

FAROOK COLLEGE (AUTONOMOUS), KOZHIKODE

Third Semester M.Sc. Chemistry Degree Examination, November 2019

MCHE3B09 – Molecular Spectroscopy

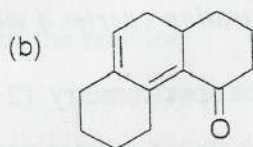
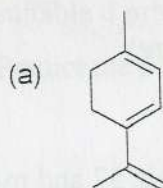
(2018 Admission onwards)

Max. Weightage: 36

Time: 3 hours

PART A*(Answer all questions. Each question carries 1 weightage)*

- Write a note on the use of Karplus equation in determination of vicinal coupling constant.
- Explain the relevance of Heisenberg's uncertainty principle in predicting the line width of spectrum.
- Explain cotton effect.
- What do you mean by 'Doppler broadening'?
- On the basis of Woodward-Fieser rules, calculate the expected position of absorption maximum for the following compounds:

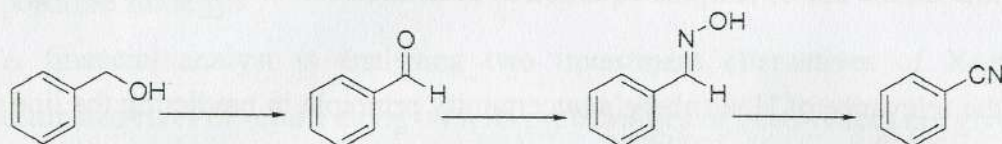


- Derive an expression for J_{\max} for the rigid rotor.
- What is the use of DEPT ^{13}C NMR spectra in structure determination of molecules?
- Describe the effect of hydrogen bonding on vibration frequency with a suitable example.
- State and explain Frank Condon principle?
- What is meant by metastable ion peak in mass spectra?
- Explain the term g-factor in ESR.
- How will you confirm the conversion of benzene to cyclohexane with ^1H NMR and ^{13}C NMR spectroscopy?

(12 × 1 = 12 weightage)**PART B***(Answer any 8 questions. Each question carries 2 weightage)*

- (a) The position of absorption of acetone varies in different solvents: 279 nm (hexane), 272 nm (Ethanol) and 264.5 nm (water). Explain.
(b) By taking suitable example explain how *cis* and *trans* isomers can be distinguished by UV spectroscopy.

14. Explain the factors contributing to chemical shift in NMR spectroscopy.
15. Write a critical note on Nuclear Overhauser Effect in NMR spectroscopy.
16. Give a brief account of the zero-field splitting in EPR spectrometry with proper example.
17. Outline the principle of Mossbauer spectroscopy. Explain the application of this technique in the characterization of compounds.
18. Discuss any two methods used for simplification of second order NMR spectra.
19. Discuss the basic principles of CD and ORD spectrometry.
20. How will you monitor the following reaction sequence by IR spectroscopy.



21. Give an account of different relaxation methods in NMR spectroscopic technique.
22. Explain the importance of isotope peaks in MS for structural elucidation.
23. Explain the effect of degeneracy on intensity of lines in rotational spectrum.
24. Briefly discuss the rotation spectrum of symmetric top molecule.

(8 × 2 = 16 weightage)

PART C

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

25. (a) Explain McLafferty rearrangement in mass spectrometry. (2 wt)
 (b) The mass spectrum of 4-methyl-1-hexene shows intense peak at m/z 57 and m/z 41. What fragmentation reaction account for these peaks? (2 wt)
26. Explain how 2D correlated spectroscopy is helpful in structural determination of molecules.
27. (i) Discuss the Quantum theory of Raman effect. Explain the criterion for the molecule to be Raman active. (2wt)
 (ii) What are normal modes of vibration of polyatomic molecule? Explain fundamental, overtone and combination bands. (2wt)
28. A compound exhibits the following spectral properties. Suggest the structure of the compound and explain the spectral data.
 MF: $C_7H_{12}O_3$; IR (cm^{-1}): 1734, 1720.
 1H NMR (δ , ppm): 4.2 (2H, q); 2.8 (2H, t); 2.6 (2H, t); 2.2 (3H, s); 1.2 (3H, t).
 ^{13}C NMR (δ , ppm): 205.3, 172.5, 60.8, 38.02, 28.2, 26.4, 12.1.

