

PH 541.4

Reg. No. :

St Aloysius College (Autonomous)
Mangaluru

Semester IV – P.G. Examination – M.Sc. Analytical Chemistry
September - 2020

ORGANIC SYNTHETIC METHODS

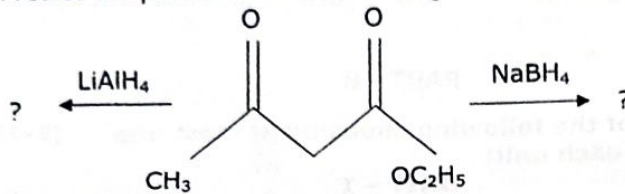
Time: 3 Hours

Max. Marks: 70

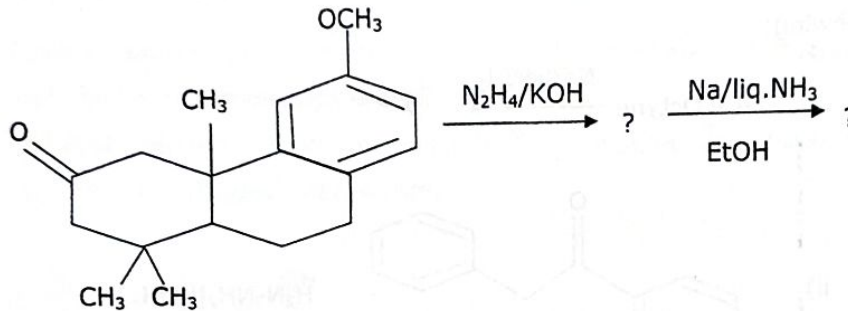
PART - A

1. Answer any **FIVE** sub divisions of the following: (5x2=10)

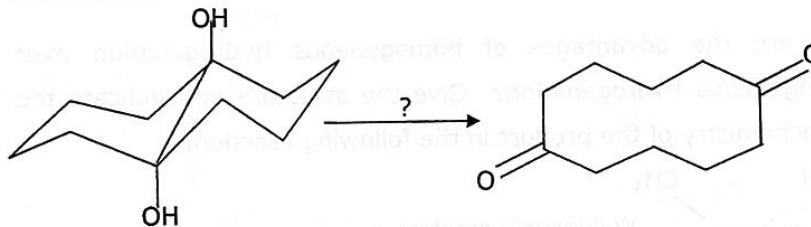
a) Predict the products in the following with suitable explanation.



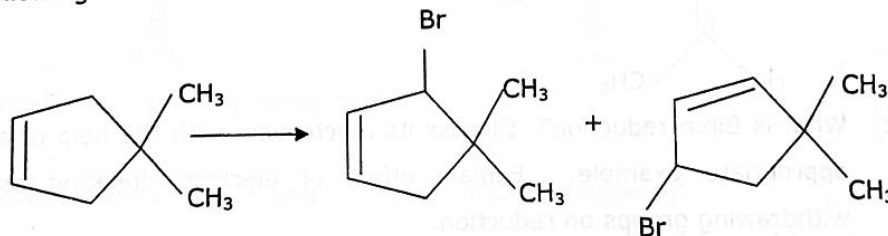
b) Predict the products in the following reactions.



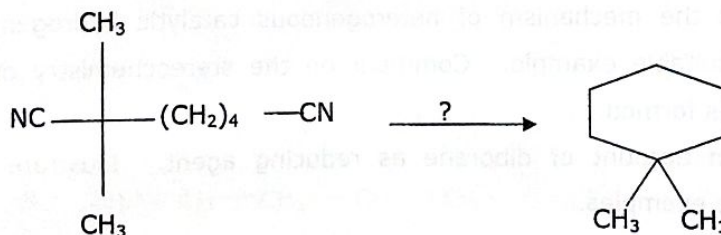
c) Suggest a reagent to effect the following conversion and outline the mechanism.



d) Suggest the reagents/reaction conditions and propose mechanism for the following reaction.



e) How is the following transformation achieved?

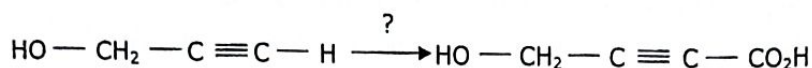


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- f) What is retro Diel's-Alder reaction? Illustrate with an example.
 g) What are synthons and synthetic equivalents? Give the synthetic equivalents for the following:



- h) How is the following transformation achieved?

