

CONTENTS

CHAPTER – 1

CONCEPT OF ATOMIC STRUCTURE

- Dual character of matter (deBroglie's hypothesis)
 - (i) Derivation of deBroglie's equation
 - (ii) Experimental verification of deBroglie's equation.
 - (iii) Experimental Verification of wave nature of electron.
 - (iv) Confirmation of quantisation of angular momentum.
 - (v) Significance of deBroglie's concept.
 - Heisenberg's uncertainty principle.
 - (i) Illustration of the principle
 - (ii) Uncertainty principle and Bohr's model
 - (iii) Applications of uncertainty principle.
 - Schrodinger's wave equation
 - Significance of wave equation.
 - (i) Eigen values and Eigen functions.
 - (ii) Wave equation for hydrogen like species.
 - (iii) Development of quantum number.
 - (iv) Significance of ψ and ψ^2 .
 - Concept of orbital
 - Shapes of orbitals.
 - Quantum numbers.
 - (i) Principal quantum number
 - (ii) Azimuthal quantum number
 - (iii) Magnetic quantum number
 - (iv) Spin quantum number.
 - Pauli's exclusion principle.
 - Shielding effect and Effective nuclear charge
 - Electronic configuration of elements.
 - (i) Aufbau principle
 - (ii) Hund's rule
 - Symmetrical distribution of charge
 - Some possible questions.
-

CHAPTER – 2

CONCEPT OF CHEMICAL BONDING

- Valence Bond Theory (Heitler-London treatment)
- Pauling-Slater's Theory.
- Molecular Orbital Theory.
- Formation of Bonding and Antibonding molecular orbital.
- Molecular orbitals due to combination of s-orbitals.
- Molecular orbitals due to combination of s- and p-orbitals.
- Molecular orbital due to combination of two p_x -orbitals.
- Molecular orbital due to combination of two p_y or p_z orbitals.
- Energy level diagram for molecular orbitals.
- Mixing of orbitals.
- Electronic configuration of molecular orbitals.
- Bond order

- Molecular orbital configuration of diatomic species.
 - (i) Hydrogen molecule
 - (ii) Hydrogen molecule ion
 - (iii) Helium molecule
 - (iv) Helium molecule ion
 - (v) Carbon molecule
 - (vi) Nitrogen molecule
 - (vii) Nitrogen molecule ion
 - (ix) Oxygen molecule
 - (x) Oxygen molecule ions.
 - (xi) Fluorine molecule
 - (xii) Carbon monoxide
 - (xiv) Nitric oxide
- Comparison between Valence Bond theory and Molecular Orbital theory.
- Hybridisation
 - (i) sp^3 -hybridisation
 - (ii) sp^2 -hybridisation
 - (iii) sp -hybridisation
- Salient features of hybridisation (Rules)
 - Electronegativity
 - Polarity in covalent bond and dipole moment.
 - Hydrogen bond
 - Addition compounds
 - Electron donor acceptor complex (EDA complex)
 - Crown ether complexes and Cryptate
 - Catenanes and Rotaxanes
 - Inclusion complex
 - Concept of Aromaticity
 - Huckel's modern theory of aromaticity.
 - Some possible questions.

CHAPTER-3

REACTIVE INTERMEDIATES

- Carbocations
 - (i) Classification
 - (ii) Structure
 - (iii) Stability
 - (iv) Generation
 - (v) Fate
- Carbanions
 - (i) Classification
 - (ii) Structure
 - (iii) Stability
 - (iv) Generation
 - (v) Fate
- Free radicals
 - (i) Classification
 - (ii) Structure
 - (iii) Stability
 - (iv) Generation
 - (v) Fate
- Carbenes
 - (i) Classification, structure and stability
 - (ii) Generation
 - (iii) Fate
- Nitrenes
 - (i) Generation
 - (ii) Fate
- Arynes
 - (i) Generation
 - (ii) Reactions
- Some possible questions

