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#### FAROOK COLLEGE (AUTONOMOUS), KOZHIKODE

### Third Semester M.Sc Degree Examination, November 2018 MCHE3B09 – Molecular Spectroscopy

(2016 Admission onwards)

Max. Time: 3 hours Max. Weightage: 36

# Part A (Answer all questions. Each question carries 1 Weightage)

- 1. Explain the relevance of Heisenberg's uncertinity principle in predicting the line width of spectrum.
- 2. Explain the Raman activity of the various modes of vibrations of pyramidal AB<sub>3</sub> molecules.
- 3. Explain why the Stock's lines are more intense than antistock's lines in Raman scattering?
- 4. What are overtones and combination bands in IR spectroscopy?
- 5. Comment on the differences between the scales in <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.
- 6. NO shows a Q branch in the vibration-rotation spectrum. Why?
- 7. How many NMR energy levels are possible for nucleus with a spin I=3/2?
- 8. Predict the EPR spectrum of the following radicals (a) <sup>12</sup>CF<sub>2</sub>H (b) <sup>13</sup>CF<sub>2</sub>H.
- 9. m- nitrophenol in neutral solution absorbs at 330nm while in alkaline solution absorbs at 380nm, in contrast p-nitrophenol has absorption maximum at 320nm in neutral solution and 400 nm in alkaline solution. Explain.
- 10. How will you confirm the conversion of benzene to cyclohexane with <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy?
- 11. How IR spectroscopy is used in identifying the nitro and cyano groups?
- 12. Explain Cotton effect.

 $(12 \times 1 = 12 \text{ Weightage})$ 

# Part B (Answer any eight questions. Each carries 2 Weightage)

13. In a given organic compound two kinds of protons exhibit signals at 50Hz and 200Hz using a 60MHz instrument. What will be their relative position using 90MHz instrument? Also convert the position of signals into delta scale.

14. Apply 1H NMR and 13C NMR spectroscopic techniques and explain how will you confirm the following oxidation conversions. Explain all characteristic features of the <sup>1</sup>H NMR and <sup>13</sup>C NMR of the substrates and the products.

a) 
$$CH_3 - CH_2 - CH_2 - OH \rightarrow CH_3 - CH_2 - CHO$$
  
b)  $CH_3 - CH(OH) - CH_3 \rightarrow CH_3 - CO - CH_3$ 

- 15. Explain Nuclear Overhauser effect based on cross polarization theory and its application in NMR.
- 16. The rotational spectrum of <sup>79</sup>Br<sup>19</sup>F shows a series of equidistant lines separated by 0.71433 cm<sup>-1</sup>. Calculate the rotational constant, moment of inertia and Br-F bond length.
- 17. Explain the various factors affecting the intensity of spectral line.
- 18. Explain McLafferty rearrangement in mass spectrometry.
- 19. Explain Karplus Equation. How it is used in structure determination?
- 20. Sketch the approximate <sup>1</sup>H NMR and <sup>13</sup>C NMR and mass spectra of 2-butanone. Explain the spectral features.
- 21. Explain Nitrogen rule and Rule of Thirteen in mass spectrometry.
- 22. Explain Off- resonance and noise decoupled spectra in NMR.
- 23. Explain the factors contributing to chemical shift in NMR spectroscopy.
- 24. Explain with energy level diagram, the quadrupolar splitting in Mossbauer spectroscopy. (8  $\times$  2 = 16 Weightage)

#### Part C

(Answer any two questions. Each carries 4 Weightage)

- 25. Define and explain quantum mechanically spin-spin coupling to first order approximation. Using tree diagram method explain AX, AX<sub>2</sub>, AX<sub>3</sub>, A<sub>2</sub>X<sub>3</sub>, and AB type coupling.
- 26. a)Discuss the use of chemical shift values in obtaining stereochemical information in proton NMR.
  - b) Predict the structure of the compound with the following spectral characteristics: Molecular formula:  $C_8H_{10}O$ ; IR peaks at 3010, 2870, 1605, 1510, 1005 and 805cm<sup>-1</sup>; NMR  $\delta$  = 2.25 singlet (3H); 3.72 singlet (3H); 6.78 doublet (2H); 7.05 doublet (2H).
- 27. Explain
  - a) Classical and Quantum theory of Raman effect
  - b) P,Q and R branches of rotation vibration spectrum.
- 28. Explain
  - a) DEPT and INEPT in NMR
  - b) Determination of T1 and T2 (relaxation time) in FT NMR

 $(2 \times 4 = 8 \text{ Weightage})$ 

M3N18137	(Pages: 2)	Reg. No:
		Name:

