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**St Aloysius College (Autonomous)**  
**Mangaluru**  
**Semester IV- P.G Examination - M.Sc. Chemistry**  
**August / September 2021**

**ORGANIC SYNTHETIC METHODS**

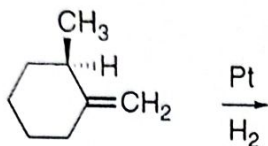
Time: 3 Hours

Max. Marks: 70

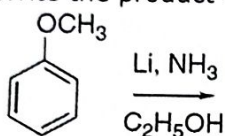
**PART - A**

1. Answer any **FIVE** sub-divisions of the following: (2x5=10)

a) Predict the major product in the following. Justify your answer.



b) Write the product in the following. Give the reaction mechanism.



- c) List out the merits and demerits of Jones reagent in oxidation reactions.  
 d) Give an example for the ozone mediated oxidation reaction. Write the reaction mechanism.  
 e) What are 1,3-dipolar addition reactions? Give an example.  
 f) Give any two reactions yielding products with new C-C double bonds (-C=C-).  
 g) Suggest a suitable protecting reagent for carbonyl groups. Write the protection and deprotection reactions.  
 h) What are synthons and synthetic equivalents? Give 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) Explain the dissolving metal reduction reactions of carbonyl compounds involving addition of hydrogen. (4)  
 b) With a suitable example, explain the stereoselectivity of hydride transfer reductions. (4)  
 c) Explain the following  
 i) Wolf-Kishner reduction and ii) Clemmensen reduction (4)
3. a) Explain the hydroboration reaction of alkenes. Comment on the regioselectivity of the reaction. (4)  
 b) Write a note on reduction reactions using arene sulphonyl derivatives of hydrazine. (4)  
 c) Explain the bimolecular reduction of esters. (4)

**UNIT- II**

4. a) Write a note on different chromium based oxidizing reagents and their application in oxidation of alcohols. (4)  
 b) Explain benzylic and allylic halogenation reaction with suitable examples. (4)

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c) Write the mechanism of oxidation reaction using osmium tetroxide.  
Mention any two synthetic applications of the reagent.

(4)

5. a) Illustrate the synthetic applications following oxidizing reagents.  
i) Periodic acid and ii) Lead tetra acetate

(4)

b) Write a note on halogenation of carbonyl compounds.

(4)

c) Discuss the dehydrogenation reactions using S and Se.

(4)

### UNIT- III

6. a) Write a note on carbene insertion reaction and its applications in organic synthesis.

(4)

b) Explain the following reactions with suitable examples.

i) Dieckmann cyclization and ii) Arndt -Eistert homologation

(4)

c) Explain the synthesis of 7-methoxy -1- tetralones.

(4)

7. a) Discuss the synthetic applications of Ene reaction.

(4)

b) Explain the chemical synthesis of Biotin.

(4)

c) Explain the following reactions

i) Thorpe condensation and ii) Robinson annulation.

(4)

### UNIT- IV

8. a) With a suitable example, explain the importance of functional group interconversion in retrosynthetic analysis.

(4)

b) Suggest any two protecting reagents for the amino group. Write the corresponding protection and deprotection reactions.

(4)

c) Perform retrosynthetic analysis of 2-methyl-6-methoxy indole 3-acetic acid and suggest a feasible synthetic route.

(4)

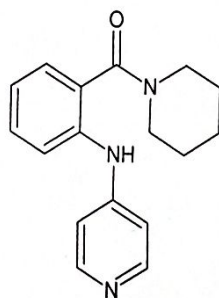
9. a) Perform retrosynthetic analysis of benzocaine and p-acetamol.

(4)

b) Give one group and two group C-C disconnections with suitable examples.

(4)

c) Propose a feasible synthetic route for the following molecule through retrosynthetic analysis.



(4)

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**August / September 2021**

**RADIATION AND PHOTOCHEMISTRY**

Time: 3 Hours

Max. Marks: 70

**PART - A**

1. Answer any **FIVE** sub divisions of the following: (5x2=10)
- State any two characteristics of alpha and beta radiations.
  - Calculate the binding energy per nucleon of the nucleus. Given mass of neutron = 1.008665 a.m.u. and mass of hydrogen atom = 1.007825 a.m.u.
  - Define the terms Rontgen and Rad.
  - Write any two applications of C-14 dating.
  - State Frank Condon principle. Mention its significance.
  - How is a photochemical reaction different from a thermal reaction?
  - Mention any two applications of photochemistry in organic synthesis.
  - Write any two differences between fluorescence and phosphorescence.