(2 × 4 = 8 weightage)

FAROOK COLLEGE (AUTONOMOUS), KOZHIKODE

Third Semester M.Sc. Chemistry Degree Examination, November 2019

MCHE3B10 – Organometallic & Bioinorganic Chemistry

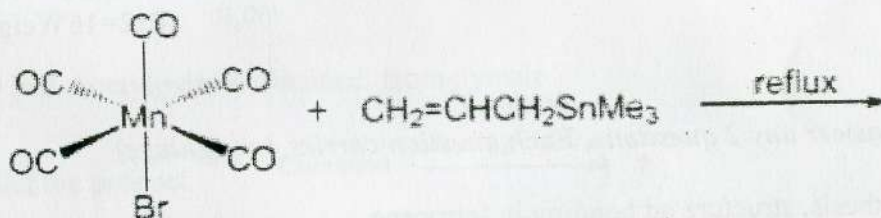
(2018 Admission onwards)

Time: 3 hours

Max. Weightage: 36

Section A*(Answer all questions. Each question has 1 weightage)*

- Determine metal-metal bond order using 18 electron rule?
A) $\text{Mn}_2(\text{CO})_5$ B) $[(\eta^5\text{-Cp})\text{Fe}(\text{CO})_2]_2$ C) $[\text{Pt}(\text{CO})_3]_2^{2+}$
- Even though $[\text{W}(\text{CO})_3(\text{PCy}_3)_2]$ is a 16 VE species but it is stable. Account for the stability?
- Specify the hapticities of the cyclopentadienyl ligand in $\text{Cp}_2\text{W}(\text{CO})_2$
- Identify which molecular orbitals of a butadiene moiety engage in π -interaction with a suitable d orbital of a metal in a η^4 -metal allyl complex?
- Predict the product of the reaction



- Comment on the number of π -electrons present in the cyclobutadiene moiety of a metal cyclobutadiene complex.
- Draw the structure of $\text{Fe}_2(\text{CO})_9$ and $\text{Mn}_2(\text{CO})_{10}$
- What are Zintl ions? Give examples?
- What is the function of SOD?
- Indicate the oxidation state of the copper ions and of the O_2 ligand in oxyhemocyanin.
- What single method: mass spec, UV-vis, NMR, microwave, or IR/Raman spectroscopy, would be best suited to verify the oxidation state of the O_2 ligand in oxyhemocyanin?
- Write short notes on anticancer drugs? **(12x1=12Weightage)**

Section B

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

13. Predict which of the complexes $[V(CO)_6]^-$, $[Cr(CO)_6]$, and $[Mn(CO)_6]^+$ has the shortest C-O bond? Explain?
14. Briefly explain Collman's reagent?
15. Sketch the pi molecular orbitals for the following. a) CO b) cyclobutadiene
16. The 1H NMR spectrum of $(C_5H_5)_2Fe(CO)_2$ shows two peaks of equal area at room temperature but has four resonances of relative intensity 5:2:2:1 at low temperature. Explain.
17. Explain Ziegler-Natta polymerizations
18. Explain Fischer-Tropsch process and water gas shift reaction.
19. Write short notes on Wade-Mingos-Lauher rules
20. What are the functions of Cytochrome P-450, catalase and peroxidase
21. Explain the term cooperativity in oxygen binding by haemoglobin.
22. Explain O_2 binding in hemerythrin.
23. Graphically compare the O_2 affinity of haemoglobin and myoglobin.
24. Explain the iron binding by transferrin.

(8x2=16Weightage)

Section C

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

25. Explain synthesis, structure and bonding in ferrocene.
26. Explain the bonding in $[Re_2Cl_8]^{2-}$
27. Explain the mechanism of Wacker process, Monsanto acetic acid process.
28. A) Explain Lewis acid role of Zn(II) and Mn(II) containing enzymes
B) Write short notes on Carboxypeptidase

(2 x 4=8 Weightage)

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Third Semester M.Sc. Chemistry Degree Examination, November 2019

MCHE3B11 – Organic Transformation & Reagents

(2018 Admission onwards)

Time: 3 hours

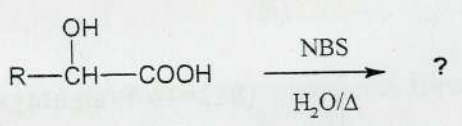
Max. Weightage: 36

Section A

Answer all questions

Each question carries a Weightage of 1.

1. What is Dess Martin Oxidation?
2. Give an example for Riley oxidation reaction.
3. Explain MPV reduction.
4. Illustrate the reduction reaction of carbonyl compounds with hydrazine using an example.
5. What is Gilman's reagent.
6. What is the product obtained for following reaction



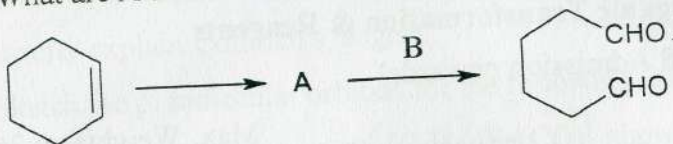
7. How is 2-Acetylpyrrole obtained from pyrrole?
8. Predict the product $\text{Quinoline} \xrightarrow{\text{Fuming H}_2\text{SO}_4} ?$
9. What are the advantages of Microwave reactions?
10. What are the different tools used for Green synthesis?
11. Give the structure and numbering of Cholesterol.
12. Suggest an example for a sesquiterpene and a diterpene.

