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M.Sc. DEGREE EXAMINATION, OCTOBER 2011

Third Semester

Faculty of Science

Branch III : Chemistry

Paper X—ORGANIC CHEMISTRY—III

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

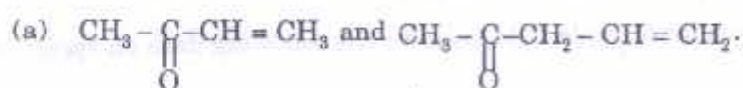Time : Three Hours   Maximum : 75 Marks

Section A

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

1. Explain why the relative intensities of the peaks in a quartet are $1:3:3:1$.

2. A trisubstituted benzene possessing one bromine and two methoxy substituents exhibits three aromatic resonance at δ 6.40, 6.46 and 7.41. What is the substitution pattern ?

3. How would you distinguish between the following isomers by MS.
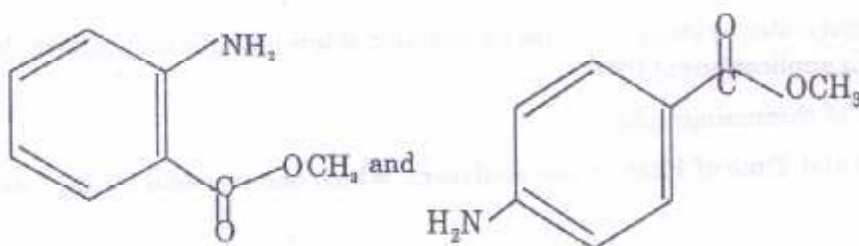
4. How would you use IR spectroscopy to distinguish between the following pairs of constitutional isomers.

   (a) $CH_3 - \underset{O}{\overset{O}{C}} - CH = CH_3$ and $CH_3 - \underset{O}{\overset{O}{C}} - CH_2 - CH = CH_2$.

   (b) $H_2C = - CH - OCH_3$ and CH_3CH_2CHO.

5. Explain briefly what is meant by quadrupole broadening ?

6. What products are formed by heating 7 – hydroxy flavone with concentrated potassium hydroxide solution ?

Turn over

7. Write down the structure of PGE$_2$ and PGF$_1$.

8. Show the reaction when ascorbic acid is boiled with hydrochloric acid.

9. What product is obtained when morphine is boiled with concentrated hydrochloric acid. Depict the reaction.

10. The region of DNA helix where G–C base pair predominates is more strongly held than the region where A – T pair is move. Explain.

11. Write down the structure of the monomers by which chitin is formed.

12. Show the anionic polymerization mechanism depicting an appropriate example.

13. Briefly explain what is density gradient centrifugation.

(10 × 2 = 20 marks)

Section B

Answer any five questions. Each question carries 5 marks.

14. Show the formation of tropinone skeleton in the biosynthesis of tropane alkaloids starting from the amino acid ornithine.

15. Comment on the stereochemistry of cholesterol.

16. Discuss the application of protecting groups and activating groups in solid phase peptide synthesis.

17. Describe the synthesis of Thymine and Adenine.

18. Briefly describe structure and property relationship of polymers.

19. Depict the synthesis of a polyester by step growth polymerization of terephthalic acid and ethylene glycol. What are the main applications of PET.

20. Explain the plate theory of chromatography.

21. Describe the quadrupole and Time of Flight mass analysers. Which one is useful for high mass range analysis.

(5 × 5 = 25 marks)

Section C

Answer any two questions.
Each question carries 15 marks.

22. An organic compound with molecular formula $C_8H_8O_3$ gave the following data on spectroscopic analysis.

    MS : m/Z – 152 (49 %), 121 (29 %), 120 (100 %), 92 (54 %)

    IR (neat v_{max} : 3205 (broad), 1675 (S), 1307 (S), 1253 (S)$^{-1}$ and 1220 (S) cm^{-1}.

    ^{1}HNMR (CDCl$_3$) : δ 3.92 (S, 3H), 6.85 (t, 1H, J = 8 H$_z$)

    7.00 (d, 1H, J = 8Hz) ; 7.44 (t, 1H, J = 8 Hz).

    7.83 (d, 1H, J = 8Hz), 10.8 (S, 1H)

^{13}CNMR (CDCl$_3$):   δ 52.1, 112.7 (S), 117.7 (d), 117.2 (d) 130.1 (d), 135.7 (d), 162.0 (S); 170.7 (S).

Deduce the structure and interpret the spectra.

23. (a) Illustrate the synthesis of papaverine.

   (b) Starting with CH$_3$COSCoA depict the biosynthetic pathway for the formation of diterpenoid.

$(8 + 7 = 15$ marks)

24. (a) Illustrate the synthesis of Vitamin - A.

   (b) Describe the structure of starch.

$(10 + 5 = 15$ marks)

25. (a) Describe the sheet conformation of protein.

   (b) Discuss the basic concept of combinatorial synthesis.

   (c) Describe the glassy and rubbery state of polymer.

$[2 \times 15 = 30$ marks]