**PART - B**

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

(5x12=60)

**UNIT - I**

- 2.a) Explain the postulates of liquid drop model for nucleus. (4)
  - b) Identify the product nucleus Y in the following nuclear reactions.  
i)  $^{227}\text{Ac} \rightarrow Y + 5\alpha + 3\beta$       ii)  $^{232}\text{Th} \rightarrow Y + 6\alpha + 4\beta$   
iii)  $^{233}\text{Pa} \rightarrow Y + 6\alpha + 4\beta$       iv)  $^{238}\text{U} \rightarrow Y + 8\alpha + 6\beta$  (4)
  - c) Write a note on NaI(Tl) Scintillation detector and semiconductor detector. (4)
- 3.a) Describe the principle and working of a Geiger-Muller counter. (4)
  - b) Discuss the features and components of a nuclear power reactor. (4)
  - c) The half-lives of the nuclei of  $^{238}\text{U}$  and  $^{235}\text{U}$  are  $4.5 \times 10^9$  years and  $7.1 \times 10^8$  years respectively. Today, the isotopic abundance of uranium is 99.28 percent of  $^{238}\text{U}$  and 0.72 percent of  $^{235}\text{U}$ . Assuming that initially these isotopes were in equal abundance and that no isotopic separation has occurred through physical and chemical changes, calculate the age of these elements on the earth. (4)

**UNIT - II**

- 4.a) Write a note on Radioactive waste management. (4)

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- b) How are transient species studied by pulse radiolysis technique? (4)
- c) Explain the ion-exchange method for radiochemical separation. (4)
- 5.a) Describe the applications of radioactive isotopes in medical and agricultural field. (4)
- b) What is a dosimeter? Explain the working of Fricke dosimeter. (4)
- c) Write a brief note on biological effects of radiation and permissible exposure doses. (4)

**UNIT - III**

- 6.a) Outline the various photophysical processes using Jablonski diagram. (4)
- b) Photobromination of cinnamic acid to dibromocinnamic acid was carried out in blue light of wavelength 440 nm at 35°C using light intensity of  $1.5 \times 10^{-3}$  J per second. An exposure of 20 minutes produced a decrease of 0.075 millimole of bromine. The solution absorbed 80 percent of the light passing through it. Calculate the quantum yield of the reaction. (4)
- c) How are the excited state species studied by flash photolysis experiments? (4)
- 7.a) Discuss by taking suitable examples the effect of solute-solvent interactions on electronic spectra. (6)
- b) What happens to the acidity constant when the molecule is electronically excited? (6)

**UNIT - IV**

- 8.a) Outline the basic differences in the measurement of fluorescence and phosphorescence intensities. (6)
- b) Derive the Stern-Volmer equation. Explain its significance. (6)
- 9.a) Explain the role of photochemistry in solar energy utilization. (4)
- b) Describe photo-isomerization reaction by taking suitable examples. (4)
- c) What are the various factors affecting fluorescence and phosphorescence? (4)

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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: (5x2=10)
- Define the following terms:
    - degree of polymerization
    - glass transition temperature
  - Between polyethylene and polystyrene, which polymer exhibits higher T<sub>g</sub> value? Explain why.
  - Write the structure of the repeating unit for each of the following polymer.
    - Teflon
    - Poly(ethylene terephthalate)
  - Sketch the characteristic DSC curve of a semicrystalline polymer sample and mention the various features.
  - How cinchonine can be obtained from cinchotoxine?
  - Give evidence for the presence of reactive methylene group in camphor.
  - State isoprene and special isoprene rules.
  - Outline the biogenesis of Adrenaline.

