Roll No. _____ [Total No. of Pages : 2

PGIIIS - N 1517 B-15
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 are compulsory

2) All questions carry **equal** marks.

1 Answer any **eight** sub questions **(2×8 =16)**

a) Distinguish between the Zero, First and Second order Perturbation terms employed in perturbation theory.

b) Define secular equation and secular determinant

c) What is a Hamiltonian operator? Represent it.

d) Distinguish between intrinsic and extrinsic defects

e) DSC technique represents a better understanding of thermal behavior of solids when compared with DTA.

f) Write the Sucker-Tetrode equation and mention the terms in it explain.

g) Define the term Ensemble, and mention the different types of Ensembles.

h) Calculate the electronic partition function for ground state of hydrogen atom.

i) What are excess thermodynamic functions? Explain.

j) Define the term 'Degree of Solvation'

2 a) Employ Schrodinger wave equation for an harmonic oscillator and give explanation for harmonic and an harmonic terms. **(5)**

b) Taking H_2 as an example, distinguish between the equation obtained for determining the energy of H_2 molecule through valence and molecular orbital theories. **(5)**

c) Give an account of Huckel theory applied to butadiene molecule (6)

OR

c) Distinguish between exchange and overlap integrals. (6)

3. a) With a flow chart explain the steps involved in asexual solid state reaction (5)

b) Represent the Fermi Energy levels in a n-and p-type semiconductors. How do the fermienergy levels change with increase in temperature. (5)

c) Taking a typical example of Mn_3O_4(M = metal). Explain the type of defects present in it (6)

OR

c) Give an account of TGA analysis in understanding the thermal behaviour of solids. (6)

4. a) Derive the classical Maxwell-Boltzmann expression for distribution of mixture of gases for ideal gas molecule. (5)

b) Describe the expression for heat capacity of solids based on Einstein's theory. (5)

c) Define partition function and give its physical significance. Express the energy, entropy and heat capacity of a ideal gas molecule in terms of Partition Function (6)

OR

c) i) The moment of inertia for $35Cl_2$ molecule is 485×10^{-40} Kg.m^2, Calculate the characteristic rotational temperature.

ii) Derive the relational partition function. (3+3=6)

5. a) i) Discuss a method to determine the critical micillar concentration (CMC) of surface actore agents employing conductance measurement

ii) Write the parameters affecting CMC (3+2=5)

b) Discuss on the Gibb's thermodynamic equation of liquid mixing (5)

c) Derive the Onsagor reciprocal relation from the principle of microscopic reversibility (6)

OR

c) Give an account of phenomenological equations in non linear region. (6)

Roll No. _____ [Total No. of Pages : 3

PGIIIS-N 1514 B-15
M.Sc. IIIrd Semester (CBCS) Degree Examination
Chemistry/Organic Chemistry
(Organic Chemistry - III (Spectroscopy))
Paper : HCT - 3.1
(Common to chemistry and organic chemistry)
(New)

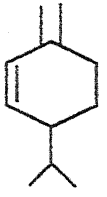
Time : 3 Hours Maximum Marks : 80

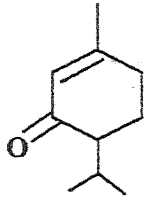
Instructions to Candidates:

1) All questions are Compulsory
2) All questions carry equal marks

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

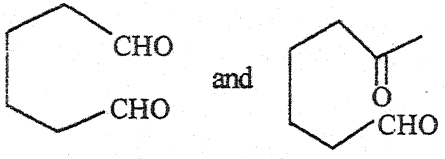
a) Using Woodward-Fieser rules calculate the λ_{max} for the following:

i) 

ii) 

b) Define the terms chromophore and auxochrome. Give one example of each.

c) How are the following compounds distinguished by IR spectroscopy?



d) Why strong bands in IR corresponds to weak bands in Raman and vice-versa?

e) Ethyne protons show upfield chemical shift value compared to ethene protons. Give reason.

f) A sweet smelling liquid with molecular formula $C_4H_8O_2$ gave the following data:

δ :3.67(S,3H), 2.32 (quartet, 2H) and 1.14(t,3H) Arrive at the structure of the compound.

g) How will you distinguish the o-m-and p-xylenes using ^{13}C NMR spectroscopy?

h) Predict the chemical shift positions for the alkene protons of 2-methyl-3-heptene

i) What is the meta stable ion in mass spectrometry? Give its importance.

j) Write the feasible structures for the ions found in the mass spectrum of benzylmethyl ketone at m/z 134,119,92,91,65,51 and 43.

2. a) Why the band positions of both the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of a compound are shifted when the solvent is changed from hexane to ethanol?

b) Predict the probable structure of a organic compound consistent with the following data.

