## Msc. II - Sem. IV - Oct 2016 Organic Chemistry-paper III

QP Code: 76703

(2½ Hours)

[ Total Marks: 60

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

(2) Figures to the right indicate full marks.

(a) Answer any two of the following:-

(i) Complete the following reactions:-

conc HNO3 + conc H2SO4

(II)

NaOEt, EtOH (IX) Me

(ii) Give two methods of synthesis of pyrimidine and discuss its electrophilic substitution reactions.

(iii) How quinoline synthesised by

ONI) Doebner-Miller synthesis

(II) The Friedlander synthesis?

 $\lambda$ lso explain, its reactivity towards nucleophiles.

- (I) Give Traube synthesis of purine.
- (II) Explain the following:-
  - (A) Electrophilic substitution in indole takes place at 3-position.

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- (B) The diazines are weaker bases than pyridine
- (C) The 1-position in isoquinoline is strongly activated than 3-position for a nucleophilic attack.
- (b) Answer any one of the following:-
  - (i) (I) Give any two methods of synthesis of indole.
    - (II) What is the action of the following reagents on N-methylindole?
      - (A) t-Buli, THF, O°C then ICH2CH2I

(B)  $HCON(CH_3)_2 + POCl_3$ , 5°C then  $H_2O$ 

(ii) Complete the following reactions:-

Br2/AICI3

COOCHA COOCHa

(a) Answer any two of the following:-

Give the occurence, biological role and structural features of steroidal hormones.

(ii) Discuss the general structure of steroids. Give the occurence and biological functions of bile acid.

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- (iii) How is 16-DPA synthesised from cholesterol?
- (iv) Give the synthesis of androsterone from 16-DPA.
- (b) Answer any one of the following:
  - (i) How is 16-DPA converted to oestadiol?
  - (ii) Write the synthesis of jasmolone. Give the structure of
- (a) Answer any two of the following:
- (i) Write the degradative evidences to establish the structure of penicillin.

  (ii) State the biological importance of form synthesis of the s
  - (ii) State the biological importance of folic acid and give the synthesis of vitamin B<sub>2</sub>.
    (iii) State the sources and biological importance of (I) vitamin K<sub>1</sub> (II) vitamin D and give the synthesis of vitamin K<sub>1</sub> from 2-methyl-1 4-naphthaguings.
  - - 2-methyl-1, 4-naphthaquinone and phytol.
  - (iv) Give the synthesis of vitamin B<sub>6</sub> from ethox acetylacetone and cyanoacetamide.
  - (b) Answer any one of the following:-
    - (i) Give the synthesis of (I) D-pencilkamine and (II) tert-butylphthalimide malonaldehyde. How is penicillin synthesised from these compounds?
    - (ii) Give the synthesis of vitamin B<sub>1</sub> along with the preparation of one intermediate used in the synthesis.
  - (a) Answer any two of the following:-
    - (i) Explain the COSY technique with a suitable example.
    - (ii) Sketch the proton decoupled <sup>13</sup>C NMR spectrum and DEPT spectra of the following compounds:
      - (I) 2-chloroethanol
      - (II) Authyl phthalate
    - (iii) Draw a schematic diagram of the HETCOR spectrum of ⇔ĩodobutane.
      - Calculate <sup>13</sup>C NMR chemical shift for all the aromatic carbons using the incremental shifts of the aromatic carbon atoms table given below, for the following compounds:
        - (I) 2-bromoanisole
        - (II) 1,3-dinitrobenzene

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	Increments in ppm			
Substituent	ipso	ortho	meta	para
Br	-5.4	3.4	2.2	-1.0
OCH <sub>3</sub>	31.4	-14.4	1.0	-7.7
NO <sub>2</sub>	19.6	-5.3	0.9	6.0

(b) Answer any one of the following:-4.

(i) An organic compound has the molecular formula  $C_9H_{16}O_{40}$ . Identify the compound and justify your answer using the spectroscopic data given below:

IR: 1740 cm<sup>-1</sup>

1H NMR: 80.77 Identify the compound and justify your answer using the spectroscopic data given below:

IR: 1740 cm<sup>-1</sup>

<sup>1</sup>H NMR: δ 0.75 (t, 3H), 0.85 (t,6H), 1.8 (m, 2H)

3.15 (t, 1H) and 4.1 (q, 4H) ppm.

 $^{13}$ C NMR :  $\delta$  11, 13, 21, 53, 61 and 170 ppm<sub>C</sub>

(ii) Explain the principle of fluorescence. Give the application of NMR in medicine.

Answer any four of the following:-5.

(a) Give two methods of preparation of coumarin. What is the action of CH3MgBr on coumarin?

(b) How will you prepare pyridazine from a 1,4-dicarbonyl compound? Explain giving an example its reactivity towards nucleophiles.

(c) How is exaltone synthesized?

(d) Write the synthesis of progesterone.

(e) Give the synthesis Expyrethrin-I.

(f) Give the sources and biological importance of tocopherols and give the synthesis α a-tocopherol

(g) The following chemical shifts were observed in the <sup>13</sup>C NMR of butylethy ether, δ 13.5, 15.0, 19.4, 32.1, 66.0 and 70.1 ppm. Match the chemical shifts with the appropriate carbons and justify your answer.

(h) Discuss the applications of ESR spectroscopy.

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