

M.Sc. DEGREE EXAMINATION, NOVEMBER 2010**Third Semester**

Faculty of Science

Branch III—Chemistry

Paper X—ORGANIC CHEMISTRY—III

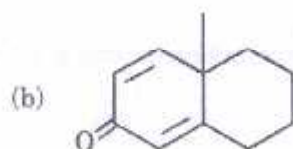
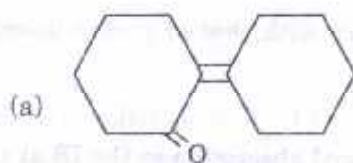
(Common with Paper X of Branch IV-A—Analytical Chemistry)

Time : Three Hours

Maximum : 75 Marks

Section A*Answer any ten questions.**Each question carries 2 marks.*

1. A trisubstituted benzene possessing one bromine and two methoxy substituents exhibit three aromatic resonance at δ 6.40, 6.46 and 7.41. What is the substitution pattern ?
2. The ketone below have λ max at 244 and 256 nm. Which Ketone has which absorption.



3. What are the masses of the charged species produced in the following cleavage pathways ?
 - (a) Alpha cleavage of 2-pentanone.
 - (b) McLafferty rearrangement of 4-methyl-2-pentanone.
4. 4-Methyl-2-pentanone and 3-methylpentanal are isomers. Explain how you could tell them apart by IR spectroscopy.
5. What product will be formed when 2-methyl piperidine is heated with Methyl Iodide and silver oxide solution.

Turn over

6. What product (s) will be formed when cyanidine chloride is heated with KOH ?
7. Write down the structure of cholesterol and mark the chiral carbons.
8. Show the mechanism of formation of acetoacetyl-s CoA by the action of malonyls CoA and Acetyls CoA. Name the enzyme catalyzing the reaction.
9. Citral is used as the starting material for the synthesis of vitamin A. Show how citral is converted in β -ionone.
10. Show the reaction involved in the ring opening polymerization of propylene oxide under a Lewis acid initiator.
11. Indicate which of the functional groups in the heterocyclic bases Guanine and cytosine functions as hydrogen bond donors and hydrogen bond acceptors ?
12. Represent a free radical polymerisation using an appropriate example.
13. What do you mean by t_R in HPLC and comment on its significance ?

(10 \times 2 = 20 marks)

Section B

*Answer any five questions.
Each question carries 5 marks.*

14. Citing suitable example explain what is NOE and compare with that of proton decoupling in structural characterization.
15. The mass spectrum of a compound with molecular formula $C_6H_{12}O$ is as follows. Peaks at m/z 43(100), 58(55), 85(30) and 100 ($M + 40\%$). It shows a carbonyl absorption in the IR at ν_{max} 1715 cm^{-1} . Give the structure and show the mechanism of formation of the peaks showing the structure of the fragment ions.
16. Depict the synthesis of quercetin using 2-hydroxy-4, 6-dimethoxy acetophenone and 3, 4-dimethoxy benzaldehyde.
17. Explain the synthesis of testosterone from cholesterol.
18. Briefly explain the basic principles of combinatorial synthesis.
19. Illustrate one method for the determination of the number average molecular weight of a synthetic polymer.
20. Discuss the use of Ziegler-Natta catalysis for the synthesis of stereoregular polymers.
21. Describe the use of crown ethers in metal extraction.

(5 \times 5 = 25 marks)

Section C

Answer any two questions.
Each question carries 15 marks.

22. Deduce the structure of the compound that gave the following spectral data :—

Mass m/z 176.131 (M^+), 131 (base peak), 103, 77. IR ν_{\max} : 1714, 1639 cm^{-1} .

^1H NMR : δ 1.31 (t 3H, $J = 7.1$ Hz); 4.2 (qt 2H, $J = 7.1$ Hz) 6.43 (d, 1H, $J = 15.8$ Hz); 7.24 – 7.57 (m, 5H), 7.67 (d, 1H, $J = 15.8$ Hz).

^{13}C NMR : 14.3, 60.4, 118.4, 128.1, 128.9, 130.2, 134.5, 144.5, 166.8 ppm.

Assign the values.

23. Illustrate the synthesis of camphor.
24. Describe the Phosphoramidite method for the synthesis of a tetranucleotide.
25. Write notes on :
- (a) Ultracentrifugation.
 - (b) Protein organisation.
 - (c) Manufacture and applications of polyurethane.

(2 × 15 = 30 marks)