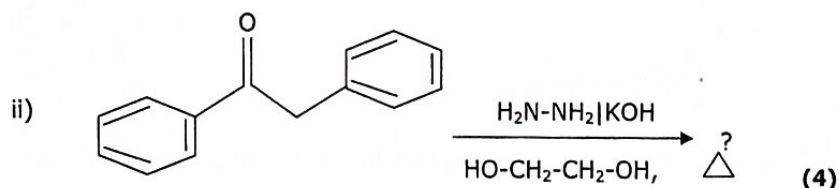
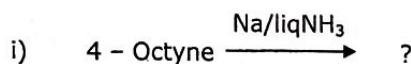


PART - B

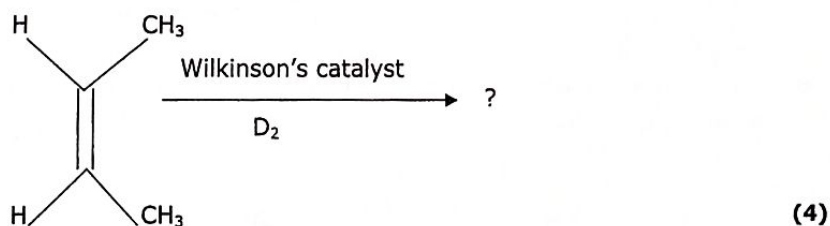
Answer any **FIVE** of the following choosing at least one full question from each unit: (5x12=60)

UNIT - I

- 2.a) Predict the product and propose suitable mechanism for the following:



- b) What are the advantages of homogeneous hydrogenation over heterogeneous hydrogenation? Give the structure and indicate the stereochemistry of the product in the following reaction.

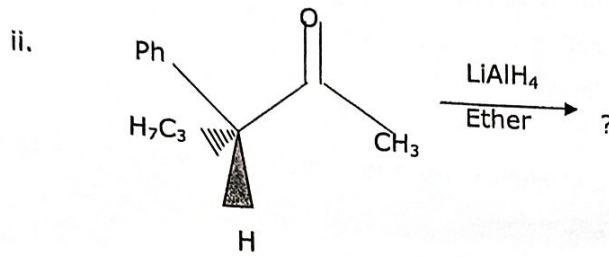
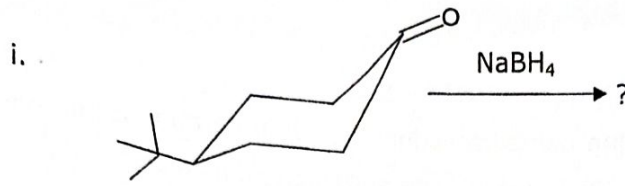


- c) What is Birch reduction? Discuss its mechanism with the help of an appropriate example. Explain effect of electron donating and withdrawing groups on reduction. (4)

- 3.a) Discuss the mechanism of heterogeneous catalytic hydrogenation using suitable example. Comment on the stereochemistry of the products formed. (4)

- b) Give an account of diborane as reducing agent. Illustrate with suitable examples. (4)

c) Predict the product/s indicating the stereochemistry. Justify the answer.

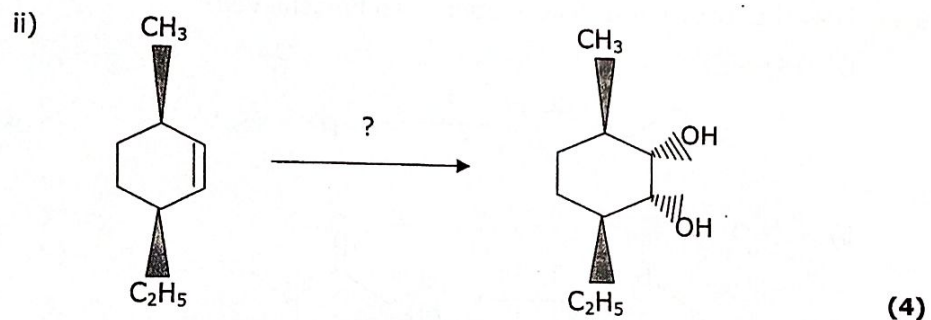
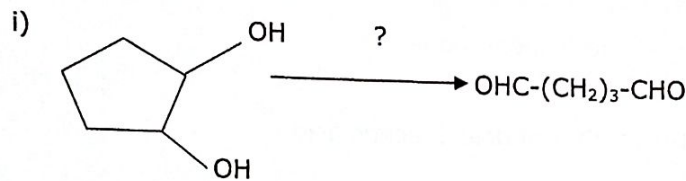