CHAPTER-4

ELECTRON DISPLACEMENT IN ORGANIC MOLECULE

- Inductive effect
(Permanent polarization)
 - (i) Positive and negative inductive effect
 - (ii) Characteristics
 - (iii) Applications
 - Resonance (Mesomerism)
 - (i) Conditions for resonance
 - (ii) Resonance hybrid and its characteristics.
 - (iii) Resonance effect
 - (iv) Applications of resonance
 - Distinctions in between inductive effect and resonance
 - Hyperconjugation
 - (i) Types of hyperconjugation
 - (ii) Applications.
 - Electromeric effect
 - Some possible questions
-

CHAPTER-5

STEREOCHEMISTRY

- Isomerism
- Structural isomerism
 - (i) Chain isomerism
 - (ii) Positional isomerism
 - (iii) Functional isomerism
 - (iv) Metamerism
 - (v) Tautomerism
- Stereoisomerism
- Geometrical isomerism
 - (i) Conditions and causes of geometrical isomerism.
 - (ii) Characteristics of geometrical isomers.
- E and Z notations.
- Determination of configuration of geometrical isomers.
- Optical isomerism
 - (i) Optical activity
 - (ii) Causes of optical activity
- Enantiomers
- Compounds displaying optical activity.
 - (i) Compound with chiral carbon
 - (ii) Compound with tervalent chiral atom
 - (iii) Compound with quadrivalent chiral atom
 - (iv) Compounds with dissymmetric plane
 - (v) Chirality due to helical shape.
- Racemic modification
- Distereomers or Distereoisomers.
- Resolution of racemic modification.
- Asymmetric synthesis.
- Absolute asymmetric synthesis.
- Fischer projection of tetrahedral carbon atom.
- Absolute and Relative configuration.
- R.S.Nomenclature (Cahn-Ingold-Prelog system).
- Concept of prostereoisomerism
- Optical activity due to chiral axis and chiral plane.

- Optical purity.
- Conformations and conformational analysis.
 - (i) Sawhorse formula
 - (ii) Newman projection formula
- Baeyer strain theory
- Sachse-Mohr theory
- Conformations of cyclohexane
- Conformations of Monosubstituted cyclohexane
- Conformations of disubstituted cyclohexane
- Conformations of decalins.
- Effect of conformation on reactivity.
 - (i) Acyclic compounds
 - (ii) Cyclic compounds
- Some possible questions.

CHAPTER-6

ORGANIC REACTIONS AND STUDY OF THEIR MECHANISM

- Homolytic and heterolytic bond cleavage
- Components of Organic reaction
- Mechanistic classification of organic reactions
 - (i) Substitution reaction
 - (ii) Addition reaction
 - (iii) Elimination reaction
 - (iv) Molecular rearrangement
 - (v) Pericyclic reaction
 - (vi) Complex reaction
- Some kinetic terms
 - (i) Rate of reaction
 - (ii) Rate equation or Rate law
 - (iii) Molecularity of a reaction
 - (iv) Order of a reaction
- The Transition state
- Thermodynamic requirements for a reaction
- Kinetic requirements for a reaction.
- Baldwin rules for ring closure.
- Kinetic and thermodynamic control.
- The Hammond postulate
- Curtin-Hammett principle
- Hammett equation :
 - Linear free energy relationship.
 - (i) Importance of Hammett equation
 - (ii) Substituent constant
 - (iii) Reaction constant
- Taft equation
- Isotopic effect
 - (i) Primary isotope effect
 - (ii) Secondary isotope effect
- Methods of determining reaction mechanism
 - (i) Product analysis
 - (ii) Determination of the intermediate
 - (iii) Crossover experiment
 - (iv) Isotopic labelling
 - (v) Stereochemical evidence
 - (vi) Kinetic evidence
- Hard and soft concept of acid base
- Hard soft acid base principle (HSAB - principle)
- Some possible questions.

