

## FAROOK COLLEGE (AUTONOMOUS), KOZHIKODE

## Third Semester M.Sc Chemistry Degree Examination, November 2023

## MCH3C09 – Molecular Spectroscopy

(2022 Admission onwards)

Time: 3 hours

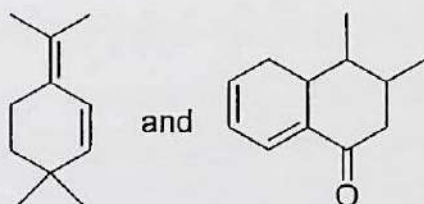
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## Section A Short Answer

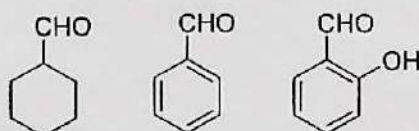
Answer 8 questions out of 12.

(Each question carries a weight of 1 (8×1 = 8))

1. Explain the relevance of Heisenberg's uncertainty principle in predicting the line width of the spectrum.
2. How will you distinguish enantiotopic and diastereotopic protons in  $^1\text{H}$  NMR spectroscopy?
3. Write a short note on NQR spectroscopy.
4. Write the Karplus equation. Draw the Karplus curve and highlight its importance.
5. Following the Woodward rules, calculate the expected  $\lambda_{\text{max}}$  value for the compounds given below.



6. What is the effect of substituting a hydrogen atom with a deuterium atom in a hydrogen molecule on rotational constant B?
7. State how many signals will arise in the  $^{13}\text{C}$  NMR spectrum of three isomeric ethers with the molecular formula  $\text{C}_4\text{H}_{10}\text{O}$ .
8. State and explain Frank Condon's principle.
9. What is meant by metastable ion peak in mass spectra?
10. Why are the Stoke's lines more intense than Anti-Stoke's lines in Raman spectra?
11. The following aldehydes exhibit carbonyl stretching bands at  $1666\text{ cm}^{-1}$ ,  $1700\text{ cm}^{-1}$ , and  $1730\text{ cm}^{-1}$ . Assign to the proper aldehyde giving justification:



12. In  $^1\text{H}$  NMR spectrum, aldehydic proton appears in the far downfield region ( $\delta = 9 - 10$  ppm). Explain.

(8×1 = 8 weightage)

**PART B**

*(Answer any 4 questions. Each question carries 3 weightage)*

13. Outline the principle of Mossbauer spectroscopy. Explain the application of this technique in the study of Fe (II) and Fe (III) cyanides.
14. Discuss the theory of ESR spectroscopy and explain the hyperfine splitting shown by NH radicals in its spectrum.
15. Explain Resonance Raman Spectroscopy. Mention its applications.
16. What is meant by coupling constant in NMR spectroscopy? Discuss various factors influencing coupling constant values.
17. Define the octant rule and explain its application in the determination of the absolute configuration of cyclohexanone compounds.
18. Highlight the application of DEPT as a spectroscopic technique to distinguish methyl, methylene, and methane protons.
19. Discuss briefly the principle and application of 2D COSY NMR.

**(4 × 3 = 12 weightage)**

**PART C**

*(Answer any 2 questions. Each question carries 5 weightage)*

20. (a) Explain the difference between first-order and non-first-order NMR spectrum with suitable examples. (2wt)
- (b) Briefly mention different chemical and instrumental methods for the simplification of a non-first-order NMR spectrum spectrum. (3 wt)
21. (a) Explain, with suitable illustration, the significance of McLafferty rearrangement in mass spectral analysis. (2wt)
- (b) The mass spectrum of toluene displays the following peaks:  $m/z$  92, 91, and 65. explain. (2wt)
- (c) Differentiate EI-MS from FAB-MS. (1wt)
22. Explain
  - (a) Classical and Quantum theory of Raman effect.
  - (b) Sketch and explain the P, Q and R branches of IR spectra of a diatomic molecule.
23. The compound with MF  $C_{10}H_{14}$  shows the following spectral data:
 

UV:  $\lambda_{max}$  265 nm ( $\epsilon_{max}$  450)

IR: 3030, 2970, 1600, 1515, 1465, and 813  $cm^{-1}$

$^1H$  NMR:  $\delta_{ppm}$  1.2 (d, 6H,  $J = 7$  Hz), 2.3 (s, 3H), 2.8 (Septet, 1 H,  $J = 7$  Hz), 7.1 (m, 4 H).

