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**St Aloysius College (Autonomous),
Mangaluru**

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

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May/June - 2023

ORGANIC SYNTHETIC METHODS

Time: 3 Hours

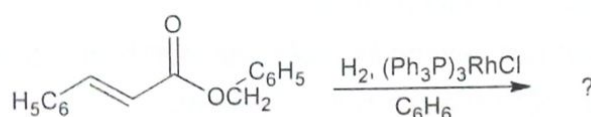
Max. Marks: 70

PART - A

1. Answer any Five sub-divisions of the following:

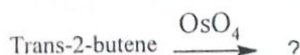
(5x2=10)

a) Complete the following reaction:



b) Explain Birch reduction, with an example.

c) Write the product in the following:

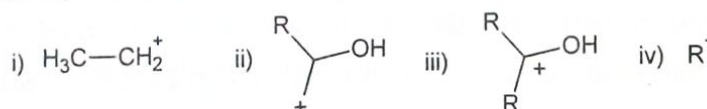


d) Ozonolysis is used for the structural elucidation of unknown organic compounds. Justify.

e) What are Heck reaction? Give example.

f) Give any one reaction yielding products with new C-C double bonds.

g) Give synthetic equivalents to following synthons:



h) Explain the term functional group addition with suitable examples.

PART - B

Answer any FIVE of the following choosing at least one full question from each unit:

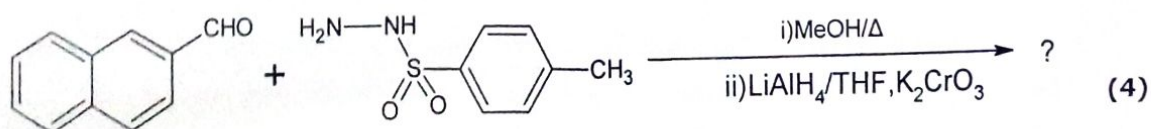
(5x12=60)

UNIT- I

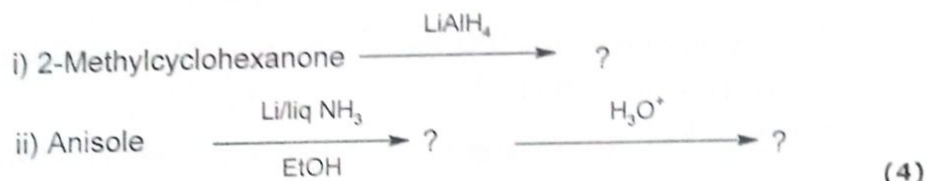
2. a) What is hydrogenolysis? Explain taking suitable example. (4)

b) What is Clemmenson reduction? Discuss the mechanism taking suitable example. (4)

c) Predict the products in the following and outline the mechanism.



3. a) Discuss the mechanism and stereochemistry of heterogenous catalytic hydrogenation. (4)
- b) Predict the products formed in the following reactions and outline their mechanisms.



- c) Write briefly on the synthetic applications of Wolf-Kishner reduction. (4)

UNIT- II

4. a) Propose the suitable mechanism for the oxidation of cyclohexanol using acidic $\text{K}_2\text{Cr}_2\text{O}_7$. (4)
- b) Discuss the oxidation of monohydric alcohols with lead tetra acetate. (4)
- c) Explain the mechanism of Beckmann rearrangement. (4)
5. a) Explain Baeyer-Villager oxidation. Give its synthetic importance. (4)
- b) Explain the oxidation of vicinal diols with HIO_4 and give its mechanism. (4)
- c) Write a note on Benzil- Benzilic acid rearrangement. (4)

UNIT- III

6. a) What is ene reaction? Discuss its synthetic applications. (4)
- b) Write a note on Robinson annulation. (4)
- c) Discuss the chemical synthesis of cubane. (4)
7. a) Write a note on carbene insertion reaction and its use in organic synthesis. (4)
- b) Explain the following reactions: i) Dickmann cyclization ii) Suzuki coupling reaction (4)
- c) Illustrate the synthesis of Penicillin-V. (4)

UNIT- IV

8. a) Illustrate one group disconnection with suitable examples. (4)
- b) Write a note on the protecting groups for carboxyl functional group. (4)
- c) Discuss the retrosynthetic analysis of the Phenacitin. (4)
9. a) Explain retrosynthetic analysis of Benzocaine Illustrate its synthesis. (4)
- b) Illustrate the C-X disconnection approach for the synthesis of 1,3-difunctionalised compounds. (4)
- c) Discuss two group C-C disconnection with suitable example. (4)