CHAPTER – 7

ORGANIC PHOTOCHEMISTRY

- Photochemical energy
 - Laws of photochemistry
 - (i) Grothus - Draper law
 - (ii) Einstein - Stark law (Law of photochemical equivalence)
 - Processes in photochemical reactions
 - Quantum yield or Quantum efficiency
 - Factors affecting quantum yield
 - Electronic excitation
 - Types of excitation
 - Photolysis
 - Fate of excited molecules
 - (i) Physical process
 - (ii) Chemical process
 - Fluorescence
 - Phosphorescence
 - Photochemical reactions of olefins.
 - Photoreduction of carbonyl compounds
 - Photofries Rearrangement
 - Norrish Type-I reaction
 - Norrish Type-II reaction
 - Paterno-Buchi reaction
 - Photochemistry of α , β -unsaturated ketone
 - Photochemistry of butadiene.
 - Barton reaction
 - Hofmann-Loeffler Freytag reaction
 - Photochemical oxidation
 - (i) Backstrom mechanism
 - (ii) Schenck's mechanism
 - (iii) Foote's mechanism
 - Photo-oxidation of alkenes
 - Photochemistry of aromatic compounds
 - Di-pi methane rearrangement
 - Photosynthesis
 - Chemistry of vision
 - Some possible questions
-

CHAPTER-8

PERICYCLIC REACTION

- Characteristics of pericyclic reactions
- Woodward Hoffmann rule
- Classification of pericyclic reactions
- Molecular orbitals of unsaturated molecules
 - (i) Ethene
 - (ii) 1, 3-Butadiene
 - (iii) 1, 3, 5-Hexatriene
 - (iv) Allyl system
- Symmetry properties of molecular orbitals
- Methods of explaining pericyclic reactions.
 - (i) Woodward Hoffmann method
 - (ii) Frontier molecular orbital approach
 - (iii) Perturbation molecular orbital theory
 - (iv) Mobius Huckel approach

- Electrocyclic reactions
 - (i) Dis and Con rotation of orbitals
 - (ii) Electrocyclic reactions in $4n-\pi$ electron system.
 - (iii) Electrocyclic reactions in $(4n+2)-\pi$ electron system
 - (iv) Explanation through correlation diagram
 - (v) Explanation through Huckel-Mobius method
- Cycloaddition Reactions
 - (i) 2+2-cycloaddition
 - (ii) 4+2-cycloaddition
 - (iii) Explanation through correlation diagram.
 - (iv) Explanation through Huckel Mobius method
 - (v) 1, 3-Dipolar cycloaddition.
- Cheletropic reactions
- Sigmatropic migration
 - (i) Sigmatropic migration of hydrogen
 - (ii) Sigmatropic migration of carbon.
- Claisen rearrangement
- Cope rearrangement
- Group transfer reaction
- Ene reactions
- Some possible questions

CHAPTER-9

ORGANOMETALLIC COMPOUNDS

- Introduction
- Metal atom functionality
 - (i) Carbanionic behaviour
 - (ii) Carbocationic behaviour
 - (iii) Free radical generation centre
 - (iv) Centre for oxidative addition and reductive elimination.
 - (v) Centre for group migration (insertion) reaction.
 - (vi) Act as leaving group in substitution and elimination.
 - (vii) Induction of carbene and carbenoid intermediate
 - (viii) Metal carbene or metal carbocation complex
 - (ix) Protection and activation by metal.
- Grignard reagent
 - (i) Preparation
 - (ii) Properties
 - (iii) Synthetic application
- Organolithium compounds
 - (i) Preparation
 - (ii) Synthetic applications
- Organocopper compounds
 - (i) Preparation
 - (ii) Synthetic applications
- Organoaluminium compounds
 - (i) Preparation
 - (ii) Synthetic applications
- Organocadmium compounds
 - (i) Preparation
 - (ii) Synthetic applications
- Organozinc compounds
 - (i) Preparation
 - (ii) Synthetic applications
- Organomercury compounds
 1. Acetoxymcury
 - (i) Preparation
 - (ii) Synthetic applications
 2. Dialkyl mercury
 - (i) Preparation
 - (ii) Synthetic applications
- Organotin
 - Preparation and synthetic application
- Some possible questions

