(2½ Hours)

[ Total Marks: 60

N. B.: (1) All questions are compulsory.

- (2) Figures to the right indicate full marks.
- 1. (a) Answer any two of the following:-

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(i) Complete the following reactions:

(II) 
$$\frac{\text{tno}_2 \text{ BF}_4}{\text{cH}_3 \text{ cn}_7 \text{ reflux}}$$
?

(II)  $\frac{\text{HNO}_3, \text{ cH}_3 \text{ co})_2\text{O}}{\text{-}70^{\circ}\text{C}}$ ?

(III)  $\frac{\text{HNO}_3, \text{ cH}_3 \text{ co})_2\text{O}}{\text{-}70^{\circ}\text{C}}$ ?

(III)  $\frac{\text{Ph} \text{ Mg Br}_7, \text{ Ni}(\text{O})}{\text{Ph} \text{ Mg Br}_7, \text{ Ni}(\text{O})}$ ?

(IV)  $\frac{\text{Ph} \text{ Mg Br}_7, \text{ Ni}(\text{O})}{\text{2}) \text{ KMnO}_4}$ ?

- (ii) (I) Explain the following:-
  - (A) Electrophilic substitution in quinoline and isoquinoline takes place in the homocyclic ring.
  - (B) Pyridine N-oxide undergoes both electrophilic and nucleophilic substitution reactions.
  - (II) Give any one method of preparation of quinoline and isoquinoline.
- (iii) How will you prepare pyrazine from
  - (I) 1,2-dicarbonyl compound
  - (II) α-aminoketone?

Discuss the electrophilic substitution reactions of diazines.

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- (iv) (I) Give any two methods of synthesis of indole.
  - (II) Complete the following reactions:-

- (b) Answer any one of the following:
  - (i) (I) Explain giving examples the nucleophilic substitution reactions of diazines.
    - (II) Discuss electrophilic substitution reactions of pyridine Noxide.
  - (ii) Complete the following reactions:-

$$(I) \qquad \frac{\text{Li Al H}_{4},}{\text{Et}_{2}O} \qquad ?$$

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- 2. (a) Answer any two of the following:-
  - (i) Give the occurence, biological role and structural features of sterols.
  - (ii) Write a note on steroidal alkaloids.
  - (iii) How is cholesterol converted to 16-DPA?
  - (iv) Give the synthesis of testosterone from 16-DPA.
  - (b) Answer any one of the following:-
    - (i) How is androsterone synthesised from 16-DPA?
    - (ii) Give the synthesis of cinerolone. Give the structure of cortisol.
- 3. (a) Answer any two of the following:-
  - (i) (I) State the sources and biological importance of (A) biotin (B) vitamin K<sub>1</sub>
    - (II) Give the synthesis of vitamin K<sub>1</sub>
  - (ii) Explain the sources and biological importance of vitamin B<sub>6</sub>.

    How will you convert ethylester of N-formyl-DL-alanine to vitamin B<sub>6</sub>.
  - (iii) How are vitamins classified? Outline the synthesis of riboflavin.
  - (iv) Write the degradative evidences to establish the structure of penicillin.
  - (b) Answer any one of the following:-
    - (i) Explain the biological importance and give the synthesis of vitamin B<sub>1</sub>.
    - (ii) DL-penicillamine and tert-butylphthalimide malonaldehyde are the intermediates required for the synthesis of penicillin. Give the synthesis of these intermediates.
- 4. (a) Answer any two of the following:-
  - (i) Calculate <sup>13</sup>C NMR chemical shifts for all the aromatic carbons using the incremental shifts of the aromatic carbon atoms from the table given below, for the following compounds.
    - (I) 2-nitrophenol
    - (II) 4-nitroaniline

	Increments in ppm			
Substituent	ipso	ortho	meta	para
NO <sub>2</sub>	19.6	-5.3	0.9	6.0
OH	26.6	-12.7	1.6	-7.3
NH <sub>2</sub>	19.2	-12.4	1.3	-9.5

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- (ii) Explain the HETCOR technique with a suitable example.
- (iii) State the number of <sup>13</sup>C peaks and assign the multiplicity of each one in <sup>13</sup>C proton decoupled NMR spectrum in the following compound.
  - (I) CF<sub>3</sub>CH<sub>2</sub>OH

(II)  $CH_3PO(OCH_3)_2$ 

- (iv) How will you distinguish between (E)-2-bromo-2-butene and (Z)-2-bromo-2-butene using NOESY spectrum?
- (b) Answer any one of the following:
  - (i) Draw the proton decoupled, DEPT-45, DEPT-90 and DEPT-135 of the compound, ethyl 2-nitropropanoate using following <sup>13</sup>C NMR values:

 $\delta$  14 , 16 , 63 , 82 and 165 ppm.

- (ii) What is ESR spectroscopy? Discuss its principle. Give the applications of NMR spectroscopy in medicine.
- Answer any four of the following:
  - (a) How is coumarin synthesised,
    - (i) by Pechmann synthesis
    - (ii) using o-hydroxybenzaldehyde and acetic anhydride?
  - (b) (i) Give Traube synthesis of purines.
    - (ii) What is the action of,
      - (I) CH<sub>2</sub>I, CH<sub>2</sub>OH, 100°C
      - (II) conc HNO<sub>3</sub>, AcOH, 120°C on purine.
  - (c) How is exaltone synthesised?
  - (d) How is oestrone converted to oestriol?
  - (e) (i) State the sources and biological importance of
    - (I) α-tocopherol
    - (II) Vitamin B<sub>12</sub>
    - (ii) What are natural insecticides?
  - (f) Give the synthesis of pyrethrin-I.
  - (g) Explain the principle of fluorescence spectroscopy.
  - (h) A compound C<sub>0</sub>H<sub>10</sub>O exhibits the following signals in <sup>13</sup>C NMR spectrum:

 $\delta$  8.2 (q), 31.6 (t), 128.3 (d), 128.6 (d) 132.6 (d), 137.2 (s) and 200 (s).

Predict the structure and justify your answer.