

FAROOK COLLEGE (AUTONOMOUS), KOZHIKODE

Third Semester M.Sc Degree Examination, November 2020

MCH3C09 – Molecular Spectroscopy

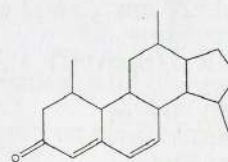
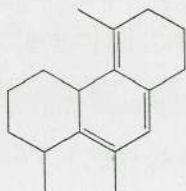
(2019 Admission onwards)

Time: 3 hours

Max. weightage : 30

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

1. Which of the following molecules are microwave active?
 CH_2Cl_2 , CHCl_3 , CH_4 , C_2H_2 , CO_2 , CCl_4
2. Discuss the selection rules for harmonic and anharmonic vibrations of a diatomic molecule.
3. The IR spectrum of CO shows an absorption band centred at 2170 cm^{-1} . Calculate the value of force constant.
4. Explain the concept of predissociation with illustration.
5. From the following nuclei which one has got highest gyromagnetic ratio and why?
 ^1H , ^3H , ^{13}C , ^{27}Al
6. How will you explain transition probabilities using Ladder operators.
7. Using Woodward Fieser rules, calculate the UV- λ_{max} of the following compounds.



8. Esters show higher $\text{C}=\text{O}$ stretching frequency than ketones. Is this statement true? Give suitable reason.
9. How will you distinguish methyl propionate from ethyl acetate by ^1H NMR spectroscopy.
10. The proton decoupled ^{13}C NMR spectrum of $\text{C}_6\text{H}_3\text{Br}_3$ gives only two signals. Write the suitable structure of the compound and explain why spectrum follows this pattern?
11. Which is the most abundant peak in the mass spectrum of toluene and how will you account this?
12. What information can be obtained by the application of octant rules to cyclohexanones. Illustrate with an example.

(8 x 1 = 8 weightage)

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

13. (a) Derive an expression for the allowed rotational energy levels of a diatomic molecule using rigid rotor model. (2 weightage)
(b) Briefly explain the different factors affecting the width and intensity of spectral lines. (1 weightage)
14. (a) From the value of O-H stretching frequency 3300 cm^{-1} calculate O-D stretching frequency. (2 weightage)
(b) Briefly discuss resonance Raman spectroscopy. (1 weightage)
15. (a) Discuss the Frank-Condon principle and its importance in understanding electronic transitions in a diatomic molecule. (2 weightage)
(b) Explain Karplus relationship. (1 weightage)
16. (a) Explain the principle and application of 2D-NMR COSY. (2 weightage)
(b) Discuss Zerofield splitting with a suitable example. (1 weightage)
17. Using spectral concepts how will you differentiate the following
(a) Cis and trans stilbene by UV spectroscopy. (1 weightage)
(b) Inter and intramolecular H-bonded compounds by IR spectroscopy. (1 weightage)
(c) Halogen compounds by mass spectrometry. (1 weightage)
18. (a) Deduce the molecular structure from the following data
Mol. Formula- $\text{C}_9\text{H}_{10}\text{O}_2$
IR- (i) 1720 cm^{-1} , 1602 cm^{-1} , 1581 cm^{-1} , 1270 cm^{-1} , 1105 cm^{-1}
1H NMR δ (ppm) (i) 1.29, 3H, t, $J=8\text{ Hz}$ (ii) 4.35, 2H, q, $J=8\text{ Hz}$,
(iii) 7.40, 3H, m
(iv) 8.81, 2H, m (2 weightage)
(b) Application of shift reagents for the simplification of NMR spectra (1 weightage)
19. (a) How will you distinguish the isomeric alcohols with $\text{C}_4\text{H}_{10}\text{O}$ by mass spectrometry (2 weightage)
(b) Discuss Nitrogen rule and Rule of Thirteen (1 weightage)

(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) UV- 284 nm, 308 nm
 - (ii) IR- 1690 cm^{-1}
 - (iii) ^1H NMR - δ (ppm)- 6.7 (dd, $J= 16\text{ Hz}, 8\text{ Hz}, 1\text{H}$), 7.40 (m, 5H), 7.45 (d, $J= 16\text{ Hz}, 1\text{H}$), 9.75 (d, $J= 8\text{ Hz}, 1\text{H}$)
 - (iv) ^{13}C NMR- δ (ppm) - 128.2, 128.3, 128.8, 131.0, 134.0, 152.0, 193.0.
 - (v) Mass- m/z - 132, 131, 103 (3 weightage)
- (b) Explain HMQC & DEPT spectra in detail (2 weightage)
21. (a) Give an account of the factors that affect the sign and amplitude of cotton effect curves. Illustrate how these parameters are useful in solving the configurational and conformational analysis of cyclic ketones. (2 weightage)
- (b) Illustrate with examples the utility of isotopic peaks in Mass spectra in the structural elucidation of organic molecules. (2 weightage)
- (c) Discuss briefly first order and non first order NMR spectra. (1 weightage)
22. (a) Explain the theory and applications of Mossbauer spectroscopy by choosing different coordination complexes. (3 weightage)
- (b) Discuss Electronic spectra of conjugated molecules using particle in a box model. (2 weightage)
23. (a) Explain quantum mechanical description of AX and AB NMR pattern. Also discuss the effect of relative magnitudes of spin-spin coupling and chemical shift on the spectrum of AB type molecule. (4 weightage)
- (b) Discuss the different factors affecting magnitude of g values. (1 weightage)