(12x1=12 Weightage)

SECTION B

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

13. What are A and B ?



14. Explain Swern oxidation with mechanism.
15. Suggest reagent and mechanism for the conversion of benzophenone to diphenylmethane
16. Write a short note on Bouveault-Blanc reduction.
17. Write one synthetic application of Crown ether and Baker's Yeast.
18. Indicate the difference in reactivity given by LiAlH_4 and NaBH_4 .
19. Explain Fischer Indole synthesis with mechanism.
20. Suggest a synthetic approach for the preparation of Guanine.
21. Outline any one synthetic method for the preparation of Oxirane and Oxazole.
22. Suggest Green and Classical synthetic methods for Grignard reactions.
23. How are Steroids classified?
24. Write a short note on Flavonoids .

(8x2=16 Weightage)

SECTION C

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

25. Write a note on the following
 - a) Oxidative cleavage of alkene.
 - b) Baeyer-Villiger oxidation.
26. Explain McMurry coupling and Shapiro reaction.
27. Compare Aldol condensation and Cannizaro reactions with respect to Green and Classical reactions.
28. What is Mitsunobu reaction? Explain its mechanism.

(2x4=8 Weightage)

FAROOK COLLEGE (AUTONOMOUS), KOZHIKODE

Third Semester M.Sc. Chemistry Degree Examination, November 2019

MCHE3E01 – Synthetic Organic Chemistry

(2018 Admission onwards)

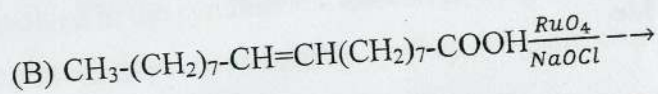
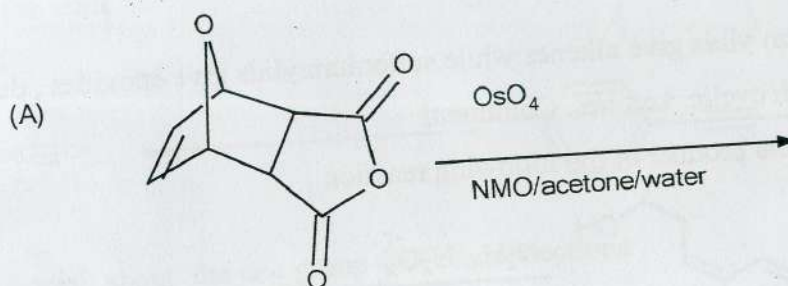
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Time: 3 hours

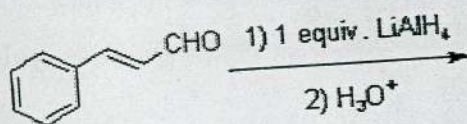
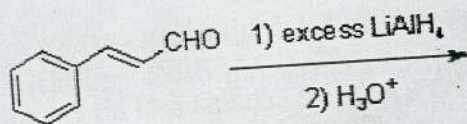
Section A

(Answer all questions. Each question carries 1 Weightage)

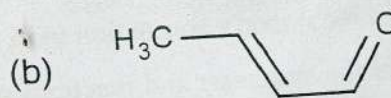
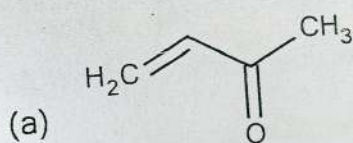
- Write down any two synthetic applications of Gilman's reagent.
- Write the product of the following reactions



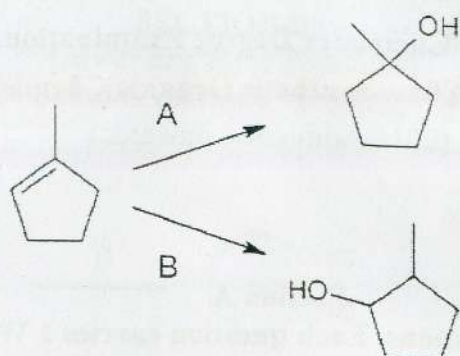
- What are the major products formed in the following reaction conditions?



