

1. Answer any *four* questions : 4×2

(a) Which property makes one nuclei NMR active ? Give examples of one NMR active and one NMR inactive nuclei.

(b) *What is Karplus* equation ? Show in figure and explain.

(c) What are the differences between ORD and CD ?

(d) What characteristic bands are observed for Random coil, β-sheet and α-helix conformation of protein structure in CD spectrophotometry?

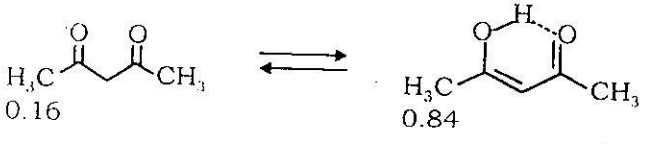
(e) Which reference compound is used for NMR in D_2O ? Write its structure.

(f) Write down the expression for specific and molar ellipticity.

2. Answer any *four* questions : 4×4

(a) A compound $C_9H_{10}O_2$ has strong infrared absorption at 1695 cm^{-1}. The ^1H NMR spectrum has five sets of lines : a triplet at δ 1.3 (3H), a quartet at δ 4.1 (2H), a doublet at δ 7.0 (2H), a doublet at δ 7.8 (2H) and a singlet at δ 9.8 (1H) ppm. Suggest a structure of this compound.

(b) What is chemical exchange ? Calculate the percentage of keto and enol forms of acetyl acetone from the integral data given below :



(Continued)

(c) A and B are two isomers having molecular formula $C_9H_{10}O_2$, deduce the structure of the isomers (A & B) with the help of given FTIR and ^1H NMR data :

For isomer A : FTIR : 1680 cm^{-1} ; ^1H NMR (δ) : 7.6 (2H, d), 6.9 (2H, d), 3.9 (3H, s), 2.0 (3H, s).

For isomer B : FTIR : 1740 cm^{-1} ; ^1H NMR (δ) : 7.2 (5H, s), 5.0 (2H, s), 1.98 (3H, s).

(d) Isomeric esters D and E have the composition $C_{11}H_{12}O_4$. Spectral data are summarized below. Deduce the structures of D and E and rationalize your answer.

Compound D : δ 8.49 (t, J = 2 Hz, 1H), 8.05 (d, J = 2 Hz, 2H), 3.94 (s, 6H), 2.46 (s, 3H) ;

Compound E : δ 8.52 (d, J = 2 Hz, 1H), 8.00 (dd, J = 8, 8 Hz, 1H), 7.28 (d, J = 8 Hz, 1H), 3.91 (s, 6H), 2.63 (s, 3H).

(e) An organic compound having molecular formula $C_{10}H_{12}O_2$ shows the following spectral data :

^1H NMR – δ (8.0, 2H, m) ; δ (7.2, 3H, m) ; δ (5.2, 1H, m) ; δ (1.3, 6H, d),

IR – 1730 cm^{-1}, 3050 cm^{-1} and 2950 cm^{-1}.

Draw the structure of the compound.

(f) An organic compound having molecular formula C_5H_8O shows following spectral data :

^1H NMR – δ (6.2, 1H, d, J = 18 Hz) ; δ (5.4, 1H, m, J = 17 Hz) ; δ (2.3, 3H, s) ; δ (1.9, 3H, d),

IR – 1685 cm^{-1}, 3020 cm^{-1},

UV-VIS – λ_{max}(EtOH) = 277 nm, ε_{max} = 4600.

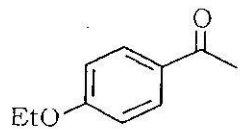
Draw the structure of the compound.

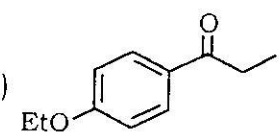
3. Answer any *two* questions : 2×8

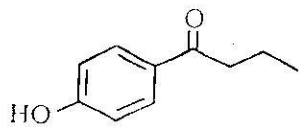
(a) (i) An organic compound exhibited the following ^1H NMR spectral data :

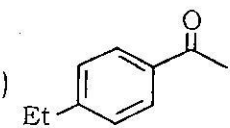
δ : 7.80 (2H, d, 8 Hz), 6.80 (2H, d, 8 Hz), 4.10 (2H, q, J = 7.2 Hz), 2.4 (3H, s), 1.25 (3H, t, J = 7.2 Hz)

The compound among the choices given below is :

(1) 

(2) 

(3) 

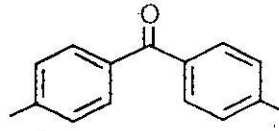
(4) 

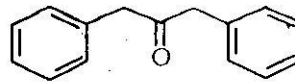
(ii) An organic compound having molecular formula $C_{15}H_{14}O$ exhibited the following ^1H NMR and ^{13}C NMR spectral data :

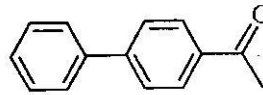
^1H NMR : δ 7.7 (d, J = 8 Hz), 7.2 (d, J = 8 Hz), 2.4(s).