(4)

UNIT - II

4.a) Taking appropriate example explain the synthetic utility and mechanism of dehydration with selenium. (4)

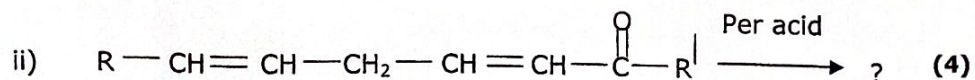
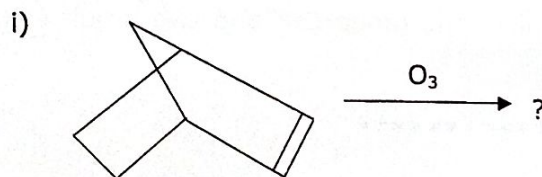
b) Suggest reaction condition suitable for effecting the following conversions. Suggest mechanism. (4)



(4)

c) Write a note on allylic halogenations. (4)

5.a) Formulate the products and mechanisms in the following?



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- b) Discuss the synthetic utility of lead tetraacetate. (4)
- c) Explain the uses of various chromium and manganese salts in the oxidation of alcohols. (4)

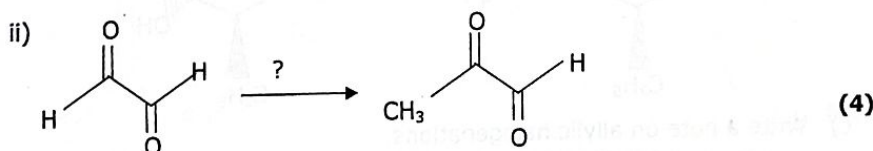
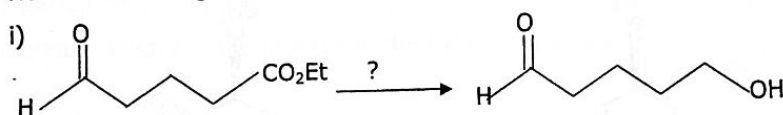
UNIT - III

6. How are the following named reactions useful in carbon-carbon bond forming reactions? Explain by taking suitable examples. (4)
- a) Carbene insertion reaction (4)
- b) Friedel-Craft's reaction (4)
- c) Robinson annulation (4)
- 7.a) Outline the synthesis of Penicillin-V and explain the precautions to be adopted during its synthesis. (4)
- b) What is Dickmann cyclisation? Explain its applications in organic synthesis using appropriate examples. (4)
- c) Outline the synthesis of 6-methoxy-tetralone. (4)

UNIT - IV

8. Propose retrosynthetic analysis for the following molecules and give their synthesis. (4)
- a) 4-Hydroxy-4-methylpentanone (4)
- b) Benzocaine (4)
- c) 2-methyl-6-methoxyindole-3-acetic acid (4)

- 9.a) How the following transformations can be achieved?



- b) Discuss the various techniques in the protection of amino group under different pH conditions. (4)
- c) With suitable examples, Explain one group C-X and two group C-X disconnections. (4)

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Mangaluru
Semester IV- P.G Examination - M.Sc. Analytical Chemistry
September - 2020

SPECTROSCOPIC METHODS OF ANALYSIS

Time: 3 Hours

Max. Marks: 70

PART - A

1. Answer any **FIVE** sub-divisions of the following: (2x5=10)
- How many ESR lines are expected in ESR spectrum of CH_3 radical? What are their intensities?
 - The Mossbauer spectrum of $\text{Fe}(\text{CO})_5$ shows splitting but that of $\text{K}_4[\text{Fe}(\text{CN})_6]$ does not. Give reason.
 - What is the function of KCl in the analysis of sodium of FES?
 - Why a high temperature nitrous oxide-acetylene flame is sometimes required in AAS?
 - What is quantum efficiency? The quantum efficiency of biphenyl and fluorine are 0.2 and 1.0 respectively, when measured under similar conditions. Why?
 - The fluorescence of aniline is pH dependent. Comment.
 - What is cotton effect?
 - Why glycerol is to be added in the determination of sulphate by nephelometry?

