

PGIIS-N 1513 B-14
M.Sc. III Semester (CBCS) Degree Examination
Chemistry
(Organic Chemistry - III/Spectroscopy)
Paper - HCT : 3.1

Time : 3 Hours

Maximum Marks : 80

Instructions to candidates:

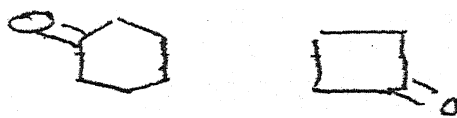
All questions are compulsory and carry equal marks

1. Answer any **eight** of the following (8×2=16)

- a) State Beer-Lambert's law, write the mathematical expression for it
- b) Calculate the λ_{\max} for the following compounds using Woodward-Fieser rules



- c) Which of the following has higher vibrational frequency for carbonyl group and why?



- d) What is finger print region? Give its importance
- e) What are deuterium exchange reactions? Mention its importance
- f) Sketch the $^1\text{H NMR}$ spectra of the following compounds and assign their approximate chemical shift values
- i) $\text{CH}_3\text{COCH}_2\text{COOCH}_2\text{CH}_3$

ii)



- g) Differentiate chemically equivalent and magnetically equivalent protons with suitable example
- h) ^{13}C nmr signals are inherently weak compared ^1H nmr signals. Justify
- i) How many isotopic peaks will appear in the mass spectrum of p-di bromobenzene? Calculate their intensities
- j) What are the masses of the two ions produced in the mass spectrum of propyl benzene by β - fragmentation
2. a) Describe the various types of transitions that occur in organic molecules after absorbing uv-vis radiation (5)
- b) Discuss the various methods of sampling used in recording the IR spectrum of an organic compound (5)
- c) How is IR spectroscopy useful in studying the hydrogen bonding and keto-enol tautomerism

Or

Discuss any three factors affecting the group frequency in IR spectroscopy (6)

3. a) Comment on chemical shift positions in benzene and 16 annulene (5)
- b) Deduce the structure of a compound having molecular formula $\text{C}_9\text{H}_8\text{O}$ and the following spectral data

UV-VIS : λ_{max} 285nm

IR : 3070, 2820, 2750, 1685, 1630, 1610, 970 and 745 cm^{-1}

^1H NMR: δ 6.62 (1H, dd, $J = 16\text{HZ}$) 7.41 (1H, d, $J = 16\text{Hz}$)

7.40(5H, m), 9.66 (1H, d, $J = 7\text{HZ}$)

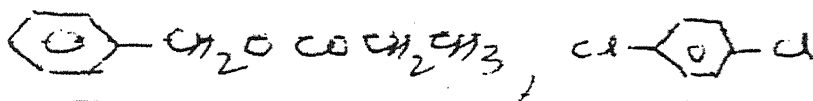
Mass spectra : $\frac{m}{z}$ 132 (M^+), 131, 103, 91, 77 and 51 (5)

- c) Explain the phenomenon of double resonance taking suitable example. Mention its importance

Or

Describe any two methods for the determination and simplification of complex nmr spectra (6)

4. a) Predict and assign the number of ^1H and ^{13}C NMR signal for the following (5)

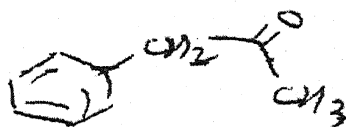


- b) Discuss the various factors influencing the coupling constant "J" in ^1H NMR spectroscopy (5)
- c) What is meant by broad band de-coupling in ^{13}C NMR? Mention its significance

Or

With a neat diagram explain the instrumentation in nmr spectroscopy (6)

5. a) Predict the fragmentation for the following compound and draw its probable mass spectrum (5)



- b) What is McLafferty rearrangement? Explain its mechanism with suitable example (5)
- c) Write note on :
- Ortho effect
 - FAB ionization

Or

Elucidate the structure of an organic compound with molecular formula $\text{C}_{12}\text{H}_{14}\text{O}_2$

With following spectral data

uv-Vis : λ_{max} 272 nm

IR: 1720 and 1625 cm^{-1}

^1H NMR : δ 7.8 (1H, d, J = 18HZ)

7.5 (2H, d, J = 8HZ)

7.1 (2H, d, J = 8HZ)

6.5 (1H, d, J = 18HZ)

4.1 (2H, q, J = 7HZ)

2.4 (s, 3H)

1.25 (3H, t, J = 7HZ)

MS : $\frac{m}{z}$ 190 (M $^{+}$ -)

