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L—12—2019

FACULTY OF SCIENCE

M.Sc. (Third Semester) EXAMINATION

MARCH/APRIL, 2019

(CBCS Pattern)

CHEMISTRY

Paper (CH-531)

(Advanced Spectroscopic Methods)

(Monday, 22-4-2019)   **Time : 2.00 p.m. to 5.00 p.m.**

Time—3 Hours   *Maximum Marks—75*

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

(ii) Figures to the right indicate full marks.

(iii) Multiple Choice Questions (MCQ) should be attempted only once on page number three of answer-book with complete answer.

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

(a) The $>C=O$ stretching frequency in *p*-nitroacetophenone is higher than in *p*-methoxy acetophenone.

(b) Use of deuterium exchange and deuterium labelling in PMR specroscopy.

(c) In case of carbonyl compounds, the $\pi \to \pi^*$ transition undergoes barthochromic shift in high polar solvent but $n \to \pi^*$ transition undergoes hypsochromic shift under same condition.

(d) An organic compound with M.F.$C_5H_{11}O$ displays the following CMR spectral data :

$$\delta : 18(q), 27.3(q), 42(d), 21.1(s)$$

Assign structure to the compound.

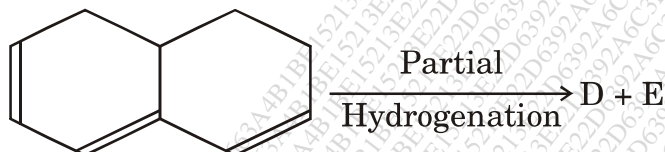(e) Calculate the fundamental modes of vibrations in the following :

(i) N_2O

(ii) BCl_4^-

P.T.O.

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

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

$$\xrightarrow[\text{Hydrogenation}]{\text{Partial}} D + E$$

(b) Dimethyl glyoxime is a bidented ligand it form more stable complex with metal Nickel (II) ion. What will be the force constant for the Ni-N bond in Nickel with dimethyl glyoxime complex ?
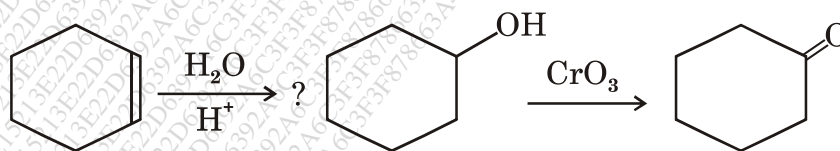
Given : Fundamental vibrational frequency of $Ni(DMG)_2$ complex is 550 cm^{-1} :

At. weight of Ni = 58.71

At. weight of N = 14

Avogadro number = 6.02×10^{23}.

(c) How will you follow the following sequence of reaction by using IR :

$$\xrightarrow[\text{H}^+]{\text{H}_2\text{O}} ? \qquad \xrightarrow{\text{CrO}_3}$$

(d) What do you understand by metastable ion ? Explain the importance of the ions in mass spectroscopy.

(e) Deduce the structure of a compound using NMR spectral data :

M.F = C_8H_7OCl

δ : 4.25 (s, 6 mm)

7.4 − 7.9 (m, 15 mm)

3. Solve the following :

(a) Deduce the structure of compound based on the following data : 8

Molecular formula : $C_{10}H_{15}N$

IR(cm^{-1}) : 3350 (broad), 1600

MS(m/z) : 149, 134, 91 (base peak)

PMR(δ) : 1.1 (6H, d, J = 7 Hz)

1.5 (1H, bs, exchange with D_2O)
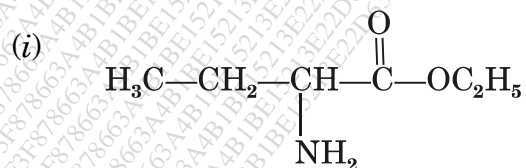
2.75(1H, septet, J = 7 Hz)

3.7(2H, s), 7.25 (5H, s)

Or

An organic compound with molecular formula $C_{10}H_{11}NO_2$ shows the following spectral data. Assign the structure and justify the spectral data :

PMR : δ 3.6 (s, 8 mm), 3.8(s, 24 mm) 6.4(m, 12 mm)

CMR : δ 162(s), 131(s), 118(s), 108(d), 100(d), 58(q), 22(t).