PART - B

Answer any **FIVE** of the following choosing at least one full question from each unit: (5x12=60)

UNIT- I

- Explain quadrupole splitting and structural elucidation of $\text{Fe}_3(\text{CO})_{12}$ using Mossbauer spectroscopy. (4)
 - Describe the principle and application of NQR spectroscopy in the study of phase transition of compounds. (4)
 - With the help of a neat schematic diagram explain the principle and working of XPS. (4)
- Illustrate the application of XPS in the determination of oxidation state of elements in compounds with suitable examples. (3)
 - Account on the magnetic hyperfine interactions. Draw and comment on the ESR spectrum of bis-salicylaldehyde copper(II) complex. (4)
 - Draw the energy level diagram and calculate the NQR transition frequencies in a nuclear quadrupole having $I=3/2$ and assuming i) $\eta = 0$ and ii) $\eta \neq 0$ (5)

UNIT- II

- Discuss the various interferences encountered in AAS? Explain how these interferences can be rectified. (5)
- Give the principle and describe the procedure for the determination of sodium in water samples by flame photometry (4)

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- c) Lithium in blood serum of a manic-depressive patient treated with Li_2CO_3 is determined by FES using method of standard addition. 100 μL of serum diluted to 1.0 mL gives an emission signal of 6.7cm on a recorder chart. A similar solution to which 20 μL of a 0.005 M solution of LiNO_3 was added gave a signal of 16.2cm. Assuming linearity between the emission signal and Li concentration, what is the concentration of Li in the serum? (3)
5. a) Discuss the cold vapour method for the determination of mercury in a given sample. (4)
- b) Explain the principle of AAS. Why is it necessary to use a hollow cathode lamp as radiation source in AAS? (5)
- c) Discuss the role temperature on absorption, emission and fluorescence. (3)

UNIT- III

6. a) Describe in detail the various factors that affect the fluorescence intensity of organic compounds. (4)
- b) Bring out the differences between fluorometer and spectrofluorometer. Sketch the block diagram of spectrofluorometer and mention the components. (4)
- c) Describe the applications of fluorimetry in the analysis of pharmaceutical and agricultural samples with suitable examples. (4)
7. a) With the help of Jablonski diagram, explain fluorescence and phosphorescence. (4)
- b) Explain different types of fluorescence quenching? Derive the equation that relates fluorescence intensity to the concentration of fluorophore. (5)
- c) Write a note on chemiluminescence. (3)

UNIT- IV

8. a) Derive Bragg's equation and explain how 'a' and 'd' are related in a cubic system. (4)
- b) Explain the principle and applications of turbidimetric titrations. (4)
- c) What are optically active compounds? Discuss the application of ORD in the determination of rate constant. (4)
9. a) Describe the principle and applications of X-ray absorption. (4)
- b) Distinguish between nephelometry and turbidimetry with respect to principle, working and instrumentation. (4)
- c) Explain the principle and applications of circular dichroism in the deduction of absolute configuration of molecules with suitable examples (4)

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Mangaluru

Semester IV – P.G. Examination – M.Sc. Analytical Chemistry
September - 2020

CHEMISTRY OF POLYMERS AND NATURAL PRODUCTS

Time: 3 Hours

Max. Marks: 70

PART - A

1. Answer any **FIVE** sub divisions of the following: (5x2=10)

- Using polystyrene as an example, write the configuration of isotactic and syndiotactic polystyrenes.
- Write the structure of the repeating units of the following polymers:
 - Polydimethylsiloxane
 - Polyacrylonitrile
 - Teflon
 - Nylon 6
- Among polyethylene and polystyrene, which polymer exhibits a higher T_g? Why?
- Sketch the characteristic DSC curve of a semicrystalline polymer sample and mention the various features.
- How codeine is converted to morphine and Thebaine.
- Give the evidence for the presence of phenolic-OH group in adrenaline.
- State special isoprene rule. Mark the isoprene units in α -pinene and zingiberene.
- Predict the products in the following:
 - Abietic acid $\xrightarrow[\Delta]{\text{Se}}$?
 - Menthol $\xrightarrow{\text{CrO}_3}$?