(6)

PGIIS-N 1520 B-14
M.Sc. IIIrd Semester (CBCS) Degree Examination
Organic Chemistry
(Natural Products)
Paper - SCT - 3.1
(New)

Time : 3 Hours

Maximum Marks : 80

Instructions to candidates:*Answer all the questions**All questions carry equal marks*

1. Answer any **eight** of the following **(8x2=16)**
- a) Illustrate anomeric effect with an example
 - b) Give the application of the BOC group in peptide synthesis
 - c) Draw the structure of cholesterol and number of carbons
 - d) What is the importance of Diels hydrocarbon in steroidal chemistry?
 - e) Explain the term special isoprene rule with an example
 - f) How is Zeisel's degradation useful in structural elucidation of alkaloids
 - g) Write the biological importance of vitamins
 - h) Mention the bases and their pairing in double helical structure of DNA
 - i) Sketch the stereochemical structure of PGE and give numbers
 - j) Bring out the structural differences between cellulose and amylopectin
2. a) Outline the strategy for solution phase and solid phase peptide synthesis. **(5)**
- b) Describe how Hudson's lactone rule and Hudson's isorotation rule are helpful in the study of monosaccharides **(5)**

- c) Discuss the general methods of structural elucidation of polysaccharides (6)

Or

Describe end group analysis to determine the sequence of amino acids in peptides

3. a) Write an account of ergosterol and its photoproducts (5)
b) Give an account of Barbier Wieland degradation to establish the nature of side chain of bile acids (5)
c) Outline the biosynthesis of cholesterol (6)

Or

Describe the synthesis of progesterone.

4. a) Outline the conversion of morphine into codeine and thebaine (5)
b) Sketch the synthesis of camphor (5)
c) Describe the procedure for the isolation of alkaloids and give their classification (6)

Or

Citing examples describe the classification of terpenes with an example in each class

5. a) Formulate the synthesis of ascorbic acid. Mention its deficiency diseases (5)
b) Describe Corey's method for the synthesis of prostaglandins (5)
c) Discuss the biological role of biotin and outline its synthesis (6)

Or

Describe recombinant DNA technology

PGIIS - N 1516 B - 14
M.Sc. IIIrd Semester (CBCS) Degree Examination
Chemistry
(Physical Chemistry - III)
Paper : HCT 3.2
(New)

Time : 3 Hours

Maximum Marks : 80

Instructions to Candidates:

- 1) All questions carry **equal** marks
- 2) All questions are **compulsory**

1. a) Calculate the value of $4!$ using Stirling approximation (8×2=16)
b) What is residual entropy? Explain
c) Write down the expression for partition function and explain the terms in it
d) Define the term "operator" in quantum mechanics
e) What is meant by Secular equation?
f) What is the essential feature of Hartree - self consistent theory
g) Distinguish between conductor and insulator on the basis of valence bond theory
h) Define 'optical reflectance'
i) Define excess molar function
j) Define chemical potential and how is it understood
2. a) Derive the expression for Fermi - Dirac quantum statistics (5)
b) Derive the expression for translation partition function. Calculate the translational entropy for gaseous iodine at 300 K (5)
c) i) Give the comparison between the three forms of quantum statistics
ii) Give an account of ensembles of localized and non localized systems. (6)

OR

Write a short note on :

- i) Ortho - para hydrogen system
- ii) Separation of partition function

3. a) Give an account of Schrodinger wave equation as applicable for a rigid rotator (5)
b) Discuss the application of Perturbation theory and give the expression for zero, first and second order Perturbation (5)
c) Write a note on :
i) Correlation diagram and
ii) Non Crossing rule (6)

OR

Write a note on :

- i) Coulomb exchange and overlap integral
ii) Comparison of VB and Mo theories

4. a) What are the general principles involved in classification of solid state reactions?(5)
b) Distinguish between different types of magnetic behaviours observed in solids. With the help of a hysteresis trace, explain the different parameters that can be identified(5)
c) Write a note on :
Thermal behaviour of solids (6)

OR

Write a note on :

- i) Optical reflectometer in solids and
ii) Photo electric phenomena in solids

5. a) Discuss on Gibbs thermodynamic of mixing and understanding of thermodynamic behaviour of mixing (5)
b) What are Phenomenological equations? Discuss (5)
c) What is critical micelle concentration? Discuss any one methods to determine it.(6)

OR

Give an account of the principle of minimum entropy production.