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

(i)

$$H_3C-CH_2-CH(-NH_2)-\overset{\overset{\displaystyle O}{||}}{C}-OC_2H_5$$
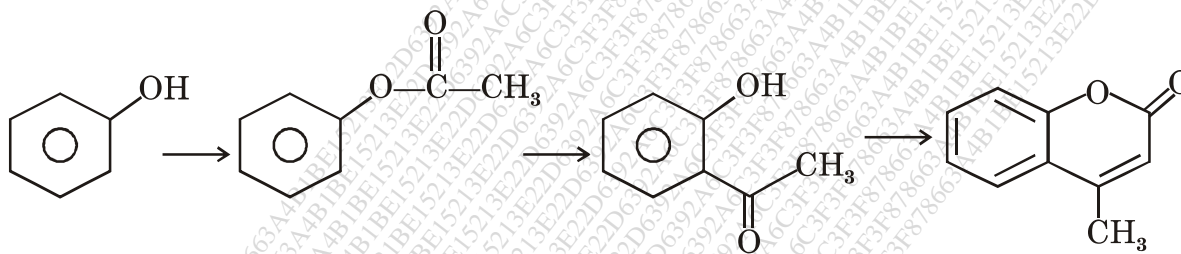
m/z : 30, 31, 58, 74, 102.

P.T.O.

(ii)
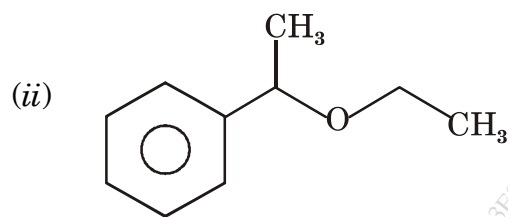
m/z : 77, 79, 105, 106, 135, 130.

Or

How will you follow the course of the following reaction by IR ?

4. Solve the following : 15

(a) An organic compound with the following spectral data :

C = 36.9%, H = 5.67%, Br = 41.0%

IR = 1735, 1250 cm^{-1}.

^{1}H NMR : 4.1 (2H, q, J = 7.5 Hz)
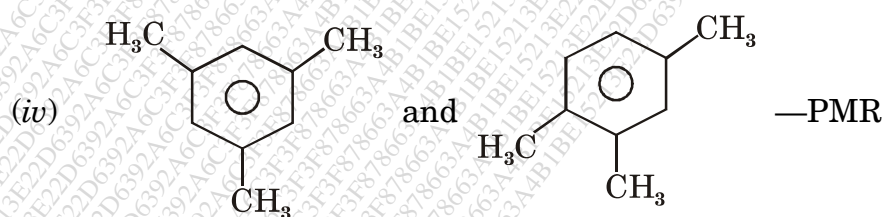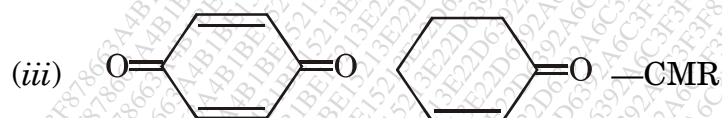
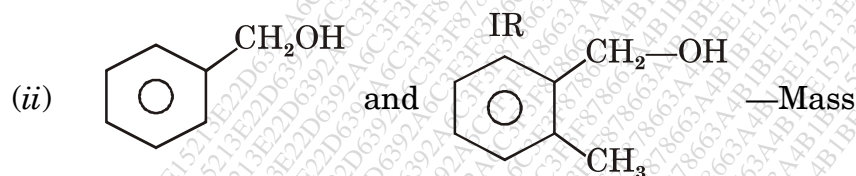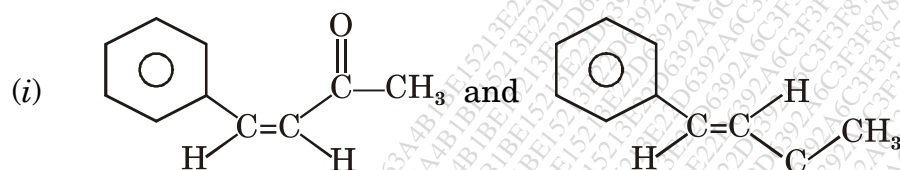3.8(2H, t, J = 7 Hz)