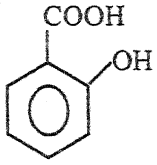
Molecular formula : $C_6H_{10}O$ (negative iodoform test)

UV(λ_{max}) : 228 nm ($\varepsilon = 7900$) IR(cm^{-1}) : 2982, 2876, 1681 and 1462.

c) Answer the following :

i) Benzal acetone (phCH=CH-$COCH_3$) shows two absorption peaks in its IR spectrum due to >C=0 group. Give reason

ii) How will you distinguish the following compounds using IR spectroscopy?



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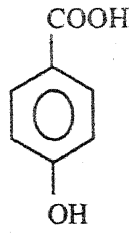
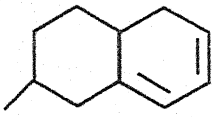


OR

c) i) Explain how does an auxochrome exerts bathochromic shift on a chromophore?

ii) How will you distinguish the following compounds using UV-Vis spectroscopy?



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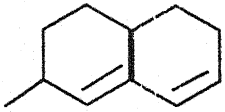


(5+5+6=16)

3. a) Discuss the various factors influencing the chemical shift in ^1H NMR spectroscopy.

b) An organic compound with molecular formula $C_5H_{12}O_4$ exhibits a broad band between 3400-3100 cm^{-1} in its IR spectrum The proton NMR showed two signals at

δ : 3.33 and 3.29 with integral ratio 2.1 respectively. Deduce the structure of the compound.

c) Write a note on :
   i) Lanthanide shift reagents in NMR spectroscopy
   ii) Double resonance or spin decoupling technique

(OR)

c) i) NOE and its applications
   ii) CIDNP and its applications **(5+5+6=16)**

4. a) What is broadband decoupling in ^{13}C NMR spectroscopy ? Mention its merits and demerits over off-resonance decoupling using appropriate example

b) Discuss 2-D homonuclear correlation experiment (^1H-^1H cos Y) with the help of suitable example. Illustrate appropriately cross peaks and diagonal peaks.

c) Deduce the structure of a compound with the help of following data and interpret its molecular formula C_8H_{14}

$UV(\lambda_{max})$: No strong band >200nm IR:2983,2938,1484 and 1338 cm^{-1}

$^1HNMR(\delta, ppm)$: $2.12(t, 4H, J = 8Hz), 1.48(sextet, 4H, J = 8Hz) and\ 0.9(t, 6H, J = 8Hz)$

$^{13}C\ NMR(\delta, ppm)$: $80.2, 22.7, 20.9 and 13.5$

(OR)

c) Write a note on
   i) Karplus equation curve and its applications
   ii) HETCOR technique **(5+5+6=16)**

5. a) Write the mass spectral fragementation patterns of toluene and n-butane.

b) Explain the nitrogen rule with suitable examples

c) Deduce the structure of an organic compound from the following data and assign the values: Molecular formula : $C_{11}H_{14}O_2$

$UV(\lambda_{max})$: 275nm

IR (cm^{-1}) : 2989, 2936, 2874, 2720, 1693, 1603, 1259 and 1101,

$^1HNMR(\delta, ppm)$: 9.91(S,1H) 7.90(d, 2H, J=8Hz) 7.04 (d' , 2H, J=8Hz)
4.10 (t, 2H, J=7Hz) 1.82 (m, 2H)
1.54(m,2H), and 1.06 (t, 3H, J=7Hz)

^{13}C NMR (δ, ppm) : 193.1, 165.2, 132.4, 129.3, 111.2 69.8, 32.2, 19.0 and 12.9

Mass (m/z) : 178(M^+), 177(100%) and 76 (46%)

(OR)

c) Write a note on
   i) McLafferty and McLafferty +1 rearrangements.
   ii) EI and CI methods of ionization in MS. **(5+5+6=16)**

Roll No. _____ [Total No. of Pages : 4

PGIIIS - N 1515 B - 15
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
All questions carry equal marks

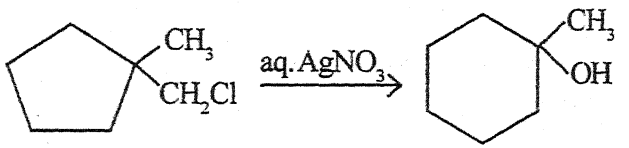
1. Answer any eight of the following: **(8×2=16)**

a) What are carbenes? Give an example of Singlet and triplet carbenes.

b) Give any two methods of generation of carbocations

c) Explain neighbouring group participation with an example

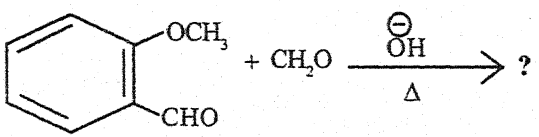
d) Outline a suitable mechanism for the following transformation



e) Account the formation of products on treatment of 2 - bromo - 2 methylbutane with sodium ethoxide.