PGIIS-N 1518 B-14
M.Sc. IIIrd Semester (CBCS) Degree Examination
Chemistry
(Inorganic Chemistry-III)
Paper - SCT-3.2
(New)

Time : 3 Hours

Maximum Marks : 80

Instructions to candidates:

- i) Answer all the questions
- ii) All questions carry equal marks

1. Answer any eight questions: (8×2=16)
 - a) What are the advantages of glazed porcelain?
 - b) Mention different types of portland cement along with their approximate compositions.
 - c) What are cytochromes? Give their significance.
 - d) Write the source and biochemical effects of SO_x.
 - e) Why is myoglobin unsuitable as an oxygen transport protein but effective as an oxygen storage protein?
 - f) What are breeder's reactors? Mention their advantages.
 - g) What is meant by induced radioactivity?
 - h) Explain the quantum yield with an example.
 - i) Define photoisomerisation reaction? Give an example.
 - j) Write the nuclear power stations in India.
2.
 - a) How is steel manufactured by open hearth furnace? Mention the advantages of this process. (5)
 - b) Write a brief note on industrial pollution with emphasis on cement industries and metallurgical processes. (5)
 - c) Discuss in detail the procedural aspects of disposal of radio active nuclear waste. How for these procedure are safe? (6)

OR

List out the raw materials used in the manufacture of glasses and the reasons for their use.

3. a) Describe the source, metabolism toxicological effects, and treatment of lead and cadmium. (5)
- b) Discuss briefly how nitrogenase helps in vivo and invitro nitrogen fixation? (5)
- c) How does electron transfer in biological system takes place by cytochromes and Iron-sulphur proteins? (6)

OR

Write a note on :

- i) Biochemical effects of Ozone and PAN
- ii) Essential and trace metals.
4. a) Describe the construction and operation of G.M. Counter. Explain its advantages. (5)
- b) Write a note on applications of nuclear science (5)
- c) Draw a schematic diagram of nuclear reactor and label the components. Explain its character features. (6)

OR

- i) Write a note on interaction of α, β, γ radiation with matter.
- ii) An ionization chamber is connected to an electrometer of capacity 0.5F and voltage sensitivity of 4 divisions per volt. A beam of α -particles causes a deflection of 0.8 divisions. Calculate the number of ion pairs required and energy of the α -particles. (Given that one ion pair requires energy of 35eV and $e=1.6 \times 10^{-19}$ coulomb.)
5. a) Discuss the possible mechanism involved in photo substitution reactions. (5)
- b) Describe the ligand-metal and metal-ligand charge transfer spectra with examples. (5)
- c) With suitable examples, discuss the metal complexes as sensitizers. (6)

OR

Write a note on:

- i) Photochemical laws.
- ii) Applications of photoredox reactions.

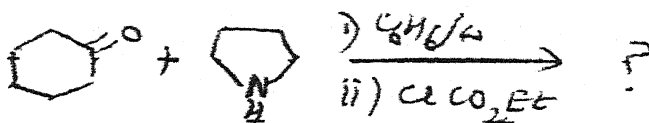
PGIIS-N 1514 B-14
M.Sc. IIIrd Semester (CBCS) Degree Examination
Organic Chemistry
(Reaction Mechanisms)
Paper HCT - 3.2
(New)

Time : 3 Hours

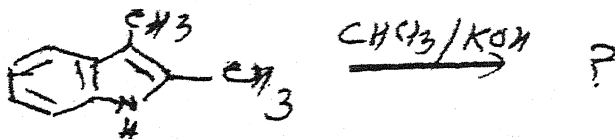
Maximum Marks : 80

Instructions to candidates :*All questions are compulsory and carry equal marks*1. Answer any **eight** of the following (8×2=16)

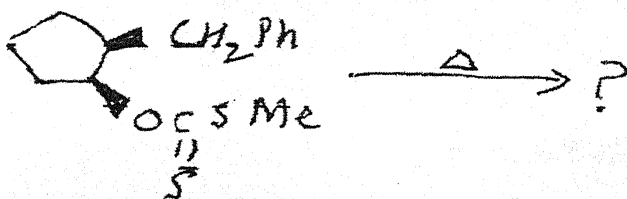
- a) What are singlet and triplet nitrenes? Which is more stable and why
b) Identify the product(s) in the following



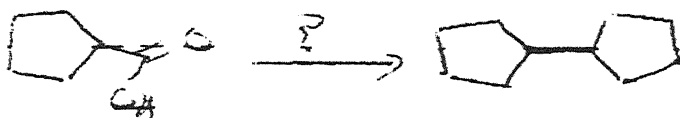
- c) Predict the product and propose suitable mechanism in the following reaction