(2 x 5 = 10 weightage)

FAROOK COLLEGE (AUTONOMOUS), KOZHIKODE

Third Semester M.Sc Degree Examination, November 2020

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. Predict the structure of $W(CO)_2(C_5H_5)_2$ assuming that it obeys the 18 electron rule.
2. Differentiate between σ -allyl complexes and π -allyl complexes.
3. Explain the fluxionality of organometallic compounds with examples.
4. What is Ziese's salt? Give its structure.
5. What are the favourable factors for oxidative- addition reactions of organometallic compounds?
6. Draw the structures of (i) $W_4(OR)_{12}$ and (ii) Mo_6Cl_{12} .
7. What is meant by isolobal analogies?
8. Explain Chevrel phases?
9. Explain the terms cooperativity and Bohr effect.
10. What are bulk and trace metal ions in biological system?
11. Explain the function of transferrin.
12. What are the functions of the enzymes catalase and peroxidase?

(8 x 1 = 8 weightage)

Section B : Short Essay

Answer 4 Questions out of 7.

Each question carries a weightage of 3

13. Explain the bonding modes of dinitrogen in transition metal complexes.
14. Explain the nature of metal- ethylene interaction in transition metal- ethylene complexes.
15. Describe the molecular orbital representation of ferrocene.
16. Explain the Cativa process using catalytic cycle.
17. State and explain Wade- Mingos-Lauher rules.
18. Explain the formation of quadruple bonding in $[Re_2Cl_8]^{2-}$.
19. Describe the biological nitrogen fixation by nitrogenase.

(4 x 3 = 12 weightage)

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

20. Discuss the bonding present in metal carbonyl complexes. Explain the structure of $\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$ and $\text{Fe}_3(\text{CO})_{12}$.
21. Describe the mechanism of reactions involved in (i) Ziegler- Natta polymerizations and (ii) Fischer- Tropsch process using heterogeneous catalysis.
22. Explain the role of alkali metal ions in biological system. Discuss the mechanism of sodium/ potassium pump.
23. What is the role of Mg in chlorophyll? Describe the function of photosystem-I and photosystem-II in photosynthesis.

(2 x 5 = 10 weightage)

FAROOK COLLEGE (AUTONOMOUS), KOZHIKODE

Third Semester M.Sc Degree Examination, November 2020

MCH3C11 – Reagents and Transformations in organic chemistry

(2019 Admission onwards)

Time: 3 hours

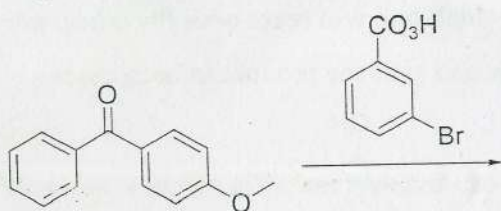
Max. weightage : 30

Section A: Short Answer

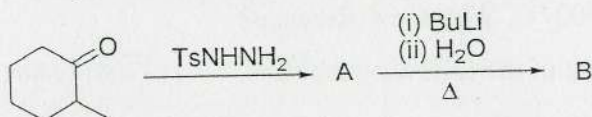
Answer 8 Questions out of 12.

Each question carries a weightage of 1

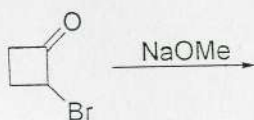
1. Outlining the mechanism, predict major product of the following reaction.



2. What is MPV reduction?
 3. Give the structure of 9-BBN. Illustrating an example, explain how does it dominate over diborane in organic syntheses.
 4. Complete and explain the reaction:



5. Give the structure of a crown ether. Briefly describe how it acts as a phase transfer catalyst?
 6. A tripeptide on partial acid hydrolysis gave two dipeptides containing Glu, Phe and Gly, Phe respectively. Treatment of the first with DNFB gave N-labelled glutamic acid and that of second gave N-labelled phenylalanine. What will be the sequence of amino acids in tripeptide? Also write the sequence for amino acids.
 7. Explain briefly any one of the methods for N-terminal amino acid analysis in protein sequencing.
 8. What are block and graft copolymers? Give one example for each.
 9. "Imidazole is an amphoteric compound, it is both more acidic and basic than alcohols and pyridine respectively." Validate the statement.
 10. Explain any one of the synthetic methods for oxiranes.
 11. What do you understand by the term 'molecular recognition'?
 12. Giving the mechanism find out major product of the following reaction.