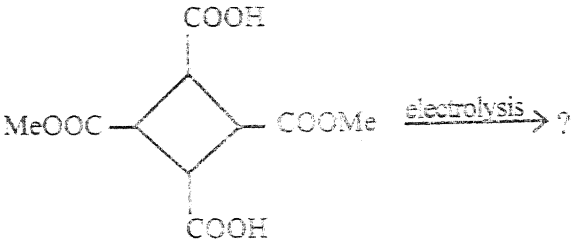
f) Explain saytzeff's rule with an example.

g) Give the product formed with mechanism.



h) What is McMurry reaction? Give the mechanism.

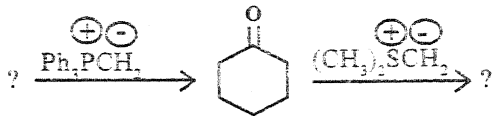
i) Predict the product with mechanism of the following



j) Give the mechanism of a push-pull reaction with a suitable example.

2. a) Discuss the methods of generation of free radicals and explain their structure and stability

b) Predict the product with suitable mechanism for the following reactions

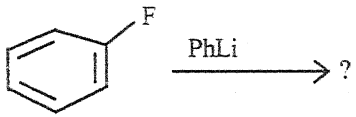


c) Discuss structure and reactions of carbenes

OR

c) Give the products formed with mechanism

i)



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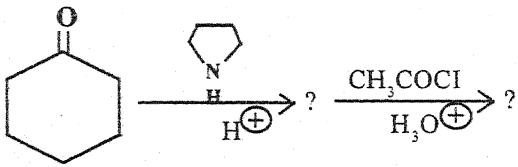
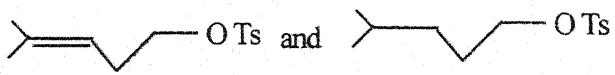
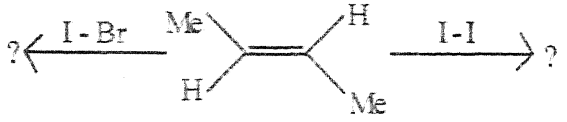


(5+5+6=16)

3. a) Compare the rate of acetolysis of following tosylates. Justify your answer.



b) Predict the Product(s) and their stereochemistry in the following reactions



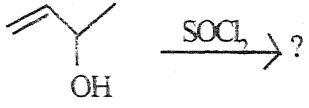
c) Write a note on

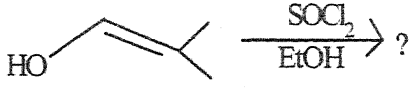
i) Trans annular rearrangement

ii) Cycloalkyl neighbouring group participation

OR

c) Discuss the SN_i' reaction observed in the following reactions.

i) 

ii) 

(5+5+6=16)

4. a) What are acetals? Outline the reaction with mechanism of 1,2 - ethanediol with cyclohexanone in presence of catalytic amount of acid.

b) State and explain cram's rule with a suitable example

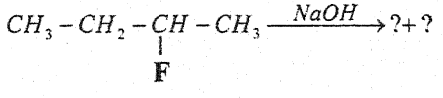
c) Write a notes on

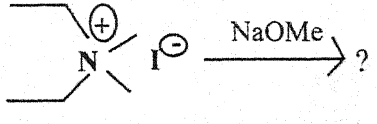
i) Barton reaction

ii) Chugaev reaction

OR

c) Predict the major product in the following

i) 

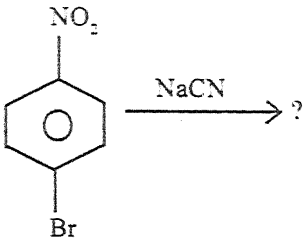
ii) 

(5+5+6=16)

5. a) What are allylic rearrangements? Discuss the mechanism of free radical allylic rearrangements with examples.

b) Give the product with suitable mechanism of the following reactions

i)



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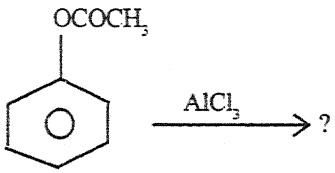


c) Synthesize following compounds with mechanism and name the reaction

i) Cinnamic acid from benzaldehyde

ii) Chlorobenzene from diazoniumbenzene salt

iii) 3- Hydrocybutanal from acetaldehyde

OR

c) Discuss the following:

i) Stobbe condensation

ii) Schmidt rearrangement. **(5+5+6=16)**

Roll No. _____ [Total No. of Pages : 2

PGIIIS-N 1521 B-15
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:

