M.Sc Sem IV May 2017
Org. Chemistry P - III

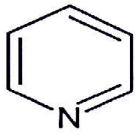
Q.P. Code: 09242

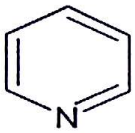
[Time: - 2½ Hours] **[Marks: 60]**

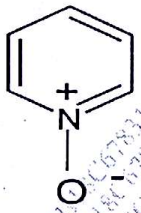
N.B: 1. **All** questions are **compulsory.**
2. **Figures** to the **right** indicate **full** marks.

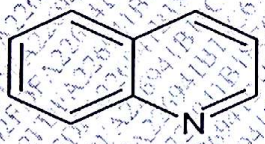
1. (a) Answer **any two** of the following:- 08

(i) Complete the following reactions:-

(I)  $\xrightarrow[C_6H_5N(CH_3)_2,\ 100\ ^\circ C]{NaNH_2}$

(II)  $\xrightarrow[180\ ^\circ C,\ aq.\ NaCl]{Hg(OOCCH_3)_2}$

(III)  $\xrightarrow[240\ ^\circ C]{Oleum\ /\ HgSO_4}$

(IV)  $\xrightarrow[2)\ H_2O]{1)\ KOH,\ 240\ ^\circ C}$

(ii) I) Explain: Pyridine N-oxide undergoes both electrophilic and nucleophile substitutions.
II) How is quinolone synthesized by Skraup method?

(iii) Pyridazine is resistant to electrophilic substitution and oxidation reactions, explain with illustration.

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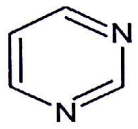
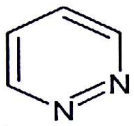
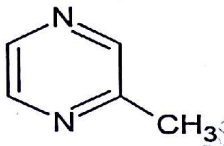
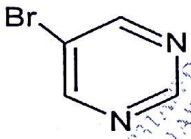
(iv) Complete the following reactions:-

(I)  m - CPBA, $CHCl_3$ / room temp.

(II)  C_6H_5COCl, $(CH_3)_3SiCN$, $AlCl_3$

(III)  1) n -BuLi / $(C_2H_5)_2O$, 2) $KMnO_4$ / $(CH_3)_2CO$

(IV)  1) $(C_6H_5)_2CO$, 2) n-BuLi , THF / -95 °C

1. (b) Answer **any one** of the following:- 04

(i) How is indole prepared by

I) Fischer synthesis

II) Reissert synthesis?

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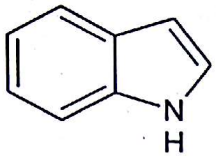
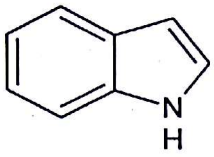
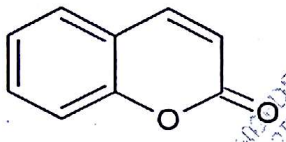
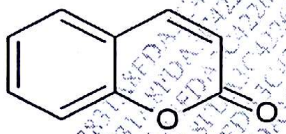
(ii) Complete the following reactions:-

(I)  $\xrightarrow[(C_2H_5)_2O]{CH_3MgI}$

(II)  $\xrightarrow[\text{Benzene}]{CH_2 = CH - NO_2}$

(III)  $\xrightarrow[CH_2Cl_2]{(C_2H_5)_3O^+ BF_4^-}$

(IV)  $\xrightarrow[C_6H_5OCH_3]{POCl_3 / ZnCl_2}$

2. (a) Answer **any two** of the following:- 08
(i) Write a note on sex hormones giving occurrence and biological role of each type.
(ii) Write a note on steroidal alkaloids.
(iii) Give the synthesis of 16-DPA from cholesterol.
(iv) How is androsterone synthesized from 16-DPA?

(b) Answer **any one** of the following:- 04
(i) How is progesterone synthesized from 16-DPA? Explain the general structure of steroids.
(ii) Give the synthesis of allethrolone. Explain the stereochemistry of oestriol.

3. (a) Answer **any two** of the following: 08
(i) Write the degradative evidences to establish the structure of penicillin-G.
(ii) Give an account of different products obtained on acid hydrolysis of cephalosporin-C.
(ii) Give the synthesis of *tert*-butyl phthalimide malonaldehyde. How is penicillin-G synthesized. from D-penicillamine and *tert*-butyl phthalimide malonaldehyde?
(iv) Write the synthesis of vitamin B_6.

(b) Answer **any one** of the following:- 04
(i) State the sources and biological importance of (I) Biotin and (II) $\propto$ – tocopherol.
(ii) State the biological importance of vitamin K_1 and write its synthesis.

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4. (a) Answer the **two** of the following:- 08

(i) An organic compound has the molecular formula C_9H_8O. Identify the compound and justify your answer using the spectroscopic data given below:
IR (cm^{-1}): 3090 (w), 2820(m), 2750(m), 1685 (s), 1630 (m), 1610 (s), 1580 (m), 1500 (m), 1450 (w), 1120 (s) and 750 (s).
^1H NMR: δ 6.7 (dd, 1H), 7.4(d,1H), 7.3 (m, 5H) and 9.7 (d, 1H) ppm.
^{13}C NMR: δ 126.2, 127.7, 128.4, 129.6, 134.9, 150.3 and 190.0 ppm.

(ii) What is DEPT? Illustrate utility of DEPT experiments to deduce structure of 4–hydroxyl-3-methyl-2-butanone.

(iii) Explain the HETCOR technique with a suitable example.

(iv) Calculate ^{13}C NMR chemical shift for all the aromatic carbons using the incremental shifts of the aromatic carbon atoms in the table given below, for the following compounds:

I. 1, 4 - dinitrobenzene

II. Catechol

Substituent	Increments in ppm			
	ipso	*ortho*	*meta*	*para*
NO_2	19.6	-5.3	0.9	6.0
OH	26.6	-12.7	1.6	-7.3

4. (b) Answer **any one** of the following:- 04

(i) Draw a schematic diagram of the COSY spectrum of 3-heptanone.

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

5. Answer **any four** of the following:- 12

(a) What is the action of the following

i. 1, 2–diaminobenzene at 160^0 C on s–triazine

ii. Br_2 at 120^0 C on s–triazine

iii. Acetic anhydride in glacial acetic acid on indole?

(b) Explain, electrophilic substitution in quinoline and isoquinoline take place in the carbocyclic ring.

(c) Give the synthesis of muscone.

(d) How is oesterone converted to oestriol?

(e) Give the synthesis of pyrethrin-I.

(f) State the biological importance of vitamin D. Draw the structure of rotenone.

(g) How will you distinguish between the three isomers of dibrombenzene, on the basis of their proton-decoupled NMR spectra?

(h) Discuss the applications of ESR spectroscopy.

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