$^{13}C$  NMR:  $\delta_{ppm}$  21.3 (q), 24.2 (q), 39 (d), 126 (d), 128 (d), 139 (s), 155 (s)

Rationalize the spectral data and assign the structure to the compound.

**(2 × 5 = 10 weightage)**



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FAROOK COLLEGE (AUTONOMOUS), KOZHIKODE

Third Semester M.Sc Chemistry Degree Examination, November 2023

MCH3C10 – Organometallic & Bio Inorganic Chemistry

(2022 Admission onwards)

Time: 3 hours

Max. Weightage : 30

**Section A**

**Answer any 8 Questions**

**Each question carries a weightage of 1 (8X1 = 8)**

1. How could a complex of the empirical formula  $[\text{Cr}(\text{CO})_3(\text{C}_6\text{H}_5)_2]$  attain the 18-electron configuration?
2. What do you mean by sigma and pi-bonded organometallic compounds? Give examples.
3. Give two reactions of ferrocene, which shows that it is more reactive than benzene.
4. What are isolobal fragments? Is  $\cdot\text{CH}_3$  and  $[\text{Mn}(\text{CO})_5]$  isolobal? Comment.
5. Explain the magnetic behaviour of  $[\text{Re}_2\text{Cl}_8]^{2-}$ .
6. What is the product formed when  $[\text{Mn}(\text{CO})_5(\text{CH}_3)]$  reacts with  $^{13}\text{CO}$ ?
7. What is a metathesis reaction? Predict the possible products of metathesis between propene and 1-butene.
8. What is the role of the ethyl aluminium in the Ziegler Natta catalyst? How does a Ziegler Natta catalyst facilitate the conversion of ethene to a representative oligomer?
9. What types of organometallic moieties can be used as pendent groups? Compare the properties of these polymers with those of traditional organic polymers.
10. Explain the Perutz mechanism in the context of the oxygenation of *haemoglobin*.
11. Validate the role of  $\text{Mg}^{2+}$  in the activity of  $\text{Na}^+/\text{K}^+$  pump.
12. What are *cytochromes*? Give two examples.

**Section B**  
**Answer any 4 Questions**  
**Each question carries a weightage of 3 (4X3 = 12)**

13. Which among the following complexes  $[\eta^6-(C_6H_6)Cr(CO)_3]$ ,  $[(CO)_2Rh(\mu-Cl)_2Rh(CO)_2]$ , and  $[(\eta^5-Cp)Ni(\mu-PPh_2)_2Ni(\eta^5-Cp)]$ , obeys the 18-electron rule? Justify.
14. Comment on the carbonyl stretching frequencies in the following compounds:  
 $Ir(CO)_6^+$ ,  $Mn(CO)_6^+$ , and  $Os(CO)_6^+$
15. Find out the cluster type of  $Co_6(CO)_{13}N^-$  and  $Fe_5(CO)_{14}N^-$
16. Write a note on the mechanism involved and the factors that influence oxidative addition and reductive elimination reactions.
17. What are organometallic dendrimers? How are they prepared?
18. Show the binding of a protein chain to the active site of *carboxypeptidase A*, clearly indicating the supporting interactions.
19. Explain the role of metalloenzymes in relation to the shape of the active site. Give examples for *oxidase* and *superoxide dismutase*.

**Section C**  
**Answer any 2 Questions**  
**Each question carries a weightage of 5 (2X5 = 10)**

20. Show the difference in bonding between Fischer and Shrock carbenes with the help of orbital interaction. In which case will the  $M=C$  bond be shorter, and why?
21. With a catalytic loop, explain how could it be possible to oxidize a terminal alkene using palladium chloride? What is the role of copper chloride in this reaction?
22. Explain the preparation, properties, structure, and bonding of simple mono and binuclear metal carbonyls.
23. (a) Identify and explain the most preferred reaction pathway when the 'iron-porphyrin-pyridine' complex binds  $O_2$  irreversibly.  
(b) Schematically explain the binding of  $O_2$  as hydroperoxide at the active site of hemerythrin.