#### FAROOK COLLEGE (AUTONOMOUS), KOZHIKODE

### Third Semester M.Sc Degree Examination, November 2018 MCHE3B10 – Organometallic & Bio inorganic Chemistry

(2016 Admission onwards)

Max. Time: 3 hours Max. Weightage: 36

#### Section A

#### (Answer all questions. Each question has 1 Weightage)

- 1. Identify the coordination sites in phenylalanine.
- 2. Explain the term co-operativity in haemoglobin.
- 3. Write the name of an enzyme which contain Zn (II) and explain its function.
- 4. Predict the structure of  $[Os_4N(CO)_{12}]$  based on PSEPT.
- 5. Write an example each for insertion reactions of CO and alkenes.
- 6. Give the structure and function of cytochrome  $P_{450}$ .
- 7. What is meant by hapticity? What hapticities are possible for 1, 4-butadiene?
- 8. How is Ziese's salt synthesised?
- 9.  $V(CO)_6$  does not dimerize to form 18electron analogous to  $Mn_2(CO)_{10}$ . Why?
- 10. Write the preparation method for a dihydrogen organometallic compound.
- 11. Draw the structure of
  - (a) Co2(CO)8
  - (b) Co<sub>4</sub>(CO)<sub>12</sub>
- 12. What are naked clusters? Write examples.

 $(12 \times 1 = 12 \text{ Weightage})$ 

# Section B (Answer any 8 questions. Each question carries 2 Weightage)

- 13. How do the structure and functions of haemoglobin differ from those of myoglobin?
- 14 State and explain 18-electron rule as applied to organometallic compounds.
- 15. How carbenes are prepared? Differentiate the structure between Fischer and Schrock

carbenes.

- 16. Describe the synthesis and structure of metal alkyne complexes.
- 17. Explain the mechanism of polymerisation of ethylene in presence of Ziegler-Natta catalyst.
- 18. Comment on the structure and functions of hemocyanin.
- 19. Discuss the structure and functions of superoxide dismutase.
- 20. Draw the catalytic cycle for Cativa process and explain the various steps involved.
- 21. Discuss the bonding present in metal carbonyl complexes?
- 22. Write an account of the classification of organometallic compounds.
- 23. Explain the CO insertion occurs into [MeMn (CO)<sub>5</sub>]. Is it a true insertion reaction? Support your answer with experimental evidences.
- 24. Draw the catalytic cycle for Wacker process and explain the various steps involved.

 $(8 \times 2 = 16 \text{ Weightage})$ 

# Section C (Answer any 2 questions. Each question carries 4 Weightage)

- 25. Explain the photosynthetic process, bringing out the functions of photosystem I and photosystem II.
- 26. How is ferrocene synthesised? Discuss its structure and reactivity.
- 27. How can we prepare dinitrogen complexes of Ru and Co? Explain the bonding modes of dinitrogen in transition metal complexes. Discuss the role of dinitrogen complexes in nitrogen fixation.
- 28. Describe the catalytic cycle and mechanism of the reactions involved in Oxo process.

 $(2 \times 4 = 8 \text{ Weightage})$ 

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#### FAROOK COLLEGE (AUTONOMOUS), KOZHIKODE

### Third Semester M.Sc Degree Examination, November 2018 MCH3B11 - Organic Transformations & Reagents

(2016 Admission onwards)

Max. Time: 3 hours

Max. Weightage: 36

# Section A Answer all questions Each question carries a Weightage of 1.

- 1. What is the use of CrO<sub>3</sub>-pyridine reagent in organic synthesis?
- 2. Give the mechanism of Swern oxidation reaction.
- 3. What is the use of Wolff Kishner reaction? Show the mechanism of the reaction.
- 4. Show the reaction and reagents in Noyori asymmetric hydrogenation.
- 5. What is Peterson reaction?
- 6. What is DIEA. Give a reaction using DIEA as a base.
- 7. Write down the mechanism of free radical polymerization?
- 8. What is meant by the secondary structure of a protein?
- 9. Give the synthesis of guanine.
- 10. Show the mechanism of Schmidt rearrangement.
- 11. Give any method for the synthesis of imidazole.
- 12. What is Fries rearrangement?

 $(12 \times 1 = 12 \text{ Weightage})$ 

#### **SECTION B**

# Answer any eight questions Each question carries a Weightage of 2.

- 13. Discuss Dess Martin oxidation reaction.
- 14. Write a note on the dihydroxylation of alkenes using OsO<sub>4</sub> and MnO<sub>4</sub> ion
- 15. Discuss the advantages and mechanism of Birch reduction.
- 16. a) Give the product of the reaction?

b) Predict a general mechanism of the above types of reactions.

