| 2M3N21247 | (Pages: 3) | Reg. No: |
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| | | Name: |

FAROOK COLLEGE (AUTONOMOUS), KOZHIKODE

Third Semester M.Sc Degree Examination, November 2021

MCH3C09 - Molecular Spectroscopy

(2019 Admission onwards)

Time: 3 hours Max. weightage: 30

Section A: Short Answer Answer 8 Questions out of 12. Each question carries a weightage of 1

- Find the rotational quantum number corresponding to the maximum intensity in the microwave spectrum of HCI. Rotational constant B=10.5 cm⁻¹.
- Write the number of fundamental vibrational frequencies in the IR spectrum of CO₂ and H₂O molecules.
- 3. What do you meant by resonance Raman spectrum? Explain.
- 4. Discuss Franck-Condon principle.
- 5. Briefly discuss T_1 and T_2 relaxation.
- 6. How many ESR lines are possible for NH₂D radical.
- How will you differentiate the following two compounds by IR spectroscopy.
 C₆H₅-CO-OCH₃ and CH₃-CO-OC₆H₅
- 8. Trans stilbene has higher λ_{max} and E_{max} than cis stilbene. Account for this?
- 9. Based on ¹H NMR how we will able to differentiate o-hydroxyacetophenone from p-hydroxyacetophenone.
- How will you differentiate isomeric xylenes by proton decoupled ¹³C NMR spectroscopy.
- Differentiate between 3-methylcyclohexene and 4-methylcyclohexene by using mass spectrometry.
- 12. State and explain axial haloketone rule.

 $(8 \times 1 = 8 \text{ weightage})$

Section B: Short Essay Answer 4 Questions out of 7. Each question carries a weightage of 3

| 13. | (a) Derive the expression for the rotational energy of a symmetr | ic top molecule and |
|-----|--|--|
| | explain the selection rules. | (2 weightage) |
| | (b) How are IR and Raman spectroscopies are complimentary to | each other? |
| | | (1 weightage) |
| 14. | (a) HCl shows IR absorption at 2990 cm ⁻¹ . Find the force consta | nt. (2 weightage) |
| | (b) Explain the concept of dissociation with illustration. | (1 weightage) |
| 15. | (a) Explain electronic spectra of conjugated molecules. | (2 weightage) |
| | (b) Differentiate between fundamental and overtone bands. | (1 weightage) |
| 16. | (a) Discuss Nuclear Overhauser Effect using suitable example as | nd illustrate its |
| | application. Explain NOE difference spectrum. | (2 weightage) |
| | (b) Write McConnell equation. Explain the terms | (1 weightage) |
| 17. | (a) An organic compound with molecular formula C7H8 shows the | ne following |
| | absorption bands in the IR spectrum in cm ⁻¹ . 3060, 3040, 2918, | 1500,750 cm ⁻¹ . |
| | Deduce the structure of the compound. | (2 weightage) |
| | (b) How solvent polarity determine the position and intensity of | electronic |
| | absorption bands. | (1 weightage) |
| 8. | (a) Deduce the molecular structure from the following data | |
| (| i) Mol. Formula- C ₉ H ₁₀ O ₂ | |
| (| ii) IR- (i) 1720 cm ⁻¹ , 1602 cm ⁻¹ , 1581 cm ⁻¹ , 1270 cm ⁻¹ , 1105 c | m ⁻¹ |
| (| iii) 1 H NMR (i) δ - 1.29 , 3H, t, J =8 Hz (ii) 4.35 , 2H, q, J =8 H | Iz, (iii) 7.40, 3H, m |
| | (iv) 8.81, 2H, m. (2 | weightage) |
| (| b) Discuss the effect of chemical exchange in NMR pattern with e | xamples. |
| | (1) (1) The property of the second of the se | weightage) |
| 9. | (a) How can we differentiate isomeric compounds with molecular | formula C ₅ H ₁₀ O |
| t | by mass spectrometry | 2 weightage) |
| (| b) Discuss HMBC spectroscopy. | (1 weightage) |
| | and the state of t | ing paratel [1] |
| | . (4) | x 3 = 12 weightage) |

