

This question paper contains 8 printed pages]

**BR—17—2016**

**FACULTY OF SCIENCE**

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

**MARCH/APRIL, 2016**

**(CBCS Course)**

**CHEMISTRY**

**Paper CH-531**

**(Advanced Spectroscopic Methods)**

**(Wednesday, 16-11-2016)**

**Time : 2.00 p.m. to 5.00 p.m.**

*Time—Three Hours*

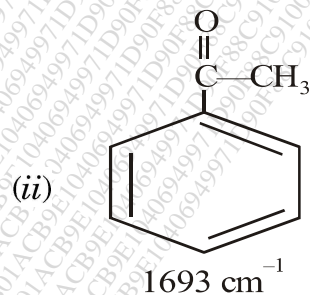
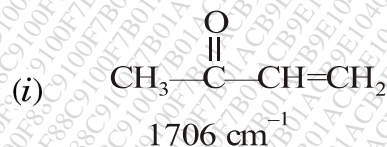
*Maximum Marks—75*

- 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.

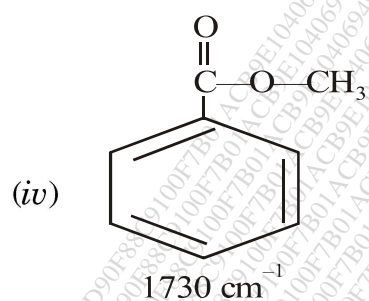
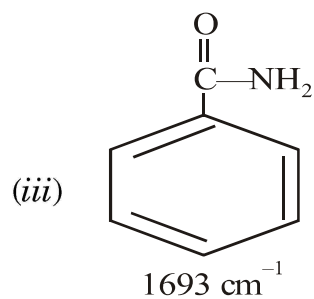
1. Attempt any *three* of the following : 15

(a) Explain acetyl acetone absorption in  $\text{H}_2\text{O}$   $\lambda_{\text{max}}$  274 and in isoctane  $\lambda_{\text{max}}$  272 nm.

(b) Discuss the  $\text{C}=\text{O}$  stretching frequencies of the following compounds :



P.T.O.



(c) Explain the role of vibrational motions and energy and dipole moment in vibrational spectroscopy.

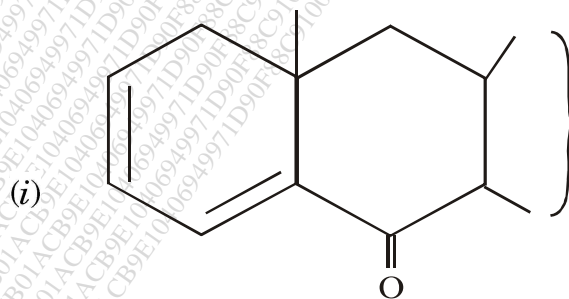
(d) TMS is used as internal standard for PMR spectrometry.

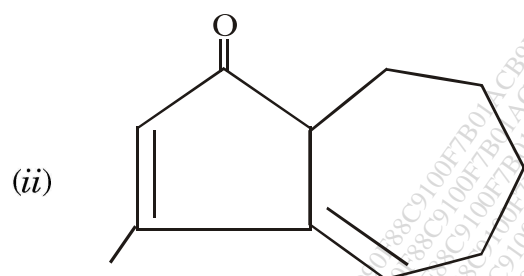
(e) Use of mas spectrometry in identification of halogens in organic compounds.

2. Attempt any *three* of the following :

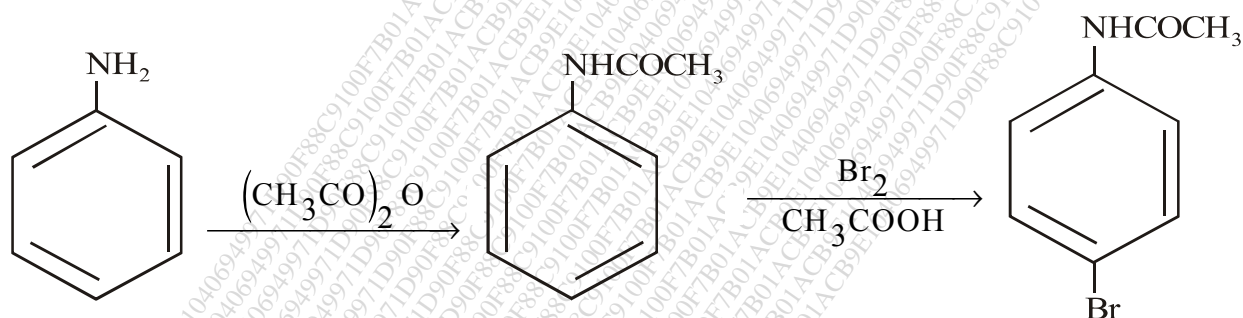
15

(a) Calculate the value of absorption maxima for the following :





- (b) How will you follow the following sequence of the reaction by using IR spectroscopy ?