## FAROOK COLLEGE (AUTONOMOUS), KOZHIKODE

Third Semester M.Sc Chemistry Degree Examination, November 2023

MCH3C11 – Reagents &amp; Transformations in Organic Chemistry

(2022 Admission onwards)

Time: 3 hours

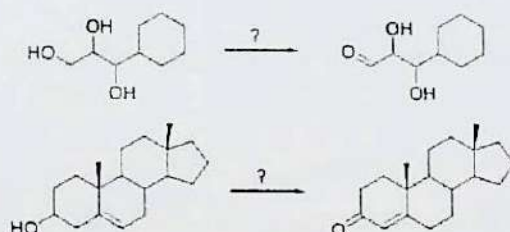
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## Section A Short Answer

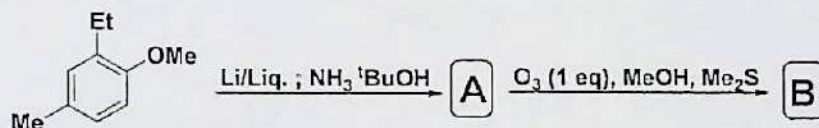
Answer 8 Questions out of 12.

Each question carries a weightage of 1 (8 X 1 = 8)

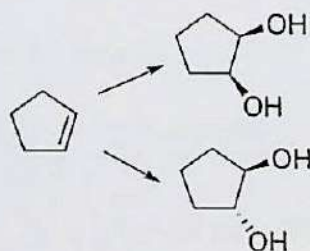
- 1) Suggest reagents for the following conversions



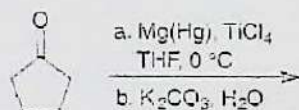
- 2) Predict the major products A and B in the following reaction sequence



- 3) How will you convert cyclohexanone to cyclohexane 1,2dione ?
- 4) Suggest reagents for the following synthetic transformations. Name the reactions, if any.

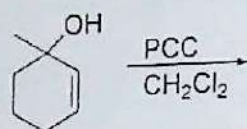


- 5) Illustrate the Bouveault–Blanc reduction using an appropriate example
- 6) Predict the product and identify the reaction



- 7) Illustrate the synthesis of imidazole from acetaldehyde

- 8) Predict the product for the following reaction



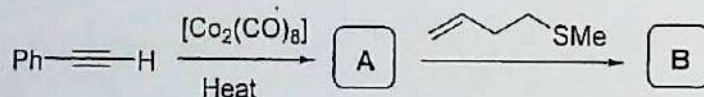
- 9) Draw the structures of Guanine and Thymine  
 10) Illustrate allylic bromination and allylic oxidation reaction using the specific reagents  
 11) What are crown ethers? Give examples.  
 12) Give two examples for the use of 1, 3 dithiane in organic synthesis

### Section B Short Essay

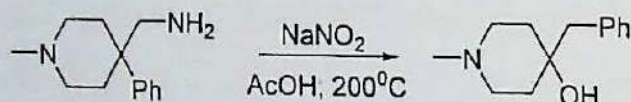
Answer 4 Questions out of 7.