Section C: Essay Answer 2 Questions out of 4. Each question carries a weightage of 5

- 20) (a) Deduce the structure and stereochemistry of the compound from the following spectral data. Explain the pattern of each and every signals with suitable explanation.
 - (i) IR-1650 cm⁻¹
 - (ii) 1 H NMR δ (ppm)- 2.4 (s, 3H), 6.8 (d, J= 16 Hz, 1H), 7.5 (m, 5H), 7.6 (d, J= 16 Hz, 1H, overlapping)
 - (iii) 13 C NMR- δ (ppm) 27.1, 127.1, 128.2, 129.0, 130.0, 135.0, 144.2, 198.0.
 - (iv) Mass- m/z- 146, 131, 103

(3 weightage)

- (b) Explain off-resonance and noise decoupled spectra with examples (2 weightage)
- 21 (a) Outline the relative advantages of ORD and CD in solving organic chemical problems. (2 weightage)
 - (b) Discuss McLafferty rearrangement in MS with suitable examples. (2 weightage)
 - (c) Briefly discuss Woodward Fieser rules for calculating absorption maxima of enones
 (1 weightage)

rospony in detail

- 22. (a) Explain the theory and applications of electron spin resonance spectroscopy in detail by selecting different compounds. (3 weightage)
 - (b) Discuss the quantum theory of Raman effect in detail

(2 weightage)

23. (a) Explain P, Q and R branches of rotation vibration spectrum

(2 weightage)

- (b) Discuss electric, quadrupole and magnetic hyperfine interactions in Mössbauer Spectroscopy. (2 weightage)
- (c) Explain the determination of bond length using microwave spectral data.

(1 weightage)

| 27 | 121 | 2.1 | 3 | 10 |
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FAROOK COLLEGE (AUTONOMOUS), KOZHIKODE

Third Semester M.Sc Degree Examination, November 2021

MCH3C10 - Organometallic & Bioinorganic Chemistry

(2019 Admission onwards)

Time: 3 hours

Max. weightage: 30

Section A: Short Answer Answer any 8 questions out of 12. Each question carries a weightage of 1

- 1. Draw the structure of Fe(CO)₅ and Fe₂(CO)₉
- 2. Give the preparation and structure of Ziese's salt.
- 3. What is hapticity? What hapticities are possible for allyl group with transition metal atom?
- 4. Write a note on fullerene complexes.
- 5. What is Collman's reagent? What is its application?
- 6. What are higher carbonyl clusters?
- 7. What are 'naked' clsters? Discuss their structures.
- 8. What is meant by isolobal analogy?
- 9. What is the significance of Hill constant?
- 10. Explain the activity of hemocyanin.
- 11. Define active and passive transport of ions across membranes.
- 12. Define entatic state. What is its necessity in metalloenzymes?

 $(8 \times 1 = 8 \text{ weightage})$

Section B: Short Essay Answer any 4 questions out of 7. Each question carries a weightage of 3

- 13. Compare the characteristics of Fischer type and Shrock type carbene complexes with examples.
- 14. Describe the molecular orbital representation of the structure of ferrocene.
- 15. Discuss the bonding in alkyne complexes.
- 16. Explain Monsanto acetic acid process using catalytic cycle.

- 17. Explain the rules for predicting the skeletal structures of high nuclearity and low nuclearity carbonyl clusters.
- 18. Discuss the structure of [Re₂Cl₈]²⁻ on the basis of molecular orbital theory.
- 19. Explain the role of Mg in chlorophyll molecule.