- (c) Calculate the force constant in  $\text{Nm}^{-1}$  of  $^{35}\text{Cl}_2$ .

Given : Fundamental vibration frequency of  $^{35}\text{Cl}_2$  is  $564.9 \text{ cm}^{-1}$ .

At. weight of Cl = 35

Avogadro's No. =  $6.022 \times 10^{23}$  grams

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

Molecular formula :  $\text{C}_8\text{H}_7\text{OCl}$

$\delta$  : 4.25 (s, 6 mm)

7.4 – 7.9 (m, 15 mm).

- (e) Explain the metastable ion peak and its application in determination structure of organic compounds.

P.T.O.

3. Solve the following :

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

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

7.1 – 7.4 (m, 5 H),

7.6 (d, 1 H  $J = 8$  Hz)

10.0 (d, 1 H  $J = 8$  Hz)

$C^{13}$  NMR : 128(d), 129(d), 131(d), 134(S), 152(d), 160(d), 195(d). 8

Or

Deduce the structure of the compound from the following spectral data : 8

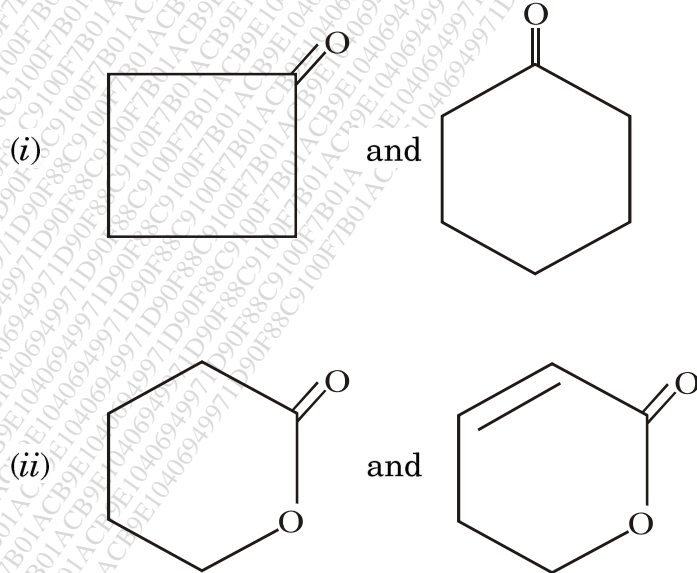
M.F.  $C_{10}H_{12}O_2$

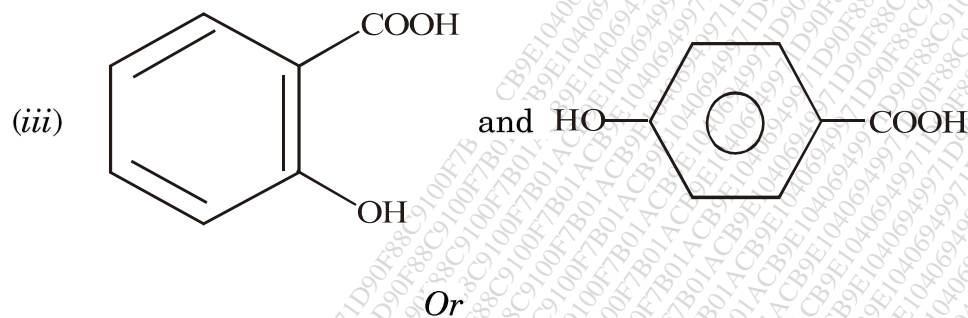
IR : 3050, 1730, 1600, 1570, 1460, 770, 700  $cm^{-1}$ .

$^1H$ -NMR : 7.3(S, 5H), 4.30(t, 2H)  $J = 7$  Hz, 2.00(S, 3H), 2.93(t, 2H)  $J = 7$  Hz.

Mass :  $m/z = 65, 91, 149, 164$ .

