

This question paper contains 7 printed pages]

**AG—12—2018**

**FACULTY OF SCIENCE**

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

**NOVEMBER/DECEMBER, 2018**

**(CBCS Pattern)**

**CHEMISTRY**

**Paper CH-531**

**(Advanced Spectroscopic Methods)**

**(Monday, 26-11-2018)**

**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 the answer book with complete answer.*

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

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

(b) CO<sub>2</sub> has zero dipole moment, but its IR is active. Explain.

(c) The UV spectrum of ethene shows absorption at 171 nm but butadiene shows absorption at 217 nm. Explain.

(d) How acetophenone, phenol and benzoic acid can be distinguished by the characteristic band in their IR-spectra ?

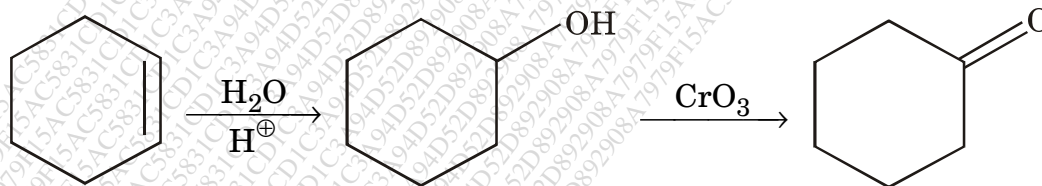
(e) Enumerate in brief principles of <sup>13</sup>C-NMR spectroscopy.

P.T.O.

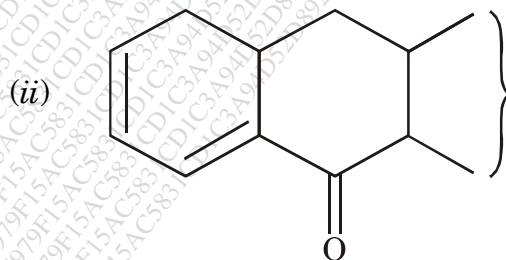
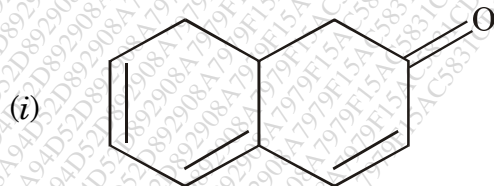
2. Attempt any *three* of the following :

15

- (a) How can we distinguish between 3-methyl cyclohexene and 4-methyl cyclohexene on the basis of mass spectroscopy ?
- (b) An organic compound with M.F.  $C_7H_{14}O$ , displays the following  $^1H$ -NMR data :
- $\delta$  : 1.05(*d*, 12 H,  $J = 7$  Hz)
- $\delta$  : 2.7(septet, 2 H,  $J = 7$  Hz).
- (c) What will be force constant for the band in  $N_2$ , if fundamental vibrational frequency is  $7 \times 10^{13} \text{ s}^{-1}$  ? (Given :  $N = 14.007$ )
- (d) How will you follow the following sequence of reaction by using IR ?



- (e) Calculate the value of absorption maxima ( $\lambda_{max}$ ) for the following :



3. Attempt any *two* of the following :

15

(a) An organic compound of molecular formula  $C_9H_8O$  exhibits the following spectral data. Identify the structure and justify your answer :

8

PMR :  $\delta$  : 6.7(*dd*, 1 H,  $J = 16$  Hz & 8 Hz)

$\delta$  : 7.1-7.4(*m*, 5 H)

$\delta$  : 7.6(*d*, 1 H,  $J = 8$  Hz)

$\delta$  : 10.0(*d*, 1 H,  $J = 8$  Hz)

$^{13}C$ -NMR : 128(*d*), 129(*d*), 131(*d*), 134(*s*), 152(*d*), 160(*d*), 195(*d*).