 $(4 \times 3 = 12 \text{ weightage})$

Section C: Essay Answer any 2 questions out of 4. Each question carries a weightage of 5

- 20. Discuss the preparation and bonding of metal-dihydrogen and metal-dinitrogen complexes.
- 21. With suitable examples, discuss the oxidative addition and reductive elimination reactions involving organometallic compounds.
- 22. Explain the structure of myoglobin and haemoglobin. Discuss the role and mechanism of action of these molecules in biological system.
- 23. What are metalloenzymes and metal- activated enzymes? Describe the function of following metalloenzymes in biological system
 - (i) cytochrome P-450, and (ii) carboxypeptidase

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FAROOK COLLEGE (AUTONOMOUS), KOZHIKODE

Third Semester M.Sc Degree Examination, November 2021

MCH3C11 - Reagents and Transformations in organic chemistry

(2019 Admission onwards)

Time: 3 hours

Max. weightage: 30

Section A: Short Answer Answer 8 Questions out of 12. Each question carries a weightage of 1

- 1. What is Sharpless asymmetric dihydroxylation reaction?
- Emphasising mechanism, explain briefly how Noyori asymmetric hydrogenation becomes useful in enantioselective reduction of ketones.
- 3. Complete the following reaction sequence. Identify each reaction and draw the mechanisms.

- 4. What is McMurry coupling?
- 5. What are β -cyclodextrins? Mention its important synthetic applications.
- 6. What is Ziegler-Natta polymerisation? Mention their advantages.
- 7. Give a synthetic route for the dipeptide, glycylvaline.

Glycylvaline

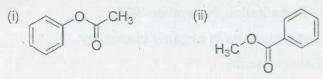
- 8. Write the structure of following polymers and the corresponding monomer units involved.

- (i) PVC (ii) Teflon (iii) Buna-S (iv) Bakelite (v) Nylon-6,6
- 9. What are molecular receptors? Give any two examples.
- 10. Write all the possible products of the following reactions. Among the products, which one is obtained as the major product and why?

(i)
$$H_3C$$
 CH_3 + CHO + $2NH_3$ CHO

(ii) CH₃(CH₂)₄CH₂MgBr +
$$O$$
 1. diethyl ether 2. H₃O⁺

- 11. Illustrate supramolecular catalysis using an example.
- 12. Which of the following compounds will give you Fries rearrangement product? Justify your answer by giving the mechanism.



 $(8 \times 1 = 8 \text{ weightage})$

Section B: Short Essay Answer 4 Questions out of 7. Each question carries a weightage of 3

13. Illustrating mechanism, predict the major product of the following reactions. Indicate the stereochemistry in each case.

(i) 0s0, (ii) OH MnO₂ NMO acetone H₂O/acetone

- 14. State and explain the synthetic importance of Bouveault-Blanc reduction.
- 15. Explain in brief the mechanism and characteristic features of MPV reduction?
- 16. Emphasising typical examples, discuss synthetic applications of:
 - (i) Crown ethers
- (ii) Diborane.
- 17. How do starch and cellulose differ in their structures? Explain.
- 18. A heptapeptide on reaction with DNFB followed by hydrolysis produces N-DNP valine. The hydrolysis of peptide by carboxypeptidase enzyme releases glutamic acid. The partial hydrolysis of peptide gives the following fragments:
 - (i) Pro Keu Val
- (ii) Ala Tyr Pro (iii) Keu Val Glu

- (iv) Val -Ala
- (v) Val Glu.

Identify the sequence of amino acids in the heptapeptide.

- 19. Explain the mechanisms of:
 - (a) Benzil-benzilic acid rearrangement reaction (b) Bayer-Villiger oxidation reaction.

 $(4 \times 3 = 12 \text{ weightage})$

Section C: Essay Answer 2 Questions out of 4. Each question carries a weightage of 5

- 20. (a) Describe the mechanism and synthetic applications of:
 - (i) Sharpless asymmetric epoxidation
- (ii) Riley reaction
- (iii) Swern oxidation reaction
- (iv) Woodward dihydroxylations
- (v) Dess- Martin oxidation.