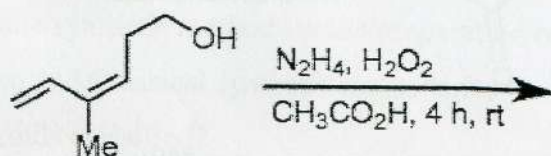
- How linear synthesis differ from convergent synthesis in retro synthetic chemistry?
- Give the method of synthesis of 1-Phenylbutan-1-one from bromopropane.
- Draw the product of the reaction with the enamine prepared from cyclopentanone and pyrrolidine, and the following molecules



- What is the disadvantage of using THP group for the protection of hydroxyl group?
- Write the reagents for the following conversions



- Explain the term 'chemo selectivity' with an example
- Write two important reactions where palladium catalyst can be used for C-N bond formation
- Phosphonium ylids give alkenes while sulfonium ylids give epoxides, during their reaction with cyclic ketones. Comment.
- Write down the product of the following reaction

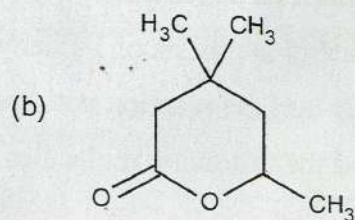
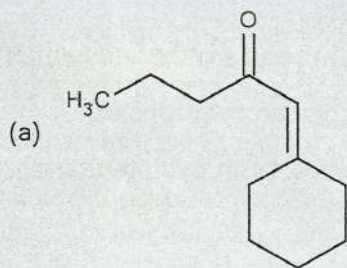


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Section B

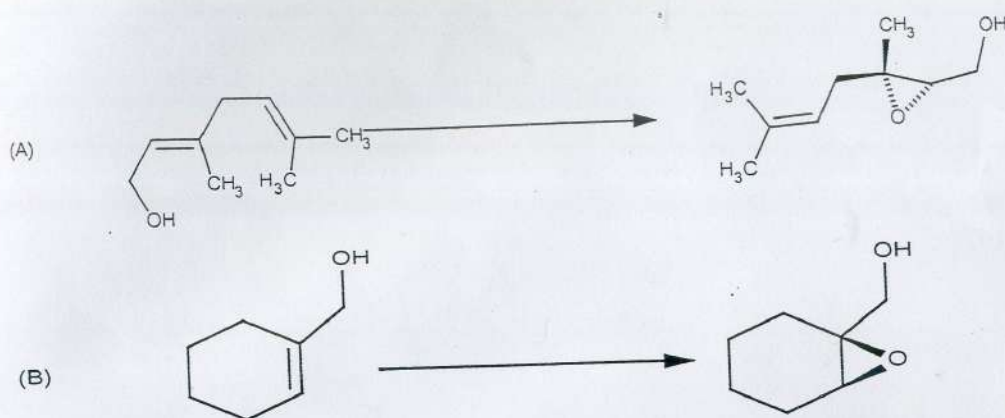
(Answer any 8 questions. Each question carries 2 Weightage)

- What is alkene metathesis? Write the mechanism of alkene metathesis.
- Propose retrosynthetic analysis of the following two compounds. Your answer should include both the synthons and the reagents that would be employed in the actual synthesis.

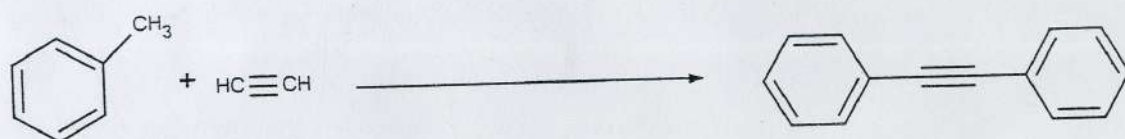


- Explain Robinson's annulation with suitable mechanism.
- Discuss the synthesis and reactions of Oxadiazole.
- Write any four synthetic uses of tri n-butyl tin hydride.
- Explain the use of 1,3 Dithiane as an acyl equivalent.
- What are the synthetic applications of Phase transfer catalyst?

20. Propose suitable catalyst, oxidising agent and proper mechanism for the following conversions



21. Write down the suitable catalyst and co catalyst in the following reaction and propose mechanism for the same



22. Write down in detail about the one group C-X disconnections .
 23. Explain the steps involved in the synthesis of vitamin D from D-Glucose.
 24. Discuss the advantages of NaBH_4 over LAH in synthetic organic chemistry

(8x2=16Weightage)

Section C

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

25. Discuss the Negishi, Heck, Stille and Suzuki palladium catalysed C-C bond forming reactions along with their mechanisms by giving at least one example for each reactions.
26. Explain the following reactions with suitable mechanisms

(a) Oppenauer oxidation

(b) Mannich reaction

(c) Swern oxidation

(d) Birch reduction

27. What are Protecting groups ? Discuss briefly on protection and deprotection of amino and carboxyl group

28. Write down the synthetic uses of the following reagents

(a) Benzene Tricarbonyl Chromium

(b) Pd/CaCO_3 poisoned with Sulphur

(c) periodic acid

(d) lead tetra acetate

(2x4=8Weightage)