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SPECTROSCOPIC METHODS OF ANALYSIS

Time: 3 Hours

Max. Marks: 70

PART - A

1. Answer any **FIVE** sub-divisions of the following: (5x2=10)
- Differentiate X-ray photoelectron spectroscopy from X-ray absorption spectroscopy.
 - Give the graphical representation of Mossbauer spectrum.
 - What is the function of atomiser in the emission system of Atomic Absorption Spectroscopy?
 - Highlight the advantages of FES.
 - How is sampling of solid compound done in photoacoustic spectroscopy?
 - Give the relation between intensity of fluorescence and concentration.
 - How are coherent and non-coherent scattered X-ray generated?
 - Does the activity of hydrogen ion effects rate of inversion of sucrose? Justify the answer.

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PART - B

Answer any FIVE of the following choosing at least one full question from each unit:

(5x12=60)

UNIT- I

- Write a note on a) Zero Field Splitting
b) Mossbauer effect (5)
 - Describe the principle and application of Auger Spectroscopy. (4)
 - ESR Frequency for a free electron is 9000 MHz. Calculate the magnetic field at which ESR is working. ($\mu_B = 9.273 \times 10^{-24} \text{JT}^{-1}$) (3)
- Write short note on:
a) Hyperfine coupling b) Kramer's degeneracy (5)
 - Describe the experimental aspects of Mossbauer spectroscopy. (4)
 - Deduce the energies of NQR levels of a nucleus with $I=1$ in an axially symmetric field. (3)

UNIT - II

- Compare and distinguish the instrumental design between atomic absorption and atomic fluorescence photometry. (5)
 - Give an insight on precision and accuracy of AAS and FES. (4)
 - List out and mention the working of plasma excitation sources. (3)

5. a) Distinguish between total consumption and premix burners. (5)
Sketch the neat labeled diagram of the same.
- b) Describe the devices used for the formation of an atomic vapour. (4)
- c) What are the errors observed in flame photometry and how to overcome those errors? (3)

UNIT - III

6. a) Explain non-radiative means of deactivation. (5)
- b) List out two advantages and limitations of phosphorimetric analysis. (4)
- c) What is the role of filters in fluorimeter. (3)
7. a) With a neat labelled diagram discuss the components of spectrofluorimeter. (5)
- b) Using two examples mention the role of fluorimetric technique in analysis biomolecules. (4)
- c) Explain the dependence of quantum efficiency for luminescence analysis. (3)

UNIT - IV

8. a) Sketch a diagram of instrumentation of nephelometry and state the factors affecting its measurement. (5)
- b) Discuss the following. i) optical activity ii) cotton curves (4)
- c) Write a note on X-ray emission. (3)
9. a) Explain optical rotatory dispersion of enantiomers of cis and trans 10-methyl-2 decalones. (5)
- b) Illustrate on the aspect of X-ray interaction of with matter. (4)
- c) How is colorimetry different from turbidimetry? Explain. (3)

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CHEMISTRY OF POLYMERS AND NATURAL PRODUCTS

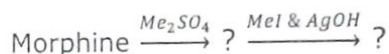
Time: 3 Hours

Max. Marks: 70

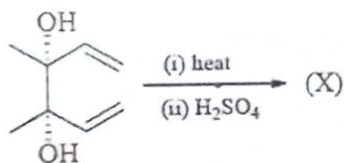
PART - A

1. Answer any **FIVE** sub divisions of the following: (5×2=10)

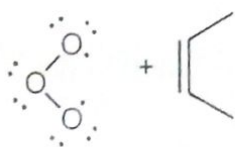
- a) How do you separate a mixture of solutes having a wide range of retention factors?
- b) Arrange in the increasing order of tensile strength based on linear, branched and network structures and justify the arrangement.
- c) Differentiate between intrinsic viscosity and relative viscosity. Which viscosity method is more suitable to calculate the molecular weight of polymer?
- d) Thermal characterisation of polymers is important. Justify.
- e) Predict the products



- f) Classify terpenoids and highlight the limitation of isoprene rule.
- g) Predict the product (X)



- h) Predict the product



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PART - B

Answer any **FIVE** of the following choosing at least one full question from each unit: (5×12=60)

UNIT - I

- 2.a) Explain with suitable example, the chain growth polymerization. (4)
- b) Define polymer fractionation. Explain in detail fractional precipitation technique. (4)
- c) A polypropylene $[-\text{CH}_2-\text{CH}(\text{CH}_3)-]$ sample contains the following composition.

