No. of Printed Pages: 4 + 6

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**SARDAR PATEL UNIVERSITY**
**M.Sc, Semester – IV (Organic Chemistry) Examination**
**Thursday, 29th November 2012**

**PS04CORC01: Spectroscopy-II**

**Time: 10:30 am to 01:30 pm** **Total Marks: 70**

**Note: Right hand figures indicate marks.**

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**Q. 1** Select the correct answer in the following. **08**

1. In IR, the C-H stretching absorption of alkyne is observed at

   a. ~2150 $cm^{-1}$
   b. ~3300$cm^{-1}$
   c. ~1000$cm^{-1}$
   d. ~1300$cm^{-1}$

2. In UV spectra the $n \longrightarrow \sigma^*$ transition is shown by

   a. Ketones
   b. Alkanes
   c. Alcohols
   d. Olefins

3. In the instrument with 1.4 Tesla magnetic field the proton will resonate at

   a. 60 MHz
   b. 90 MHz
   c. 100 MHz
   d. 300 MHz

4. In the PMR spectrum, mesitylene(1,3,5-trimethyl benzene) will give

   a. 2 signals
   b. 3 signals
   c. 4 signalls
   d. 6 signals

5. In $^{13}C$ NMR, phenanthrene will give

   a. 14 signals
   b. 6 signals
   c. 5 signals
   d. 7 signals

6. The solvent $CDCl_3$ in $^{13}C$ NMR spectrum will give

   a. a doublet at 100 δ
   b. a triplet at 77 δ
   c. a singlet at 180 δ
   d. a singlet at 40 δ

7. In mass spectra, the metastable ion peak is observed

   a. as diffused peak at non integral m/z value
   b. at heighest m/z value
   c. as two lines with equal intensity
   d. at M-15 position

8. In HETCOR spectra, the connectivity observed between $^{1}H$ and $^{13}C$ is

a. $^{2}J$
b. $^{3}J$
c. $^{2}J$ and $^{3}J$
d. $^{1}J$

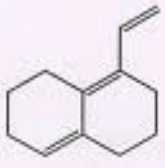
**Q. 2** Answer the following **(Any Seven)**. **14**

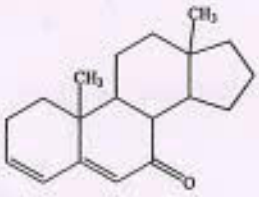
1. Explain Fermi resonance observed in IR spectroscopy.
2. With suitable example explain the terms chromophores and auxochromes.
3. The symmetrical stretching vibration in $H_2O$ is IR active whereas the same is inactive in $CO_2$. Explain.
4. Sketch the expected PMR spectrum for ethyl acetate by taking approximate δ value for each signal.
5. Assign the spin systems (Pople notations) for 1-nitropropane and p-chloro nitrobenzene.
6. How will you differentiate o-, m- and p- xylenes on the basis of proton decoupled $^{13}C$ NMR spectra.
7. Write the important characteristic properties of DEPT-90 and DEPT-135 spectra.
8. With suitable example explain Mclafferty rearrangement observed in mass spectroscopy.
9. Sketch the $^{1}H$-$^{1}H$ COSY spectrum for ethyl benzene by taking approximate δ value for each signal.

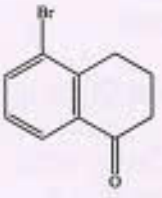
**Q. 3** **A.** Answer the following. **06**

**(i)** State and explain the Beer-Lambert law.
**(ii)** Discuss in detail the characteristic IR absorptions in aldehydes and esters.

