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III Semester M.Sc. Degree (CBSS – Reg./Sup./Imp.) Examination, October 2022 (2019 Admission Onwards) CHEMISTRY

CHE 3C.09: Organic Chemistry - III

Time: 3 Hours Max. Marks: 60

SECTION - A

Answer **all** questions in **one** word or **one** sentence. **Each** question carries **1** mark.

- Aniline absorption shifts from 230 nm in neutral medium to 203 nm in acidic medium. Why?
- 2. What is the significance of the fingerprint region in the IR spectra?
- 3. How many different types of protons are there in allyl chloride?
- 4. Predict the number of peaks on the ¹³C NMR spectrum of p-dimethoxy benzene and m-dimethoxy benzene.
- 5. What are the major fragments and their m/z values in the mass spectrum of nitrobenzene?
- 6. What is a metastable ion? What is its significance?
- 7. Draw the structure of coumarin. What is its use in medicine?
- 8. Sketch the structures of the pyrimidine bases present in DNA. (8×1=8)

SIRSECTION L BGE

Answer **any 8** questions. Answer may be **two** or **three** sentences. **Each** question carries **2** marks.

9. Propene and propyne show C-C multiple bond stretching in IR spectrum, while ethylene and ethyne do not show such bands. Why?



- 10. Explain how *cis*-stilbene is distinguished from *trans*-stilbene using UV spectra.
- 11. Comment on the aromatic nature of cyclooctatetraene on the basis of its NMR spectrum.
- 12. An organic compound having the molecular formula C_3H_7Cl exhibits the following signals in the 1H NMR spectrum : (i) δ 0.9 (3H, t); δ 1.6 (2H, m); δ 3.3 (2H, t). Suggest the probable structure.
- 13. Calculate the λ_{max} and ϵ_{max} for the following molecules using Woodward-Fieser rules.

- 14. Explain the term off-resonance decoupling.
- 15. What is nitrogen rule? Explain the rule taking the example of nitrobenzene.
- 16. Explain the principle of TOF analyser.
- 17. Phenetole in its mass spectrum exhibits an ion peak at $\frac{m}{z}$ 94. Explain its formation.
- 18. Name the following compounds based on Hantzsch-Widman system of nomenclature.





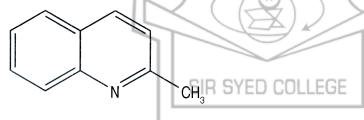
- 19. Pyrrole is more reactive at 2-position than 3-position in electrophilic substitution reactions. Explain.
- 20. Give any method of synthesis of oxirane.

 $(8 \times 2 = 16)$

SECTION - C

Short paragraph questions. Answer any 4 questions. Each question carries 3 marks.

- 21. An organic molecule having molecular formula C_2H_5NO shows in its IR spectrum and absorption band at 1680 cm⁻¹. When reduced with LiAlH₄ it forms C_2H_7N whose IR spectrum lacks the peak at 1680 cm⁻¹, instead it exhibits a band at 3300 cm⁻¹. Suggest the probable structure.
- 22. a) An organic compound in hexane exhibits λ_{max} at 305 nm and in ethanol at 307 nm. What should be the nature of the transition and why?
 - b) Sketch the first order NMR spectrum of ethanol.
- 23. Explain Nuclear Overhauser Effect.
- 24. What is FAB? What are its advantages and disadvantages?
- 25. a) Explain Mclafferty rearrangement with an example.
 - b) Give a synthesis of the following:



26. How is pyrimidine ring constructed ? Give one method of synthesis of thymine. ($4\times3=12$)



SECTION - D

Essay type questions. Answer 4 questions. Each question carries 6 marks.

27. a) The principal flavour constituent of cinnamon is a compound whose mass spectrum shows the molecular ion at m/z 132 (C_9H_8O), with the base peak at m/z 131, and a significant peak at m/z 103. IR spectrum : 1690 cm⁻¹ (s); UV spectrum : 284 (intense), 308 (weak) nm. ¹H NMR spectrum: δ 9.75 (1H, d, J = 8 Hz), 7.45 (1H, d, J = 16 Hz), 7.4 (5H, m) and 6.7 (1H, dd, J = 16, 8 Hz). Deduce the structure of the molecule and comment on its stereochemistry with respect to the NMR spectrum.

OR

- b) Discuss the various factors affecting the positions frequencies of absorption in the IR spectrum.
- 28. a) An organic compound having the molecular formula $C_9H_{10}O_2$, gave the following spectral data :

UV : λ_{max} 274 nm (ϵ = 2050)

IR: v 3031, 2941, 1724, 1608, 1504, 1060 and 830 cm⁻¹

¹H NMR δ : 2.35 (3H, s); 3.82 (3H, s) and 7.20 –7.85 (4H, m)

MS (m/z): 150, 145, 119.

What is the probable structure of the compound?

OR

- b) Discuss the terms:
 - i) Lanthanide shift reagents and
 - ii) CIDNP.
- 29. a) Write short notes on:
 - i) MALDI and

ii) El.

OR

- b) What are the common methods for the simplification of complex spectra in NMR spectroscopy? Explain with suitable examples.
- 30. a) Explain the synthesis strategies for the synthesis of indole and benzofurans citing examples.

OR

b) Describe the methods of synthesis of selenophanes, tellurophanes and naphthyridines. (4×6=24)