Each question carries a weightage of 3 (4 X 3 = 12)

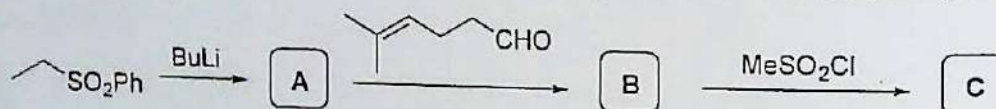
- 13) Discuss the mechanism of Swern oxidation. What are the advantages of this method?  
 14) Discuss the structure of (i) Proteins and (ii) DNA  
 15) Illustrate the Merrifield Solid phase peptide synthesis  
 16) Predict A and B in the following reaction sequence. Identify the reaction and give a mechanistic explanation for your prediction



- 17) Provide the mechanism for the following synthetic transformation



- 18) Predict A, B and C in the following reaction sequence. Name the reaction, if any



- 19) Briefly discuss the heterogeneous catalytic hydrogenation reactions

**Section B Essay**

**Answer 2 Questions out of 4.**

**Each question carries a weightage of 5 (2 X 5 = 10)**

- 20) Discuss the salient features of (i) Sharpless Asymmetric Epoxidation and (ii) Sharpless Asymmetric Dihydroxylation reactions
- 21) Discuss the synthetic applications of (i) Lead Tetraacetate and (ii) DCC and (iii) DDQ
- 22) Discuss the different methods for the synthesis of (i) Benzofuran (ii) Benzothiophene (iii) Benzothiazole and (iv) Benzimidazole
- 23) Discuss the mechanism underlying the Passerini and Ugi Multicomponent reactions and illustrate their synthetic applications



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FAROOK COLLEGE (AUTONOMOUS), KOZHIKODE

Third Semester M.Sc Chemistry Degree Examination, November 2023

MCH3E01 – Synthetic Organic Chemistry

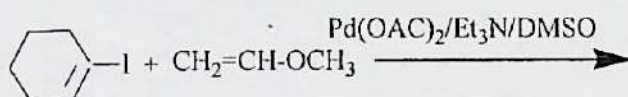
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Time: 3 hours

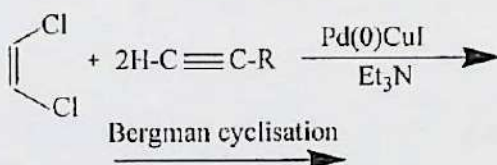
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**Section A Short Answer****Answer 8 Questions out of 12.****Each question carries a weightage of 1 (8 X 1 = 8)**

1. Explain hydroboration reaction taking suitable example
2. What is the use of periodic acid in organic synthesis ?
3. Complete the following reaction



4. Predict the product in the following reaction

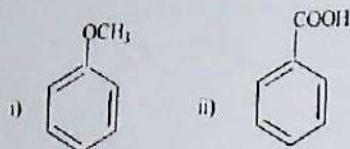


5. Explain Wacker oxidation reaction
6. What do you understand by the term activating groups in synthesis?
7. Illustrate umpolung reaction with suitable example.
8. How are terpenoids classified based on the structure?
9. Write a note on the classification of steroids.
10. Write about the stereochemical outcome of Sharpless asymmetric epoxidation reaction.
11. Explain Sonogashira coupling reaction with suitable example
12. What are flavonoids?



**Section B Short Essay**  
**Answer 4 Questions out of 7.**  
**Each question carries a weightage of 3 (4 X 3 = 12)**

13. Explain the mechanism of Swern oxidation reaction taking suitable example
14. What are the synthetic application of Tri-n-Butyl tin hydride and Benzene Tricarbonyl Chromium?
15. Explain the mechanism of Birch reduction, what is the major product formed when following compounds undergo Birch reduction



16. With suitable diagram explain the stereochemistry of heterogeneous catalytic hydrogenation reaction
17. What are the synthetic applications of Negishi and Hiyama coupling reactions?
18. Explain the disconnection approach in organic synthesis taking suitable example.
19. Discuss the general structure of Anthocyanin

**Section C**  
**Essay Answer 2 Questions out of 4.**  
**Each question carries a weightage of 5 (2X5 = 10)**

20. Explain the synthesis of longifolene
21. Illustrate the structure elucidation of atropine
22. Explain the role of following reagents in organic chemistry by taking at least two examples each.
- |                      |                        |                             |
|----------------------|------------------------|-----------------------------|
| i) PCC               | ii) per acids          | iii) aluminium isopropoxide |
| iv) lead tetracetate | v) Ruthenium tetroxide |                             |
23. Explain the Heck, Kumada and Suzuki- Miyaura coupling reactions.