21. Giving mechanism, complete the following reactions.

(iv) O HO-CH₂-CH₂-OH A
$$\stackrel{1. \text{ NaNH}_2, \text{ NH}_3}{2. \text{ CH}_3\text{I}}$$
 B $\stackrel{\text{H}_2\text{O}}{\text{HCI}}$ C

- 22. Explain any two synthetic methods for the following.
 - (i) Adenine

- (ii) Guanine (iii) Uracil (iv) Thymine (v) Aziridine.
- 23. Explain the mechanism and synthetic applications of:
 - (i) Negishi coupling reaction
- (ii) Orton rearrangement reaction

(iii) Peterson reaction

- (iv) Lossen rearrangement reaction
- (v) Demjanov rearrangement reaction.

| 2M3N21250 | (Pages: 3) | Reg. No: |
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FAROOK COLLEGE (AUTONOMOUS), KOZHIKODE

Third Semester M.Sc Degree Examination, November 2021 MCH3E01 – Synthetic Organic Chemistry

(2019 Admission onwards)

Time: 3 hours Max. weightage: 30

Section A: Short Answer Answer 8 Questions out of 12. Each question carries a weightage of 1

- Give examples of chromium based oxidants for selective oxidation of alcohols to aldehydes?
- 2. Write down the mechanism of Wacker oxidation of alkenes to ketones.
- 3. Highlight the synthetic utility of Tri-n-butyl tin hydride reagent.
- 4. Give an example for Pd-catalyzed amine arylation reaction.
- Chlorobenzene is normally unreactive towards methoxide ion, whereas the tricarbonyl chromium complex of chlorobenzene undergoes substitution of chlorine by methoxide. Explain.
- 6. Give the application of SeO₂ reagent in organic synthesis.
- 7. How will you bring about the following conversion successfully using a suitable protecting group?

- 8. What are Synthons? Suggest synthetic equivalents for the synthons R⁻ and +CH₂OH.
- Using disconnection approach, design a suitable synthesis for the following molecule:

- 10. Write a brief note on the applications of Wilkinson's catalyst.
- 11. Suggest a method for the synthesis of Quinoline.
- 12. How will you establish that enolate anions are involved as intermediates in conjugate additins of lithium alkylcuprates?

 $(8 \times 1 = 8 \text{ weightage})$

Section B: Short Essay Answer 4 Questions out of 7. Each question carries a weightage of 3

- 13. Write a descriptive note on chemoselectivity in metal hydride reductions.
- 14. What is Umpolung strategy in organic synthesis? Give examples of organic syntheses employing various umpolung reagents.
- 15. Write a descriptive note on the preparation and synthetic applications of organo silicon and boron reagents.
- 16. Explain the importance of protecting groups in organic syntheses. What are the major strategies of protection and regeneration of amino and alcohol functional groups?
- 17. (a) Explain two group C-C disconnections with respect to Diels-Alder reaction and 1,3-Difunctionalised compounds. (2 weightage)
 - (b) Discuss one-group C-X disconnections with suitable examples. (1 weightage)
- 18. Give general methods for the synthesis of the following heterocycles:
 - (a) Indoles
- (b) Azepines
- (c) Triazoles
- 19. Outline the Corey's synthesis of longifolene. Which step do you consider as the key step in this synthesis? Justify.

 $(4 \times 3 = 12 \text{ weightage})$

Section C: Essay Answer 2 Questions out of 4. Each question carries a weightage of 5

- 20. Discuss the importance of the following reactions in organic synthesis:-
 - (a) Woodward and Prevost hydroxylation reactions

(2 weightage)

(b) Sharpless asymmetric epoxidation

(2 weightage)

- (c) Dissolving metal reductions of aromatic and conjugated systems. (1 weightage)
- 21. Draw the structures of the products formed in the following reactions. Give the name of the reaction and explain the general mechanism of the reaction.

(a)
$$-Si$$
 $SnMe_3$ + OSO_2CF_3 $Pd(PPh_3)_4$ OSO_2CF_3 $Pd(PPh_3)_4$ $Pd(PPh_3)_4$

- 22. Highlight the synthetic applications of the following:-
 - (a) Dieckmann reaction
 - (b) Mannich reaction
 - (c) Stork-enamine reactions
 - (d) Phosphorous Ylides
 - (e) Phase transfer catalysts
- 23. (a) Discuss two-group C-C disconnections with reference to Michael addition and Robinson annulation. (3 weightage)
 - (a) Discuss the guidelines for choosing suitable disconnections in retrosynthetic analysis. (2 weightage)