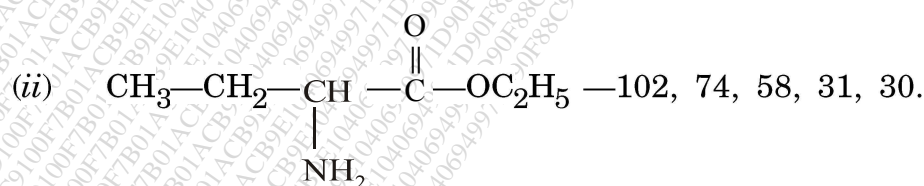
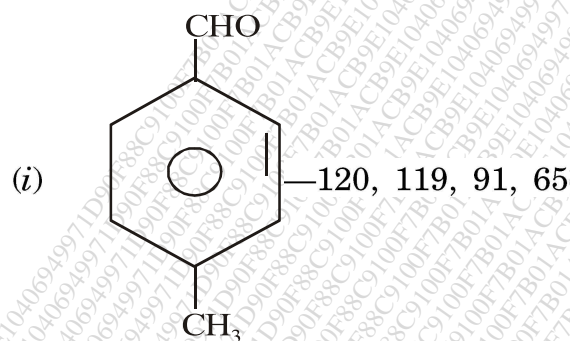
(b) How will you distinguish between the following pairs on the basis of IR spectroscopy ? 7





Explain the genesis of the ions in mass spectra :

7



4. Solve the following :

(a) A compound with MF  $\text{C}_{16}\text{H}_{22}\text{O}_4$ .

8

IR : 2900(S), 1720(S), 1250, 1120, 740(m).

PMR :  $\delta$  : 1.0(d, 6H), 2.0(m, 1H)

4.1(d, 2H), 7–7.5(m, 4H)

$^{13}\text{C}$ —NMR : 21.63(q) 28.46(d), 69.63(t), 131.7(s), 130(d), 133(d), 170(s).

P.T.O.

WT

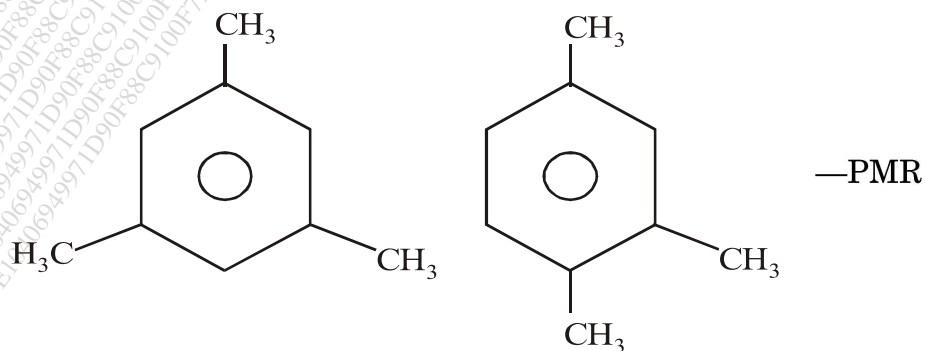
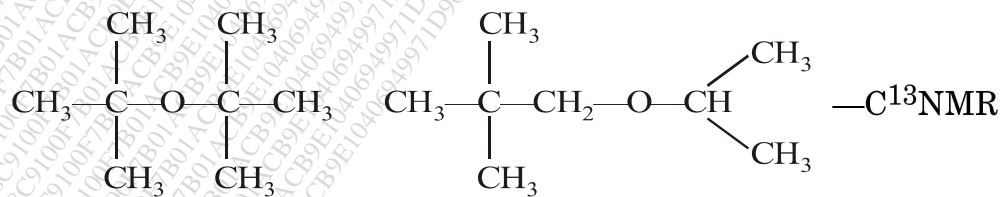
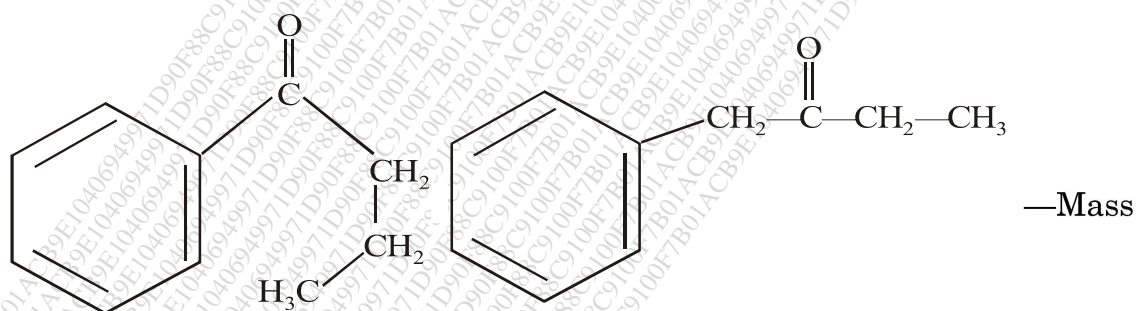
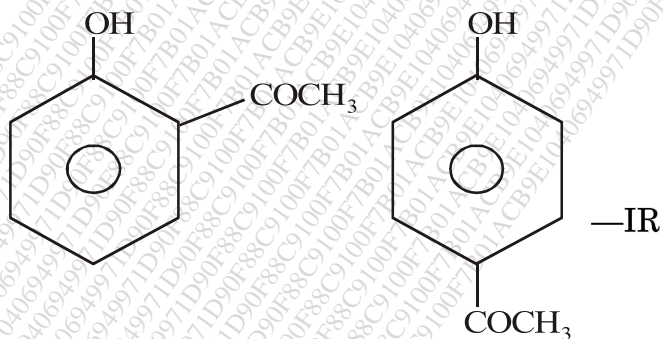
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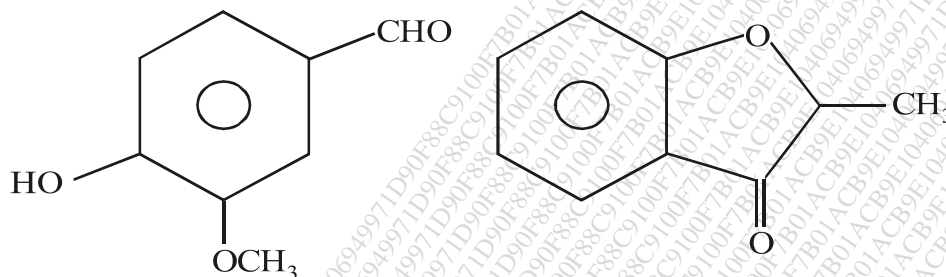
Or