**B.** Calculate $\lambda_{max}$ for the following molecules. **06**

(i) 

(ii) 


(iii) 


**OR**

**B.** Answer the following. **06**

(i) How can you differentiate o-hydroxy acetophenone and p-hydroxy acetophenone on the basis of their IR sprctra?
(ii) In IR, s-trans benzal acetone absorbs at 1674 $cm^{-1}$ while s-cis benzal acetone absorbs at 1699 $cm^{-1}$. Explain.
(iii) Draw the relative energy level diagram for the following electronic transitions.
$\pi \rightarrow \pi^*$, $\sigma \rightarrow \sigma^*$, $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$

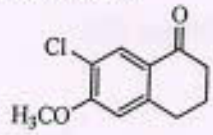
**Q. 4 A.** **(i)** What is coupling constant in PMR? Explain vicinal and germinal couplings in detail. **03**

**(ii)** List the important methods for the simplifications of PMR spectra. Discuss the use of shift reagents in detail. **03**

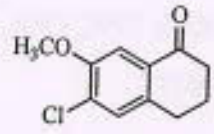
**B.** **(i)** A compound with molecular formula $C_6H_{12}O_2$ shows the following signals in PMR spectrum. Assign the structure. **03**

| Signal position(δ) | Multiplicity | Protons |
|---|---|---|
| 0.9 | Doublet | 6H |
| 1.9 | Multiplet | 1H |
| 2.1 | Singlet | 3H |
| 3.85 | Doublet | 2H |

**(ii)** What is nuclear overhauser effect? How will you distinguish following compounds using NOE-PMR spectra? **03**




(i)




(ii)

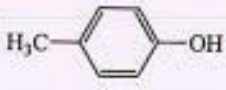
**OR**

**B.** **(i)** Sketch the expected PMR spectrum for 3-methyl-2-pentanone by taking approximate δ value for each signal. **03**

**(ii)** What is chemical shift equivalent? Dimethylformamide, in its PMR spectrum shows two separate signals for two methyl groups at room temperature but it shows only one signal for two methyl groups at 123 °C. Explain. **03**

**Q. 5 A.** Do the $^{13}C$ NMR chemical shift calculations for the following molecules. **06**

**(i)** $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2$

**(ii)** 


**(iii)** $CH_3\text{-}CH_2\text{-}CH_2\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$

**B.** **(i)** Sketch the proton coupled and proton decoupled $^{13}C$ NMR spectra for p-methoxy benzaldehyde by taking approximate chemical shift value for each signal. **03**

**(ii)** Indicate the position and multiplicity of the signals for the following solvents in $^{13}C$ NMR. **03**

**(a)** Acetone-$d_6$ **(b)** DMSO-$d_6$ **(c)** Benzene-$d_6$

**OR**

**B. (i)** A bicyclic hydrocarbon with molecular formula $C_8H_{14}$ shows only two peaks in proton decoupled $^{13}C$ spectrum. The DEPT spectra indicated that those signals are for CH and $CH_2$. Assign the structure to the compound. **03**

**(ii)** Sketch the $^{1}H$-$^{13}C$ HETCOR spectrum for 2-butanol by taking approximate δ value for each signal. **03**

**Q. 6 A.** Do the mass fragmentation for the following molecules. **06**
(a) 2-methyl-2-pentanol (b) 2-pentanone (c) 3-pentanone

**B. (i)** Discuss FAB and MALDI techniques used in mass spectroscopy. **03**

**(ii)** What is metastable ion peak in mass spectroscopy? A parent ion with mass 91, results a daughter ion of mass 65, calculate the position of the meta stable ion peak. **03**

**OR**

**B.** A compound has molecular formula $C_{10}H_{12}O_2$. It gives the following spectral analysis. Interpret the spectral data and assign the structure to the compound. **06**

**IR ($cm^{-1}$) :** 1711, 3000, 2950, 1500, 1600 and 820.

**PMR :**

| δ | Multiplicity | No. of protons |
|---|---|---|
| 2.1 | Singlet | 3H |
| 3.6 | Singlet | 2H |
| 3.8 | Singlet | 3H |
| 6.9 | Doublet | 2H |
| 7.1 | Doublet | 2H |

**$^{13}C$ NMR :**

| $^{13}C$ (δ) | DEPT-90 | DEPT-135 |
|---|---|---|
| 30.0 | - | positive |
| 50.0 | - | Negative |
| 55.0 | - | positive |
| 114.0 | positive | positive |
| 127.0 | - | - |
| 130.0 | positive | positive |
| 159.0 | - | - |
| 207.0 | - | - |

**Mass:**

**m/e :** 164($M^+$), 149, 133, 121, 107, 43

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