Or

A compound with MF  $C_{10}H_{12}O$  displays the following spectral data :

8

IR : 1690, 1600, 1580, 1490, 770, 690  $cm^{-1}$

PMR :  $\delta$  : 1.3(*d*, 6 H)

$\delta$  : 5.3(*septet*, 1 H)

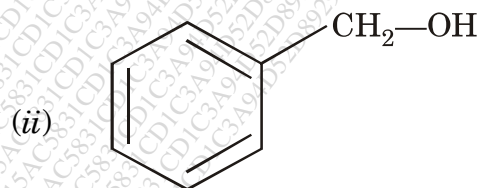
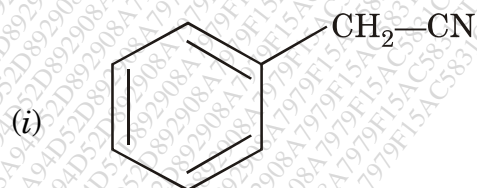
$\delta$  : 7.3-7.7(*m*, 5 H)

$^{13}C$ -NMR : ( $\delta_{ppm}$ )

22(*q*), 68(*d*), 128(*d*), 129(*d*), 131(*s*), 135(*d*), 175(*s*).

(b) Explain the genesis of the ions :

7

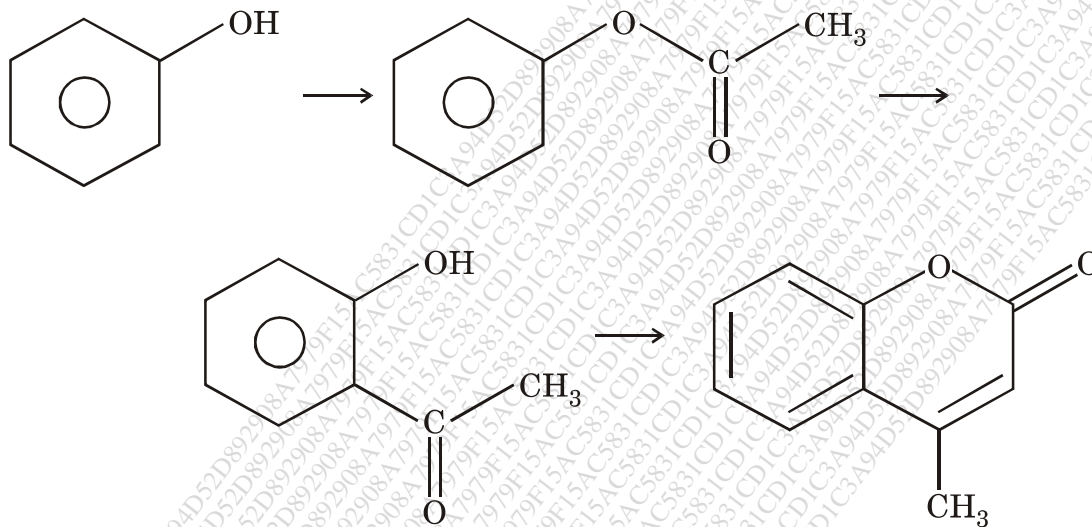


P.T.O.

Or

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

7



4. Attempt any *two* of the following : 15

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

Molecular Formula : C<sub>11</sub>H<sub>11</sub>N

UV : 272 nm (ε 1800)

IR : 2212, 1604, 845, 814 cm<sup>-1</sup>

PMR (δ) : 1.03(3 H, *t*, J = 7 Hz)

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

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

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

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

7.72(1 H, *d*, J = 16 Hz)



Or

A compound with M.F.  $C_6H_5NO$  displays the following spectral data :

UV : 265 nm

IR : 2720, 1710, 1600, 1500, 850  $cm^{-1}$

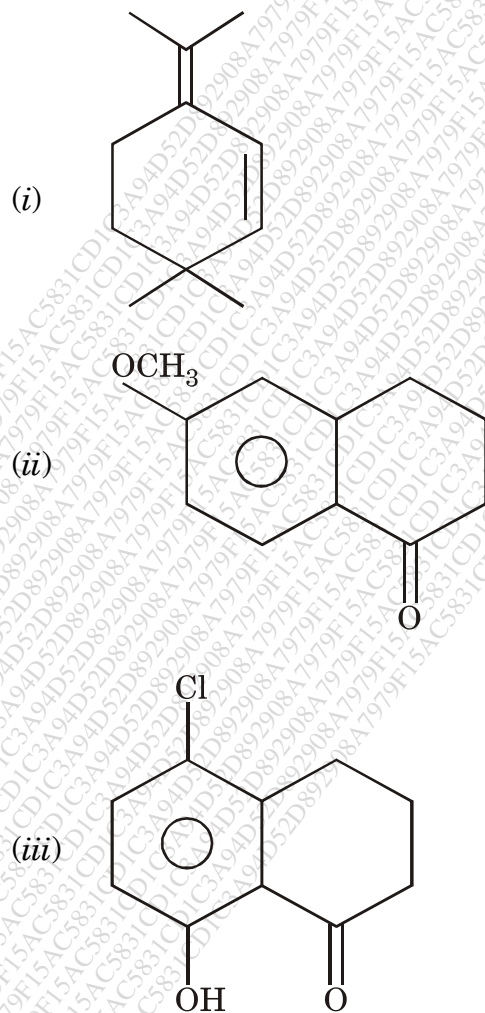
PMR :  $\delta$  : 7.24(d, 10 mm)