Distinguish between the following pairs by using the indicated spectral method :

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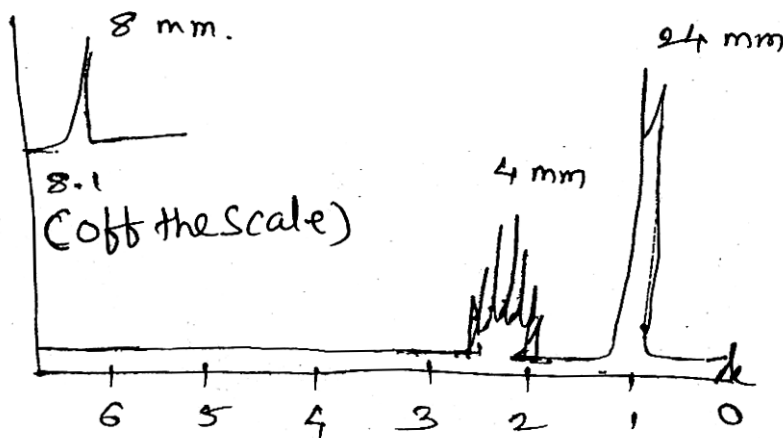


- (b) Calculate  $\lambda_{\max}$  for the following compound by A.I. Scott rules. 7



Or

A compound C<sub>4</sub>H<sub>9</sub>NO shows the following PMR spectra deduce its structure. 7



5. (A) Select the *correct* answer from the following Multiple Choice Questions and rewrite complete answer : 5

(i) Which of the following correct basic value of heteroannular diene ?

- (a) 210 (b) 215  
(c) 230 (d) 253

P.T.O.

- (ii) In IR spectrum a medium band appears at  $2720\text{ cm}^{-1}$  is a good evidence for the presence of .....
- (a) Ester (b) Keto  
(c) Ether (d) Aldehyde
- (iii) Number of modes of vibration of trans  $\text{N}_2\text{F}_2$  are .....
- (a) 4 (b) 5  
(c) 6 (d) 7
- (iv) The ' $\delta$ ' scale of  $^{13}\text{C}$ -NMR is .....
- (a) 0—220 ppm (b) 0—20 ppm  
(c) 0—110 ppm (d) 0—10 ppm
- (v) Presence of M+ and M+2 peaks in mass spectrum is 1 : 1 intensity, which indicate presence of halogen atom is .....
- (a) Cl (b) Br  
(c) I (d) F

(B) Write short notes on any two :

10

- (a) Shielding and deshielding effect in PMR  
(b) McLafferty Rearrangement  
(c) Types of electronic transitions in UV spectroscopy.