



**MAK-003-001506**

Seat No. \_\_\_\_\_

**B. Sc. (Sem. V) (CBCS) Examination**

**October / November – 2016**

**Chemistry - 502**

*(Organic Chemistry and Spectroscopy)*

*[New Course]*

**Faculty Code : 003**


**Subject Code : 001506**

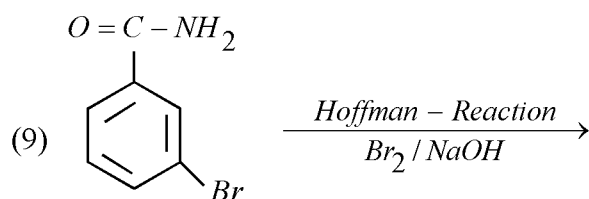
Time :  $2\frac{1}{2}$  Hours]

[Total Marks : 70

- Instructions :**
- (i) All questions are **compulsory**.
  - (ii) All questions of Q. no. 1 carry 1 mark each.
  - (iii) Question no. 2 and 3 carry 25 marks each.

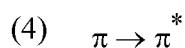
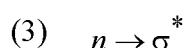
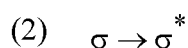
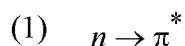
**1** Give correct answers of following questions in short : **20**

- (1) Write the structure of Glucosazone.
- (2) Give reaction for n-octane from coniine.
- (3) Give single reaction of catachol from veratric acid.
- (4) Diphenyl amine +  $2S \xrightarrow{I_2}$  \_\_\_\_\_
- (5)   $MgBr + PCl_3 \longrightarrow$  \_\_\_\_\_
- (6) 2-chloro ethanol + Thiourea  $\rightarrow$  \_\_\_\_\_
- (7) What is polysaccharides ? Explain with example.
- (8) Maltose +  $2H_2O \xrightarrow{H^+} A + B$  \_\_\_\_\_



(10) Write the structure of Tartaric acid.

(11) Answer the following transitions in their decreasing order of energy :



(12) Define frequency and give value of velocity of light.

(13) Write the expected infrared peaks for methyl ester.

(14) Give the range of IR region in both units  $\text{cm}^{-1}$  and  $\text{wn}$ .

(15) When molecule is rotated  $810^\circ$ , it gives equivalent orientation find out value of  $k$  and  $n$  in  $C_n^k$ .

(16) Define Inversion centre  $i$  in symmetry.

(17) Give possible transitions in benzene in U.V. Spectra.

(18) In  $-\text{CHO}$  group  $-\text{C}-\text{H}$ , stretching vibration is observed at \_\_\_\_\_  $\text{cm}^{-1}$ .

(19) Which material is used for prism in IR Spectra ?

(20) In IR spectra Nujol is useful for only range of \_\_\_\_\_  $\mu$  to \_\_\_\_\_  $\mu$  (micron).

2 (a) Answer any **three** of the following :

6

(1) Explain reaction of Fructose with HCN

(2) Give synthesis of Dulcin.

(3) Give synthesis of Thiazine

(4) Give one reaction for each for the synthesis of Lithium aluminium hydride and sodamine.

(5) Explain reaction of Glucose with  $\text{H}_2\text{NOH}$ .

(6) Give reaction of Orange - II from sulphanilic acid.

- (b) Answer any **three** of the following : 9
- (1) Give synthesis of Ibuprofen.
  - (2) Give synthesis of Pyrazole
  - (3) Give conversion of D(-) Fructose from D(-) Arabinose.
  - (4) Give synthesis of Saccharin from Anthranilic acid
  - (5) Give synthesis of Dioxane.
  - (6) Give synthesis and uses of Alizarin.
- (c) Give answers briefly : (any **two**) 10
- (1) Explain Fries Rearrangement.
  - (2) Explain determination of ring size of glucose by methylation method.
  - (3) Give any one method for the synthesis of Nicotine.
  - (4) Explain step-up reaction :  
Kilani and Swodan method
  - (5) Prove the constitution of Coniine
- 3 (a) Answr any **three** of the following : 6
- (1) Explain proper rotational axis.
  - (2) For  $\text{NH}_3$  molecule, prove that  $C_3 \times \sigma_a \neq \sigma_{ra} \times C_3$ .
  - (3) What is chromophore; give two examples.
  - (4) Calculate theoretical number of vibrational degree of freedom in HCN and  $\text{C}_6\text{H}_5\text{CH}_3$ .
  - (5) Which solvent is used as mulling agent in infrared spectra ?  
Give its useful range.
  - (6) UV-spectra of Aniline in acidic solution is similar to benzene; explain.
- (b) Answer any **three** : 9
- (1) Explain  $C_1$ ,  $C_2$  and  $C_3$  point group with example.
  - (2) Find out point group of 1,3 and 1,4 dichlorobenzene and explain why different point groups are obtained.
  - (3) Explain Bathochromic and Hypsochromic shift in UV spectra.
  - (4) Explain Finger print region in IR spectra.