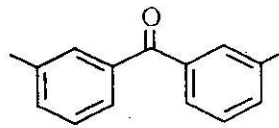
^{13}C NMR : δ 190.0, 141.0, 136.0, 130.0, 129.0, 21.0

Identify it :

(1) 

(2) 

(3) 

(4) 

(b) (i) Compound A, $C_8H_8O_3$, shows the following spectral data :

UV : λ_{max} (EtOH) 215, 235, 285 and 320 nm ;
λ_{max} *(EtOH–NaOH)* 260, 303 and 355 nm.

^{1}H-NMR (d) : 9.80 (s, 1H), 7.40 (m, 2H), 7.10 (s, 1H, disappeared on deuterium exchange), 7.0 (1H, d, J = 8 Hz), 3.95 (s, 3H)

MS (m/z) : 152 (M^+, 100%), 151 (96%) and 123 (8%).

Suggest a probable structure for the compound.

(ii) Compound B, $C_9H_{11}NO$, shows the following spectral data :

UV : λ_{max} 235 (ε 8650) and 320 (ε 28300)

FTIR (cm^{-1}) : 1695, 1600 (s), 1567, 1526, 808, 720 and bands immediately above and below 3000 cm^{-1}, well-defined doublets at 2820) and 2740 cm^{-1}.

^{1}H NMR (δ) : 9.72 (s, 1H), 7.75 (d, 2H, J = 9 Hz), 6.70 (d, 2H, J = 9 Hz), 2.98 (s, 6H)

MS (m/z) : 149 (M^+), 148 (base peak) and 120.

4+4

(c) (i) Discuss "nuclear decay scheme for ^{57}Fe Mössbauer resonance".

(ii) Derive the expression for "recoil energy". Explain why recoilless emission and absorption of Y-ray is essential for Mössbauer spectroscopic study.

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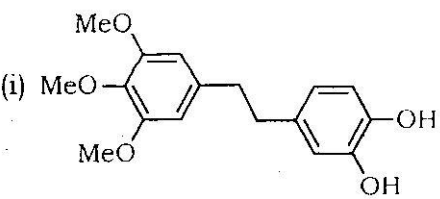
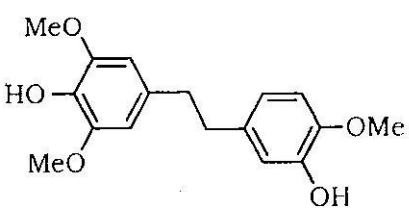
(d) (i) (1) How mass spectral analysis can be used to distinguish the structural isomers ? Explain with the help of suitable examples.

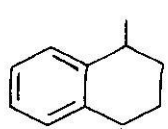
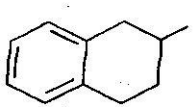
(2) Prove that in the benzylic system the mass spectral fragmentation is not straight forward rather it passes through stable tropyliumcation intermediate.

(3) Differentiate the following compounds with the help of mass spectroscopy :

(i) 

and

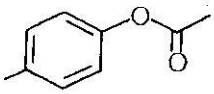


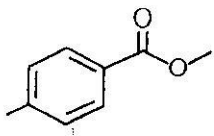
(ii)  and 

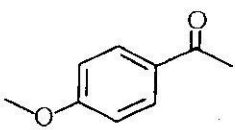
(ii) The structure of the compound which displays the following spectral data is

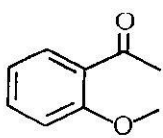
IR 1690, 1100 cm^{-1}

^1H NMR : δ 7.8 (d, J = 8 Hz, 2H), 6.9 (d, J = 8 Hz, 2H), 3.8 (s, 3H), 2.8 (s, 3H).

(1) 

(2) 

(3) 

(4) 

^{13}C NMR : δ 197, 165, 130, 129, 114, 56, 26.

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