$\delta$  : 8.70(d, 10 mm)

$\delta$  : 10.40(s, 5 mm)

Assign the structure to the compound.

(b) Calculate  $\lambda_{max}$  for the following compounds by A.I. Scott rules : 7

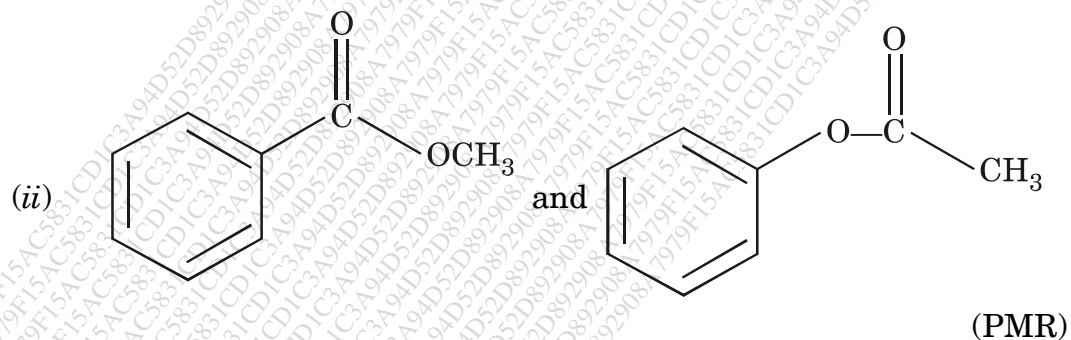
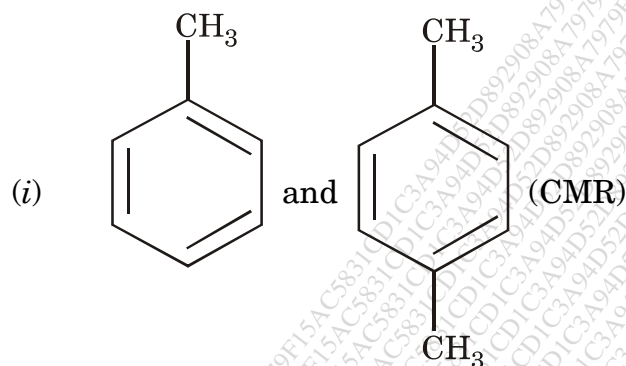


P.T.O.

Or

Distinguish between the following pairs by using indicated spectral method :

7



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

5

(i) Base peak in mass is obtained due to :

- (a) Less stable ion
- (b) Most stable ion
- (c) Metastable ion
- (d) None of the above

(ii) How many fundamental vibrations are expected with  $\text{SO}_2$  molecules ?

- (a) 5
- (b) 2
- (c) 3
- (d) 1

- (iii) Electromagnetic radiation used in  $^1\text{H}$  NMR spectroscopy :
- (a) Radio
  - (b) IR
  - (c) Microwave
  - (d) None of the above
- (iv) In the  $\alpha$ -cleavage of acetone the  $m/z$  ratio is :
- (a) 35
  - (b) 43
  - (c) 20
  - (d) 45
- (v) Which one of the following is the correct basic value of  $\lambda_{\text{max}}$  for homoannular diene ?
- (a) 214 nm
  - (b) 215 nm
  - (c) 217 nm
  - (d) 253 nm
- (B) Write short notes on any *two* :
- (i) Spin-spin coupling in PMR
  - (ii) MacLafferty rearrangement
  - (iii) Solvent effect in UV spectroscopy.

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