PART - B

Answer any **FIVE** of the following choosing at least one full question from each unit: (5x12=60)

UNIT - I

- Differentiate between step growth and chain growth polymerization. (4)
 - Explain the viscometric method of determination of molecular weight of a polymer. (4)
 - A polydisperse sample of polymers has 10% of molecules of molecular weight 10,000, 80% of 20,000 and 10% of 40,000. Calculate the number average and weight average molecular weights. (4)
- 3.a) Explain the use of gel permeation chromatography technique in isolation and purification of polymers. (4)

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- b) Discuss the Flory-Huggins theory of polymer dissolution. (4)
- c) Solution viscosity measurements give an idea about the size and shape of polymer molecules in solution. Justify. (4)

UNIT - II

- 4.a) Discuss the factors affecting the T_g of polymers. (4)
- b) Elucidate the use of DSC technique in polymer characterisation. (4)
- c) Explain the method of vapour phase osmometry in the determination of polymer molecular weight. (4)
- 5.a) Explain how the structure of a polymer influences the following properties: (4)
- i) Tensile strength ii) Flexural strength
- b) How do you correlate the glass transition temperature, crystallinity and melting point of a polymer with the structure of that polymer? Explain with suitable example. (4)
- c) Discuss the uses of thermogravimetric analysis of polymers. (4)

UNIT - III

- 6.a) Give the synthesis of piperine. (4)
- b) Explain the use of Emode's degradation in the determination of the structure of an alkaloid. (4)
- c) Outline the steps involved in the determination of structure of nicotine. (4)
- 7.a) Outline conversion of ethyl quininate to (±)-quinine. (4)
- b) Write the steps involved in the synthesis of papaverine from dimethoxy benzene. (4)
- c) Outline the reactions that indicate the following: (4)
- i) Presence of methylene group in papaverine.
- ii) Attachment of -CHOH group directly to the benzene ring in adrenaline. (4)

UNIT - IV

- 8.a) How do you fix up the positions of three double bonds in zingiberene? (4)
- b) Discuss how the structure of geraniol was established. (4)
- c) Give the synthesis of farnesol. (4)
- 9.a) Write the steps involved in the synthesis of dihydroabiatic acid. (4)
- b) Explain the structure of santonin by its degradation studies. (4)
- c) Indicate the reagents that are used to bring about the following conversions. (4)
- Pinene glycol \longrightarrow pinonic acid \longrightarrow Pinic acid \longrightarrow cis-norpinic acid
- Give the structures of all these compounds and write the synthesis of any one of them. (4)

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Mangaluru**

**Semester IV – P.G. Examination – M.Sc. Analytical Chemistry
September - 2020**

APPLIED ANALYSIS AND AUTOMATION

Time: 3 Hours

Max. Marks: 70

PART - A

1. Answer any **SEVEN** sub divisions of the following: (7x2=14)
- What are the factors affecting reaction rate?
 - Mention the types of kinetic methods.
 - What is enzyme specificity?
 - Compare the differences between BOD and COD.
 - Mention the importance of automatic elemental analyser.
 - Explain Resazurin test.
 - Define quality assurance.
 - Explain the types of ISO series.
 - What is the significance of tolerance?

PART - B

Answer any **FOUR** of the following choosing at least one full question from each unit: (4x14=56)

UNIT - I

- 2.a) Explain the importance of half life. (3)
 - b) Explain any two methods for the determination of reaction rates. (3)
 - c) Discuss the determination of GOT enzyme. (4)
 - d) Write a note on enzyme catalysis with example. (4)
- 3.a) Explain the micro determination of iodide in complex materials. (3)
 - b) Discuss enzyme activity. (3)
 - c) Explain the significance of GPT enzyme and its determination. (4)
 - d) Discuss the major classes of enzymes with example for each. (4)

UNIT - II

- 4.a) List out the minerals in milk and butter. (3)
 - b) Mention the procedure for determination of mercury in biological materials. (3)
 - c) Discuss Flow Injection Analysis. (4)
 - d) Write a note on analysis of fat content. (4)
- 5.a) What are the types of automated techniques? (3)
 - b) Explain working of centrifugal fast scan analyser. (3)
 - c) Write a note on mode of action of snake venom. (4)
 - d) Explain methods for the determination of crude protein. (4)

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UNIT - III

- 6.a) Explain ISO 17025 series importance. (3)
- b) What are the procedures for current trends in quality control? (3)
- c) Give a comparative account of QA and QC with reference to pharma industry. (4)
- d) Write a note on ISO 14001 series. (4)

- 7.a) Write a detailed note on different aspects of specification. (3)
- b) What are the different Indian laws related to quality control in various industries. (3)
- c) Explain the cost aspects of quality decisions. (4)
- d) Give a detailed account of ISO 9001 series. (4)