- 17. What are the synthetic applications of 1,3 dithiane.
- 18. Discuss the reactivity of LiAlH<sub>4</sub> and LiBH<sub>4</sub> in reduction reactions.
- 19. Discuss the structure of RNA.
- 20. What is the role of protecting groups in the sequence determination of proteins? Illustrate with example.
- 21. Show the synthesis and reactions of imidazole and oxazole.
- 22. How can we synthesize uracil and thymine?
- 23. What is the organic rearrangement reaction useful in the conversion of nicotinic acid to 3-amino pyridine? Show the reaction.
- 24. Write a note on Heck reaction? Discuss the mechanism.

 $(8 \times 2 = 16 \text{ Weightage})$ 

#### SECTION C

### Answer any two questions Each question carries a Weightage of 4.

- a) Give the mechanism for heterogeneous catalyzed hydrogenation reaction b)
  Discuss the reduction of carbonyl groups using i) hydrazine ii) diimide and iii)
  semicarbazide.
- 26. Write a short note on
  - a) PTC
  - b) conversion of cellulose to rayon and
  - c) synthetic rubber
- 27. Give the mechanisms of Negishi, Sonogashira and Suzuki reactions.
- 28. a) Give the synthesis and reactions of Lithium dimethyl cuprate.
  - b) Write a note on the use of Pb(OAc)<sub>4</sub> in organic synthesis

 $(2 \times 4 = 8 \text{ Weightage})$ 

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### FAROOK COLLEGE (AUTONOMOUS), KOZHIKODE

### Third Semester M.Sc Degree Examination, November 2018 MCHE3E01 – Synthetic Organic Chemistry

(2016 Admission onwards)

Max. Time: 3 hours

Max. Weightage: 36

### Section A (Answer all questions. Each question carries 1 Weightage)

1. Give the uses of PCC as an oxidizing agent in organic synthesis?

2. Compare the stereochemistry of the reduction of epoxides using LiAlH<sub>4</sub> and alanes with suitable examples?

3. Complete the following reaction?

4. Explain how the following conversion can be carried out?

5. Give a synthetic route for the conversion of an aromatic aldehyde in to an  $\alpha$ ,  $\beta$  unsaturated acid?

6. Comment an example for the use of silylating reagent for selective protection of a functional group in organic synthesis?

7. How will you carry out the following reaction?

8. Write two important reaction where palladium catalyst can be used for C-O bond formation?

9. Discuss regioselectivity with respect to Michael reaction?

10. Discuss retrosynthetic analysis of following compound?

11. Explain synthesis and reaction of Tetrazole?

12. Write the structure of Vitamin C?

 $(12 \times 1 = 12 \text{ Weightage})$ 

# Section B (Answer any 8 questions. Each question carries 2 Weightage)

- 13. Explain the Woodward and Prevost oxidation of alkenes with stereochemistry and mechanism?
- 14. Briefly discuss the synthetic applications of alkyl boranes?
- 15. Write the reaction with mechanism of
  - (a) Stork enamine reaction
- (b) Robinson annulation
- 16. What are the requirements for a protecting group. Illustrate the use of the following as protecting group in organic synthesis?
  - (a) BOC group
- (b) CBZ group
- 17. How will you compare the reactivity of carbonyl groups in aldehydes, ketones and carboxylic acids?
- 18. Explain Heck reaction with mechanism and synthetic applications?
- 19. Outline retrosynthetic analysis and synthesis of the following compounds?

- 20. Discuss the structure, synthesis and reactions of
  - (a) Benzofuran
- (b) Benzimidazole
- 21. Explain with mechanism and applications.
  - (a) Wacker oxidation (b) Birch reduction
- 22. Discuss the synthetic utility of Gilman Reagent for C-C bond forming reactions?
- 23. Write briefly the mechanism and synthetic applications of palladium catalyzed amin earylation reaction?
- 24. Discuss one group C-X disconnections in detail?

 $(8 \times 2 = 16 \text{ Weightage})$ 

### Section C (Answer any 2 questions. Each question carries 4 weightage)

- 25. Explain the reaction and mechanism of following reactions?
  - (a) Aldol reaction
  - (b) Dieckmann reaction
  - (c) Mannich Reaction
  - (d) Claisen Reaction
- 26. Explain the following coupling reactions with mechanism.
  - (a) Sonogashira coupling
  - (b) Negishi Coupling
  - (c) Suzuki-Miyaura Coupling
  - (d) Stillecarbonylative coupling
- 27. Explain protection and deprotection methods of
  - (a) Alcohols
- (b) Carboxylic group
- 28. Illustrate the synthetic utility of following reagents
  - (a) IBX
  - (b) Aluminiumisopropoxide
  - (c) Metal hydrides
  - (d) Hydrazine.