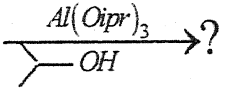
1) Answer ALL the questions
2) All questions carry equal marks

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

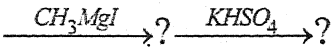
a) Lactose is a reducing sugar Justify.

b) Explain why cyanogen bromide specifically cleaves the carboxyl end of methionine?

c) What is Diels hydrocarbon? How is it obtained?

d) Predict the product and propose a mechanism cholesterol 

e) Write the product in the following reaction

Estrone 

f) Out line the steps involved in the following transformation

$\alpha - santonin \rightarrow Hyposantonin$

g) Draw all possible stereo chemical structures of ephedrine and comment on their activity.

h) What are the prostaglandins? Give their biological importance.

i) Distinguish between replication and transcription

j) How do you convert vitamin A_1 into A_2 ?

2. a) How do you establish the presence of pyranose ring in D-glucose by methylation and oxidation?

b) Out line the steps involved in the synthesis of the following tripeptide Ala.Gly. Cyst

c) Describe any two methods of determination of C-terminal and N-terminal amino acid residue of a polypeptide.

(OR)

c) Write an account on general methods of structural elucidation of polysaccharides. **(5+5+6=16)**

3. a) Discuss the utility of Barbier-Wieland degradation in the structural elucidation of steroids.

b) Outline the synthesis of cortisone

c) How do you bring about the following transformations.

i) *Diosgenin → progesterone*

ii) *Cholesterol → Testosterone*

(OR)

c) Write notes on

i) Cardiotonic glycosides

ii) Irradiation products of ergosterol **(5+5+6=16)**

4. a) How is the structure of camphor established by chemical evidences?

b) Give the synthesis of quinine

c) How are the following established?

i) Phenanthrene nucleus in morphine.

ii) Dimethoxy isoquinoline in papaverine.

(OR)

c) Give the synthesis of

i) Abietic acid

ii) Capsorubin **(5+5+6=16)**

5. a) Sketch the corey's synthesis of P&E_1

b) Explain the salient features of Crick-watson model of double helical structure of DNA.

c) How are the following established?

i) Presence of 1,4 - naphthoquinone system in Vitamin K_1

ii) Nature of sulphur atom in Biotin.

(OR)

c) Write an account of

i) Recombinant DNA

ii) Genetic code. **(5+5+6=16)**

Roll No. _____ [Total No. of Pages : 3

PGIIIS-N 1519 B-15
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:

1. Answer **all** the questions
2. All questions carry **equal** marks.

1. Answer any **eight** questions. **(8×2=16)**

a) Define Portland cement? Write its types.

b) What is annealing?

c) Write the source and biochemical effects of O_3 and PAN.

d) What is the principle function of nitrogenase?

e) Define the terms ferritin and transferrin.

f) Write the advantages and disadvantages of nuclear reactors.

g) State photo chemical laws.

h) Differentiate between photo isomerization and photo recemization reactions.

i) Write down the expression relating to disintegration constant and half life of radio nuclide.

j) Mention the harmful effects of metallurgical industrial pollution.

2. a) Explain the manufacture of steel by using Bessemer converters method. (5)

b) Discuss the storage and disposal procedures for the nuclear waste. (5)

c) Describe the manufacture and properties of portland cement. (6)

OR

Discuss indetail pollution caused by thermal power plants and explain the treatment technologies for the control of thermal pollution.

3. a) Discuss the source, biochemical effects and treatment options for cyanide and arsenic. (5)

b) What are the functions of haemoglobin and myoglobin? What are the principle similarities in their structures? (5)

c) Write a note on biological nitrogen fixations. (6)

OR

What do you mean by ferredoxins? Give the examples of different types of ferredoxins and discuss their structural features.

4. a) Draw a schematic diagram of nuclear reactor and label the components and write its character features. (5)

b) Discuss the construction and operation of scintillation counters. (5)

c) What are breeder reactors? How do they differ from others? Mention their advantages. (6)

OR

Discuss the parent daughter decay growth relationship with reference to

i) Parent long-lived than daughter $\left(\tau_p > \tau_d\right)$

ii) Parent and daughter nearly the same half life. $\left(\tau_p \approx \tau_d\right)$

5. a) Explain the photo redox reactions? Give examples. Discuss their applications. **(5)**

b) What is charge transfer spectra? Discuss the ligand-metal and metal-ligand charge spectra with suitable example. **(5)**

c) How does energy dissipation occur? Discuss in detail. **(6)**

OR

Write a note on

i) Metal complexes as sensitizers and

ii) Photo reduction reactions.