- (5) Calculate stretching frequency of (C–O) bond for IR spectra (where  $K=5 \times 10^5$  dyn/cm)
- (6) Distinguish the following compounds :  
Phenyl acetic acid and p-tolueic acid by IR spectra.

(c) Answer any **two** (briefly) : 10

- (1) Prove that in staggered ethane

$$S_n^n = E \text{ where } n \text{ is even number.}$$

- (2) Give symmetry point groups of following molecules with figure and symmetry elements :

- (i) Eclipsed Ferrocene
- (ii)  $\text{XeOF}_4$
- (iii) 1,3,5 Trichlorobenzene
- (iv) Glyoxal
- (v) 9-chloro Anthracene

- (3) Assign the structure to a compound having following characteristics.

Molecular formula =  $\text{C}_8\text{H}_4\text{O}_3$

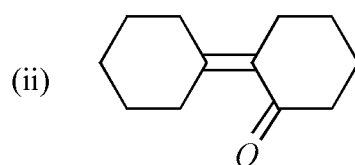
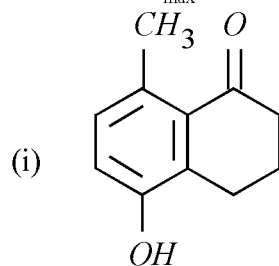
I.R. data : 3020 (m), 1860 (m), 1710 (m), 1600 (m), 1580 (m), 1210, 1060 (m),  $750 \text{ cm}^{-1}$ .

- (4) Assign the structure to a compound having following data :

M.F. =  $\text{C}_8\text{H}_8\text{O}_2$

I.R. data =  $3035, 2980 \text{ cm}^{-1}, 2750$  and  $2680 \text{ cm}^{-1}, 1690, 1580, 1550 \text{ cm}^{-1}, 1220, 830 \text{ cm}^{-1}$ .

- (5) Calculate  $\lambda_{\text{max}}$  for the following :



### Spectral Data

U.V. :

Empirical rules for Dienes :

(A) Homoannular    (b) Heteroannular  
 $\lambda = 253 \text{ nm.}$          $\lambda = 215 \text{ nm.}$

|  |        |        |
|--|--------|--------|
| Increments for double bond extending conjugation | 30 nm. | 30 nm. |
| Exocyclic double bond                            | 5      | 5      |
| Alkyl substitution or ring residue               | 5      | 5      |
| Homocyclic Diene components                      | 39     | 39     |
| Polar groups :                                   |        |        |
| - COCH <sub>3</sub>                              | 0      | 0      |
| - OR   | 6      | 6      |
| - Cl, -Br  | 5      | 5      |
| - NR <sub>2</sub>                                | 60     | 60     |

(C) Simple Diene :

Parent  $\lambda = 217 \text{ nm.}$

Polar groups :

|                              |      |
|------------------------------|------|
| Alkyl subst for ring residue | 5 nm |
| - Cl, -Br                    | 17   |
| -OH                          | 5    |
| -OR                          | 5    |
| -NR <sub>2</sub>             | 60   |
| -SR                          | 30   |

(D) Empirical Rules for Enones and Dienones :

|                                   |                       |
|-----------------------------------|-----------------------|
| (a) Z = C                         | $\lambda$             |
| (1) 6 membered ring or acyclic    | 215                   |
| (2) 5 membered ring               | 202                   |
| (b) Z = H                         | 207                   |
| (c) Z = OH or OR                  | 193                   |
| (d) Acyclic dienone               | 245                   |
| Increment for :                   |                       |
| Double bond extending conjugation | 30                    |
| Alkyl group of ring residue       | $\alpha$ 10           |
|                                   | $\beta$ 12            |
|                                   | $\gamma$ or higher 18 |
| Exocyclic double bond position    | 5                     |
| Homocyclic diene component        | 39                    |

| Polar groups        | $\alpha$ | $\beta$ | $\gamma$ | $\delta$ other |
|---------------------|----------|---------|----------|----------------|
| -Cl                 | 15       | 12      | .        | .              |
| -OH                 | 35       | 30      | 50       | 50             |
| -OR                 | 35       | 30      | 17       | 31             |
| -NR <sub>2</sub>    | .        | 93      | .        | .              |
| -O                  | .        | 75      | .        | .              |
| -NHCOR              | .        | 95      | .        | .              |
| -OCOCH <sub>2</sub> | 6        | 6       | .        | 6              |
| -SR                 | .        | 85      | .        | .              |
| -Br                 | 25       | 30      | .        | .              |
| -NO <sub>2</sub>    | .        | 95      | .        | .              |