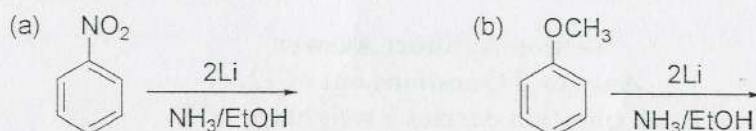


(8 x 1 = 8 weightage)

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

13. What is Sharpless asymmetric epoxidation reaction? Explain its mechanism.

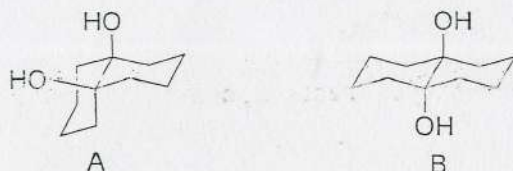
14. Complete the following reactions and comment on the formation of products.



15. What is Noyori asymmetric hydrogenation reaction? Elaborate its mechanism.

16. Among the following compounds A and B, which one will react with $\text{Pb}(\text{OAc})_4$ very easily?

Emphasizing mechanism, justify your answer and give the product in both cases.



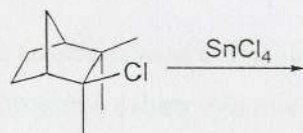
17. Explain the structure and synthesis of glutathione.

18. Why does polymerization occur only at relatively low temperatures often below $200\text{ }^\circ\text{C}$?

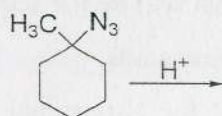
What occurs at higher temperatures? Formaldehyde polymerizes only below about $100\text{ }^\circ\text{C}$

but ethylene still polymerizes up to about $500\text{ }^\circ\text{C}$. Why the difference?

19. (a) Giving reason, find out the major product of the following reaction.



(b) Giving mechanism, predict the major product of the following reaction.



(4 x 3 = 12 weightage)

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

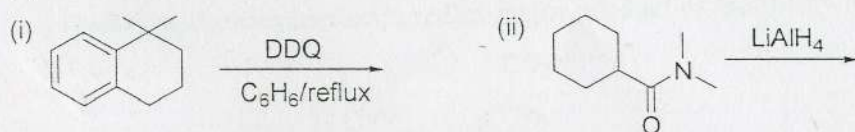
20. Elaborate the mechanism and synthetic applications of:

- (i) Dess- Martin oxidation (ii) Swern oxidation (iii) Riley reaction
 (iv) Sharpless asymmetric dihydroxylation (v) Jacobsen epoxidation.

21. (a) Giving examples, elaborate the synthetic applications of:

- (i) Gilman's reagent (ii) β -cyclodextrins (iii) ionic liquids.

(b) Illustrating mechanism, find out the major product of the reactions:



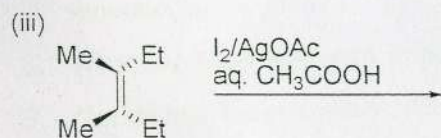
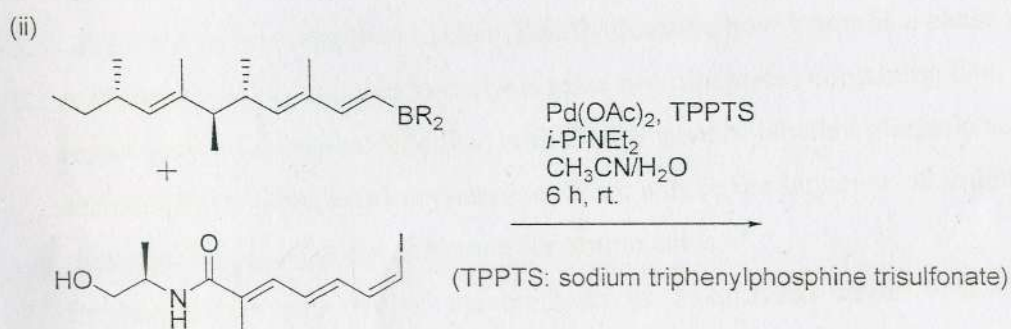
22. Write notes on:

- (i) Molecular receptors for different types of cations, anions and neutral molecules.
 (ii) The importance of H bonds in crystal engineering.
 (iii) Supramolecular photochemistry.