1.8(2H, M), 1.25 (3H, t, J = 7.5 Hz)

2.4(2H, t, J = 7.2 Hz)

Mass (m/z) : 194 (M$^+$), 196 (m^{+z})

Deduce structure.

Or

Distinguish between the following pairs by using indicated spectral method :

(i)

 and

(ii)

 and —IR —Mass

(iii)

  —CMR

(iv)

 and —PMR

(b) Calculate λ_{max} for the following compound by A.I. Scott rules :
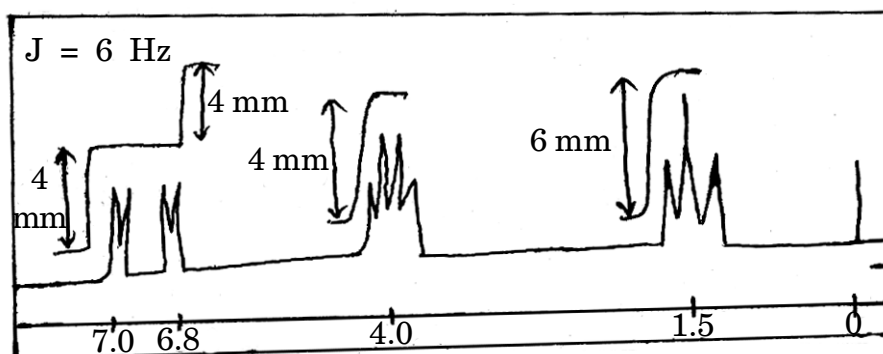
 and
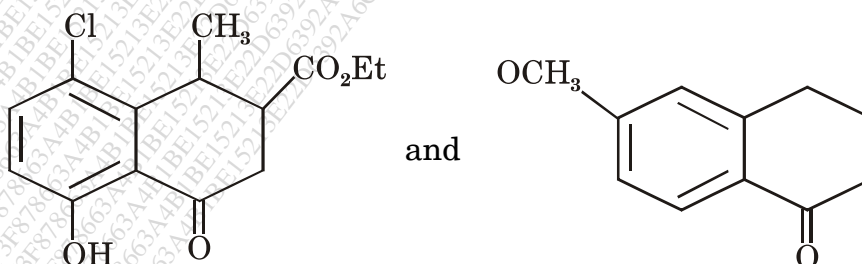
P.T.O.

Or

A compound having M.F C_8H_9OBr shows the following NMR spectrum. Deduce its structure :

5. (A) Select the *correct* answer from the following multiple choice questions and rewrite the complete answer : 5

    (i) Diene or conjugated polyene in UV spectrum displays :

        (a) R-Band   (b) K-Band

        (c) B-Band   (d) E-Band

    (ii) How many fundamental vibrations are epected with CO_2 ?

        (a) one   (b) two

        (c) three   (d) five

    (iii) Which one is the correct basic value of λ_{max} for homoannular diene ?

        (a) 214 nm   (b) 253 nm

        (c) 217 nm   (d) 215 nm

    (iv) Gyromagnetic ratio in ^{13}CNMR spectroscopy is :

        (a) 26753 radian guess S^{-1}

        (b) 6728 radian guess S^{-1}

        (c) 9850 radian guess S^{-1}

        (d) 4980 radian guess S^{-1}

(v) The presence of chlorine and bromine can be easily detected by :

(a) UV   (b) CMR

(c) IR   (d) Mass

(B) Write short notes on (any *two*) :   10

(a) Spin-spin coupling in PMR.

(b) Stretching and bending vibrations in IR.

(c) MacLafferty rearrangement.

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