- d) The rate of hydrolysis of 2-phenylthioethyl chloride is faster than 1-chloropropane. Explain.
e) Give the mechanism of cannizaro reaction
f) Illustrate the mechanism of Meerwein Pundoff reduction with suitable example
g) Write the product and propose mechanism in the following

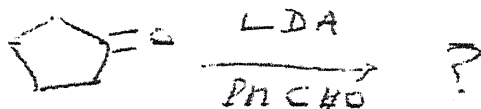


h) How do you achieve the following conversion



i) Give an example of a push-pull reaction

j) Predict the product and propose mechanism

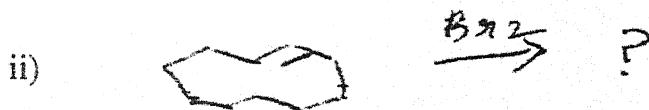
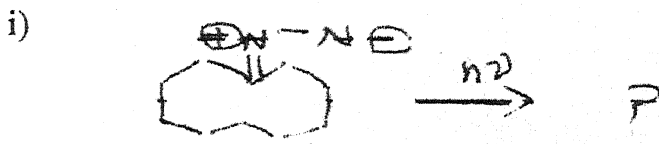


2. a) What are non-classical carbocations? Discuss their stability (5)
b) What are carbenes? Discuss their structure and stability (5)
c) How are free radicals generated? Discuss briefly the reactions of free radicals

Or

Discuss the shape of carbocations, carbanions and carbon free radical intermediates (6)

3. a) What is neighbouring group participation? Give the mechanism of a ngp involving π -bonds (5)
b) Write an account on nucleophilic substitution reactions at trigonal carbon atom (5)
c) Predict the product(s) formed with suitable mechanism



Or

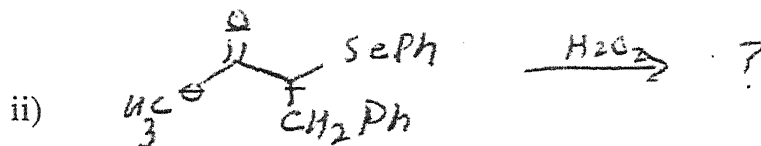
Discuss the mechanism of neighbouring group participation reaction involving phenyl and cyclopropyl rings (6)

4. a) Explain Cram's rule with suitable example (5)
b) Describe the stereochemistry of eliminations in non-cyclic system (5)
c) Write notes on
i) Barton reaction
ii) Hydride transfer reactions

Or

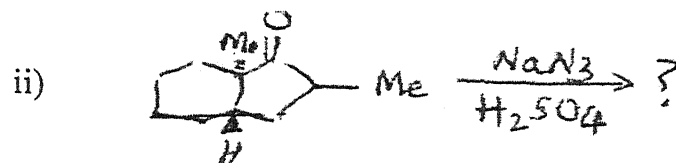
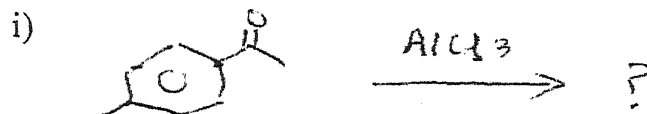
Predict the products and propose mechanism in the following

(6)



5. a) Compute the following and propose mechanisms

(5)



b) What is aldol condensation? Write the mechanism of crossed aldol condensation (5)

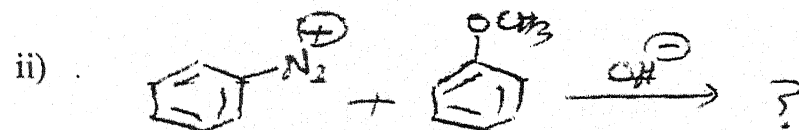
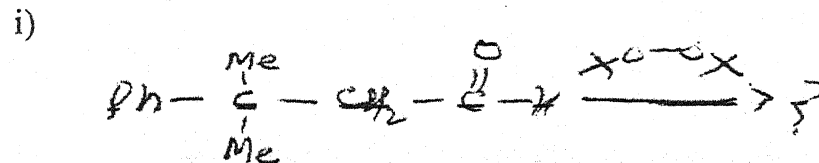
c) Explain the synthetic utility of the following in organic synthesis

i) Perkin reaction

ii) Sandmeyer reaction

Or

Predict the product with suitable mechanism in the following



(6)