23. (a) Describe the mechanism and synthetic applications of:

- (i) Lossen rearrangement reaction (ii) Dienone-Phenol rearrangement reaction.

(b) Illustrating mechanism and stereochemistry, complete the following reactions.



(2 x 5 = 10 weightage)

FAROOK COLLEGE (AUTONOMOUS), KOZHIKODE

Third Semester M.Sc Degree Examination, November 2020

MCH3E01 – Synthetic Organic Chemistry

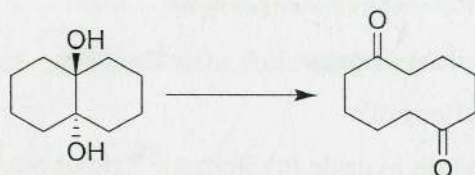
(2019 Admission onwards)

Time: 3 hours

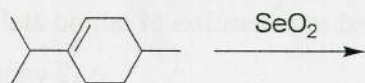
Max. weightage : 30

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

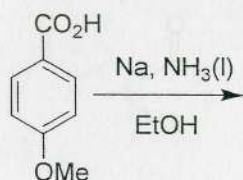
1. How will you accomplish the following conversion?



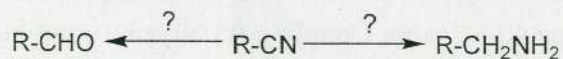
2. Predict the product of the following reaction:



3. Predict the product of the following reaction. How will you explain the formation of the product?

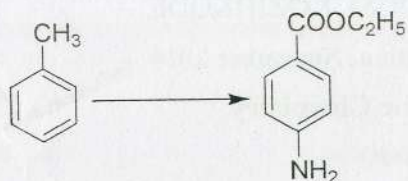


4. How will you carry out the following reactions using metal hydride based reagents?



- What is Mannich reaction? Give an example.
- Identify the product formed by hydroboration of $Me_3C-CH=CMe_2$ and subsequent alkaline peroxide oxidation of the alkylborane.
- What is the role of $CuCl_2$ in the Wacker oxidation reaction?
- Which other reactant, reagents and catalysts are needed to prepare $Ph-CH_2-CH=CH_2$ from $PhBr$ by stille coupling reaction?
- Suggest a synthetic method each for Tetrazoles and Oxadiazoles.
- Suggest a method for the synthesis of Quinoline.

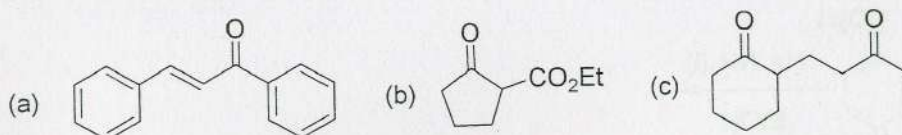
11. Explain the terms "Synthons" and "Synthetic equivalents" giving suitable examples.
 12. Propose a logical disconnection for the following synthetic transformation:



(8 x 1 = 8 weightage)

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

13. Give an account of Woodward and Prevost hydroxylation reactions.
 14. Explain the following in the context of organic synthesis:-
 (i) activating groups (ii) umpolungstrategy (iii) ylides
 15. Briefly discuss the synthetic applications of :-
 (a) Gilman's reagent (b) Tri-n-butyl tin hydride (c) Benzene Tricarbonyl Chromium
 16. (a) Highlight the importance of protecting groups in organic synthesis. (1 weightage)
 (b) What are the major strategies of protection and regeneration of amino and alcoholic functional groups? (2 weightage)
 17. How would you employ base-catalyzed reactions in the synthesis of the following compounds?.

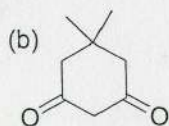
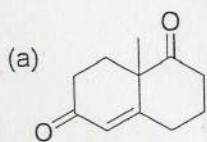


18. Explain the following Pd catalysed coupling reactions with mechanism
 (a) Sonogashira Coupling (b) Suzuki-Miyaura Coupling (c) Hiyama coupling
 19. Outline the synthesis of Vitamin C from D-Glucose.

(4 x 3 = 12 weightage)

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

20. Write an account of the catalysts used, their selectivity and the stereochemical outcome in homogeneous and heterogeneous catalytic hydrogenations.
21. Write notes on:
- (a) Combinatorial chemistry (1 weightage)
 - (b) Sharpless asymmetric epoxidation-Reagents and applications (2 weightage)
 - (c) Phase transfer catalysts – Principle and applications (2 weightage)
22. Discuss various steps of the retrosynthetic analysis of longifolene and outline the corresponding synthesis.
23. Explain the term retrosynthetic analysis. Propose a retrosynthetic analysis and sequences of reactions for the following target compounds.



(2 x 5 = 10 weightage)