**PART - B**

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

**UNIT – I**

- 2.a) Explain the use of gel permeation chromatography in isolation and purification of polymers. (5)
  - b) With a suitable example, explain the mechanism of chain growth polymerization. (4)
  - c) Write a note on viscosity of polymer solutions. (3)
- 3.a) Describe fractional precipitation of polymers. (5)
  - b) Write a brief account of weight average and viscosity average molecular weight concepts. (4)
  - c) Discuss the effect of crystallinity on the properties of polymers. (3)

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**UNIT - II**

- 4.a) Explain osmometry method of determination of molecular weight. (5)  
b) What is glass transition temperature? Explain Tg-transitions and associated properties. (4)  
c) Discuss the application of ebulliometry method in molecular weight determination. (3)
- 5.a) Outline the principle of Thermo gravimetric analysis in polymer characterization. (5)  
b) Write a note on mechanical properties of polymers. (4)  
c) Explain the procedure for determining Tg using DSC technique. (3)

**UNIT - III**

- 6.a) How do you Synthesis Papaverine? (5)  
b) How do you ascertain the position of carboxyl and hydroxyl groups in Reserpine? (4)  
c) Account for the presence of phenanthrene nucleus and ether linkage in Morphine. (3)
- 7.a) Outline the synthesis of piperine. (5)  
b) Describe Hoffmann's and Embde's degradation. (4)  
c) Discuss the use of the following reagents in structure determination of compounds: i) O<sub>3</sub> (ii) CrO<sub>3</sub> (3)

**UNIT - IV**

- 8.a) Describe the Wagner's work for establishing the structure of  $\alpha$ -pinene. (4)  
b) Outline the steps involved in the commercial synthesis of camphor. (4)  
c) Sketch the synthesis of Farnesol. (4)
- 9.a) Discuss how the structure of santonin was established by degradation studies. (5)  
b) Write a note on structural features of squalene. (4)  
c) Explain the chemical synthesis of geraniol. (3)

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**SOLID STATE AND NANO CHEMISTRY**

Time: 3 Hours

Max. Marks: 70

**PART - A**

1. Answer any **SEVEN** sub divisions of the following: (7x2=14)
- For a simple cubic crystal lattice, calculate the glancing angle of the incoming beam along [001] direction with the [201] plane.
  - You are given an X-ray powder pattern of a cubic crystal. How will you determine whether the structure is simple, body-centred or face-centred cubic?
  - Give the Wierl equation and name the terms involved.
  - What is chemic vapour deposition? Illustrate.
  - Depict the band structure for p-type and n-type semiconductors.
  - What is piezoelectricity? Name any two piezoelectric materials.
  - What are nanoparticles? Give two examples.
  - Give two applications of nanomaterials in biotechnology.
  - What is self-assembly?

**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 Weisseberg method of structural determination of solids. (4)
  - b) Derive Bragg's equation for X-ray diffraction and explain the terms involved. (4)
  - c) Discuss the identification of unit cells from systematic absences in X-ray diffraction. (3)
  - d) Explain the structural elucidation of simple gaseous molecules by electron diffraction technique. (3)
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- 3.a) Discuss any four factors affecting X-ray intensities. (4)
  - b) The X-ray powder diffraction pattern of AgCl obtained using radiation of wavelength  $1.54\text{\AA}$ . The peaks are labeled with  $2\theta$  values: 27.80, 32.20, 46.20, 54.80, 57.45, 67.45. On the basis that the structure is cubic, index the first six reflections. Calculate the unit cell parameter and the density of AgCl (Assume the following atomic weights: Ag, 107.868; Cl, 35.453) (4)
  - c) Give the different stages of single crystal structure determinations. (3)
  - d) Describe Laue method of X-ray diffraction. (3)

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**UNIT - II**

- 4.a) Give the comparative account on the thermodynamics of Schottky and Frenkel defect formation. (4)
- b) Explain the Czochralski and Verneuil method of crystal growth. (4)
- c) Describe the properties and applications of dielectric materials. (3)
- d) Explain Hall effect. (3)
- 5.a) Give an account of band theory of solids. (4)
- b) Write short note on (4)
- i) Sol-gel method
- ii) Colour centres
- c) Discuss the origin of depletion region at p-n junctions. (3)
- d) Explain the physical methods of preparation of thin films. (3)

**UNIT - III**

- 6.a) Discuss the classification of nanomaterials in detail. (4)
- b) How SEM & TEM can be used for characterization of nanomaterials? (4)
- c) Discuss the preparation, properties and applications of nano composites. (3)
- d) What is the principle of nanooptoelectronic devices? (3)
- 7.a) Explain sol-gel and hydrothermal synthesis of nanomaterials. (4)
- b) Write notes on i) smart materials ii) Xerogels (4)
- c) Discuss briefly on the applications of nanomaterials in catalysis. (3)
- d) Elaborate on optical properties of nanoparticles. (3)

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