

[Time: 2½ Hours]

[ Marks:60]

Please check whether you have got the right question paper.

- N.B.:**
1. All questions are compulsory.
  2. Figures to the right indicate full marks.

**Q.1** a) Attempt any two of the following:- **08**

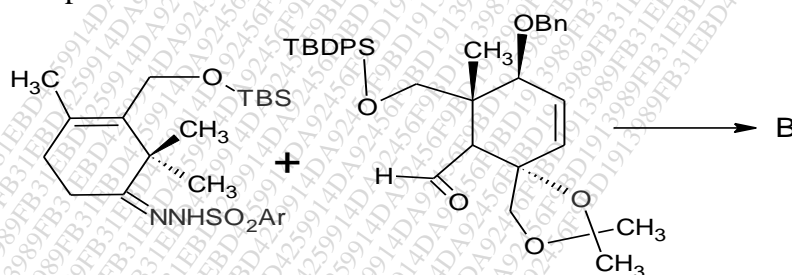
- Give analytical evidences in support of the constitution of  $\beta$ -carotene.
- Write notes on
  - Amino sugars
  - Deoxy sugars
- Explain the structural features and applications of
  - Chitin
  - Heparin
- Give the synthesis of disparlure from 6-methylhept-1-ene

b) Attempt any one of the following:- **04**

- What are insect pheromones? Discuss the various types of pheromones.
- Give the analytical evidences of
  - Numbers and position of hydroxyl groups in cyanidine chloride
  - n-propyl side chain in coniine

**Q.2** a) Attempt any two of the following:- **08**

- How the 8 membered (B) ring in Taxol is synthesized from the following compounds?



- Give the synthesis of Griseofulvin from phloroglucinol.
- How would you convert 2-cyclohexenone and Isobutylene into isocaryophyllene?
- How would you convert 6-methoxytryptamine and cyclohexanecarboxaldehyde derivative into reserpine?

b) Attempt any one of the following:- **04**

- Give the synthetic strategy for synthesis of Longifolene.  
Draw the structure of PGE<sub>1</sub> and give biological importance of prostaglandins.
- Give analytical evidence for the structure elucidation of PGF<sub>1 $\alpha$</sub>

**Q.3** a) Answer any two of the following:

**08**

- What are chemical shift reagents? Explain the use of shift reagents in NMR spectroscopy.
- Using spin system notation designate the type of spin system in the following compounds.

(I) 1, 1, 2-trichloroethane

(II) 5-nitro-m-xylene

(III) Phenylethylacetate

(IV)  $\beta$ -chlorophenatole

- Calculate  $^{13}\text{C}$ NMR chemical shifts for all the aromatic carbons using incremental shifts of the aromatic carbon atoms from the table given below for the following compounds:

(I) m-nitrobenzaldehyde

(II) o-toluidene

Substituents	Increments in ppm			
	<i>ipso</i>	<i>ortho</i>	<i>meta</i>	<i>para</i>
-NO <sub>2</sub>	+19.6	-5.3	+0.9	+6.0
-NH <sub>2</sub>	+19.2	-12.4	+1.3	-9.5
-CH <sub>3</sub>	+9.3	+0.7	-0.1	-2.9
-CHO	+8.2	+1.2	+0.6	+5.8

- Deduce the structure:

Molecular formula C<sub>9</sub>H<sub>8</sub>O

IR (cm<sup>-1</sup>) : 3090 (w), 2820 & 2750, 1685 (s), 1630 (m), 1610, 1580, 1500, 1450, 1400, 1120, 750.

PMR ( $\delta$ ppm): 9.7 (d, 1H), 7.5 (m, 5H), 6.4 & 6.8 (two doublets  $^3J=16$  Hz).

CMR ( $\delta$ ppm): 190 (d), 150.3(d), 134.9(s), 129.6(d), 128.4(d), 127.7(d), 126.2(d)

Mass spectrum : M<sup>+</sup> at 148

b) Attempt any one of the following:

**04**

- The following chemical shifts were observed in  $^{13}\text{C}$ NMR spectrum of anisole in  $\delta$ ppm.

54.8      114.1      120.7      129.5      159.9

Match the chemical shifts with the appropriate carbons and justify your answer.

- Explain long range coupling with suitable examples.

**Q.4** a) Answer any two of the following:

**08**

- Explain COSY technique with suitable example.
- Sketch the proton decoupled  $^{13}\text{C}$ NMR spectrum and DEPT-45, DEPT-90, DEPT-135 spectra of the following compounds:

(I) Ethylbenzene

(II) 4-hydroxy-3-methyl-2-butanone

- Explain NOESY technique with suitable example.

- An organic compound with molecular formula C<sub>7</sub>H<sub>14</sub>O<sub>2</sub> exhibit strong absorption at 1715 cm<sup>-1</sup> in its IR spectrum. Its  $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR data is as follows:

$^1\text{H}$ NMR ( $\delta$ ppm) : 0.9(d, 6H), 1.53(m, 1H), 1.69(m, 2H), 2.05(t, 2H), 4.10(s, 3H)

$^{13}\text{C}$ NMR ( $\delta$ ppm) : 171, 63, 37, 25, 22, 21.

Assign the structure to the compound and draw its HETCOR spectrum.

**Q.4** b) Attempt any one of the following:

**04**

- What is NOE? What is its significance? Explain with suitable examples.
- A compound with average molecular weight 137 shows following spectral data.  
 $^1\text{H}$ NMR ( $\delta\text{ppm}$ ) : 3.5 (t, 2H), 2.0 (quintet, 2H), 1.5 (sextet, 2H), 1.0 (t, 3H)  
 $\text{M}^+$  peak 136 & 138 (ratio 1:1)  
 Predict the structure to the compound and draw its COSY spectrum.

**Q.5** Attempt any four of the following:

**12**

- Give the synthesis of cyanidin chloride by Robinson method.
- Give the synthesis of ubiquinone from 3, 4, 5-trimethoxyacetophenone.
- Draw the structure of  $\text{JH}_2$ .  
 Give a brief account aryl acetic acid as plant growth regulators.
- Give applications of gibberelic acids.
- State whether the following statements are true or false and justify your answer.
  - Mesitylene gives only one signal in its  $^{13}\text{C}$ NMR spectrum.
  - 1-chloropentane can be better identified from its  $^{13}\text{C}$ NMR rather than  $^1\text{H}$ NMR.
  - $^1\text{H}$ NMR spectrum of methyl alcohol shows one doublet and one quintet at  $-40^\circ\text{C}$ .
- How will you distinguish three isomers of dinitrobenzene on the basis of their proton decoupled  $^{13}\text{C}$ NMR spectra?
- Sketch and explain HETCOR spectrum of 2-pentanone.
- Match the columns & justify your answer

**A**

**B**

1. COSY

a) Determination of stereochemistry

2. HETCOR

b)  $^1\text{H}$ - $^1\text{H}$  correlation

3. NOESY

c)  $^1\text{H}$ - $^{13}\text{C}$  correlation

d) Determination of molecular weight

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