Degree of polymerization	300	700	800
% of composition	25	35	40

Calculate \overline{M}_n & \overline{M}_w of polypropylene sample by neglecting the end groups. (4)

- 3.a) Differentiate between suspension and emulsion polymerization. Mention any two limitations of each technique. (4)
- b) Discuss the mechanism of ring opening metathesis polymerisation. (4)
- c) Which among the linear and network polymers have highest crystallinity? Explain the effects of crystallinity on the properties of polymers. (4)

UNIT - II

- 4.a) Explain ultracentrifugation method of determination of molecular weight of polymer. (4)
- b) Whether T_g of a polymer is exothermic or endothermic process in DSC thermogram? List out any three factors affecting the T_g of polymers. (4)
- c) Discuss the technique of reinforcement in polymers with an example. (4)
- 5.a) Describe osmometry method of determination of molecular weight of polymer. (4)
- b) Why TGA is recommended before DSC analysis. Discuss the instrumentation setup of TGA. (4)
- c) Natural rubbers cannot be used directly for manufacturing tyres. Elaborate the statement with reason and explain the solution with mechanism. (4)

UNIT - III

- 6.a) Account for the point of attachment between quinuclidine nucleus and quinoline nucleus in quinine. (4)
- b) Explain the biogenesis and precursors of alkaloids. (4)
- c) Write the isolation and synthetic route for the synthesis of Menthol. (4)
- 7.a) Formulate the stereospecific synthesis of Papaverine. (4)
- b) Describe the isolation and structure elucidation of alkaloids. (4)
- c) Discuss how spectroscopy is used for structural elucidation of terpenoids. (4)

UNIT - IV

- 8.a) Classify pericyclic reactions. (4)
- b) How FMO analysis can be used to study Diels-Alder reaction? (4)
- c) Explain cheletropic reactions with suitable example. (4)
- 9.a) Describe using suitable example suprafacial and antarafacial sigmatropic rearrangement of hydrogen. (4)
- b) Sketch and explain the correlation diagram of electrocyclic reaction when polyene has 4n electrons. (4)
- c) With suitable rearrangement reaction predict the most favourable product of allyl vinyl ether. (4)

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APPLIED ANALYSIS AND AUTOMATION

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Max. Marks: 70

PART – A

1. Answer any **SEVEN** sub divisions of the following: (7x2=14)
- Differentiate between Order and molecularity with suitable examples.
 - How the graphical method is most useful in determining the order of a reaction?
 - What is meant by Michaelis-Menten constant k_m ?
 - What is the working principle of ammonia analyzer?
 - What is flow injection titration?
 - Write the principle of inhibition test of milk sample.
 - What is the difference between ISO 9001 and ISO 17025?
 - What is the Significance of Tolerance?
 - What are the four responsibilities of Quality Control?

PART – B

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

UNIT – I

- Show that a second-order reaction behave like a first order, if concentration of one reactant is at least ten times greater than that of another reactant. (3)
 - Discuss the effect of pH in an enzyme catalyzed reaction. (3)
 - Explain the determination of cobalt in the given sample. (4)
 - In a reaction when initial concentration doubles, the half-life is reduced to half. What is the order of reaction? (4)
- How conductometric method is helpful in determination of reaction rates? (3)
 - Explain the significance of GPT enzyme and its determination. (3)
 - A reactant reacts 30% in 30 min. If the reaction follows a second order kinetics, find rate constant and remaining concentration of reactant after 60 min. (4)
 - Describe the micro determination of inorganic species. (4)

Contd...2

UNIT – II

- 4.a) Mention the procedure for the determination of arsenic in biological materials. (3)
- b) Write a note on milk adulteration. (3)
- c) Describe the working of segmented flow method. (3)
- d) Explain the mode of action of snake venom poisoning. (5)
- 5.a) What is dispersion? Explain the factors affecting it. (3)
- b) Explain the working principle of BUN analyzer. (3)
- c) Explain the methylene blue test and resazurin test for milk. (4)
- d) Give the general method for the determination crude fibre and ash content in the food sample. (4)

UNIT – III

- 6.a) Give an account of ISO 14001 and laws related to Quality Control in petrochemical industries. (4)
- b) Comment on the importance of Sampling Techniques in pharmaceutical industry. (3)
- c) What is Quality Control? Discuss its role in raw materials and finished products. (4)
- d) What is Specification? Discuss different aspects of Specification? (3)
- 7.a) Discuss the Quality Assurance laws. (4)
- b) Write a note on ISO 17025 for Testing and Calibration? (3)
- c) Discuss cost aspects of Quality Decisions. (4)
- d) What is pharmaceutical Quality Assurance? And why is it important? (3)