(e) Empirical Rules for Benzoyl Derivative :

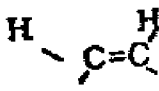
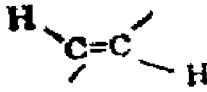
| Parent Chromophor :       | mm  |
|---------------------------|-----|
| Z = alkyl or ring residue | 246 |
| Z = H                     | 250 |
| Z = -OH or -OR            | 230 |

| Increment for each substituent :  | Q  | M  | R  |
|-----------------------------------|----|----|----|
| Alkyl or ring residue             | 3  | 3  | 10 |
| -OH; -OCH <sub>3</sub> -OR        | 7  | 7  | 25 |
| -O                                | 11 | 20 | 78 |
| -Cl                               | 0  | 0  | 10 |
| -Br                               | 2  | 2  | 15 |
| -NH <sub>2</sub>                  | 13 | 13 | 58 |
| -NHCOCH <sub>2</sub>              | 20 | 20 | 45 |
| -NHCH <sub>3</sub>                | .  | .  | 78 |
| -N(CH <sub>2</sub> ) <sub>3</sub> | 20 | 20 | 85 |

IR

| Infra - Red Data            |   |                                     |
|-----------------------------|---|-------------------------------------|
| Alkene (stretching)         | -C-H  | 2850-2960(v)                        |
| Alkene                      | =C-H  | 3100-3200(m)                        |
| Alkyene                     | =C-H  | 3200-3300(s)                        |
| Aromatic                    | ArC-H   | 3010-3100(m)                        |
| Aromatic ring               | C=C   | 1500-1600(v)<br>(two to three)      |
| Alkene                      | >C=C<   | 1610-1680(v)                        |
| Alkyene                     | -C=C <sup>2</sup> .                             | 2100-2260(s)                        |
| Alkene (Bonding)            | -C-H  | 1340(w)                             |
|                             | -C(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> | 1430-1470(m) &<br>1880-1385(s)      |
|                             | -C(CH <sub>2</sub> ) <sub>3</sub>               | 1865 (s)                            |
| Aldehyde                    | -C-H  | 2820-2980(w) & 2650-2760(s) doublet |
| Aldehyde                    | C=O   | 1740-1720(s)                        |
| Ketone                      | C=O   | 1725-1710(s)                        |
| Carboxylic acid             | C=O   | 1725-1705(s)                        |
| Ester                       | C=O   | 1750-1730(s)                        |
| Amide                       | C=O   | 1670-1640(s)                        |
| Anhydride                   | C=O   | 1810-1760(s) & 1740-1730 doublet    |
| Alcohols, Ethers, esters    |   |                                     |
| Carboxylic acids, Anhydride | C-O   | 1300-1000(s)                        |

Alcohols, phenols :

|                      |   |               |
|----------------------|---|---------------|
| Free                 | O-H   | 3650-3600(sh) |
| bonded               | O-H   | 3500-3200(b)  |
| Carboxylic acids     |   |               |
| Free                 | O-H   | 3500-3650(m)  |
| H-bonded             | O-H   | 2500-3200(b)  |
| amines (stretch)     | N-H   | 3330-3500(m)  |
| Bnding               | -N-H  | 1640-1550(m)  |
| Nitrile              | -C=N  | 2210-2280(s)  |
| Ether                | -O-   | 1070-1150(s)  |
| Alkene bending       |   |               |
| disubstituted Cis.   |  | 690(s)        |
| disubstituted Trans. |  | 960-970(s)    |

Aromatic substitution :

Type C-H out of plane bending

No. of adjacent H atom.

range cm

|   |                  |             |
|---|------------------|-------------|
| 5 | (Two bends) Mono | → 700 ± 650 |
| 4 | one Ortho        | → 750 ± 20  |
| 3 | (Two) Meta       | → 710 ± 750 |
| 2 | one Para         | → 850 ± 20  |
| 1 |                  |             |