CHAPTER – 10

ALIPHATIC NUCLEOPHILIC SUBSTITUTION

- Introduction
- SN_2 – mechanism
 - (i) Salient features
 - (ii) Evidences in favour of SN_2 mechanism
- SN_1 – mechanism
 - (i) Salient features
 - (ii) Evidences in favour of SN_1 -mechanism
- Ion pairs in SN_1 – mechanism
- Mixed SN_1 and SN_2 (Border line) mechanism
- SET mechanism
- SN_i – mechanism
- Nucleophilic substitution at allylic carbon
- Nucleophilic substitution at aliphatic trigonal carbon
- Nucleophilic substitution at vinylic carbon
- Neighbouring group participation
 - (i) Characteristics of neighbouring group mechanism
 - (ii) Examples of neighbouring group participation.
- Factors influencing reactivity of nucleophilic substitution.
 - (i) Effect of the structure of substrate
 - (ii) Effect of nucleophile
 - (iii) Effect of solvent
 - (iv) Effect of leaving groups at carbonyl carbon
- Ambient nucleophile
- Factors influencing regioselectivity in ambient nucleophiles.
- Ambient substrate
- Some possible questions.

CHAPTER – 11

ALIPHATIC ELECTROPHILIC SUBSTITUTION

- Unimolecular mechanism (SE_1)
 - (i) Salient features
 - (ii) Stereochemistry
 - (iii) Evidences in favour of SE_1 mechanism
- Bimolecular mechanism (SE_2 and SE_i)
 - (i) Salient features of SE_2
 - (ii) Salient features of SE_i
 - (iii) Evidences in favour of SE_2 (front) attack.
 - (iv) Evidences in favour of SE_2 (back) attack
- Distinctions in between SE_2 and SE_1
- Electrophilic substitution at allylic substrate
- Factors influencing reactivity
 - (i) Effect of structure of the substrate
 - (ii) Effect of leaving group.
 - (iii) Effect of solvent
- Some examples of aliphatic electrophilic substitution
 - (i) Hydrogen as leaving group
 - (ii) Electrophilic substitution with double bond shift
 - (iii) Halogen as electrophile and hydrogen leaving group
 - (iv) Nitrogen as electrophile
 - (v) Sulfur as electrophile
 - (vi) carbon as electrophile
 - (vii) Nitrosation reaction.
- Some possible questions.

CHAPTER – 12

AROMATIC ELECTROPHILIC SUBSTITUTION

- Arenium ion mechanism
 - (i) Salient features
 - (ii) Evidences supporting arenium ion mechanism
 - Pi-complex mechanism
 - Evidences in favour of π -complex mechanism
 - SE_1 -mechanism
 - Some typical aromatic electrophilic substitution
 - (i) Nitration
 - (ii) Sulfonation
 - (iii) Halogenation
 - (iv) Friedel-Crafts reaction
 - Orientation and reactivity
 - Classification of the substituents
 - Ortho-para ratio
 - Ipso attack
 - Rearrangement followed by ipso attack
 - Orientation of benzene with more than one substituent
 - Quantitative treatment of reactivity in the substrate
 - Quantitative treatment of reactivity of the electrophile.
 - Vilsmeier - Haack reaction
 - Gatterman - Coch reaction
 - Reimer - Tiemann reaction
 - Hoesch reaction
 - Diazonium coupling
 - Some possible questions
-

CHAPTER – 13

AROMATIC NUCLEOPHILIC SUBSTITUTION

- Introduction
- Ar SN_2 - mechanism
 - (i) Salient features
 - (ii) Evidences favouring Ar SN_2 -mechanism
- Ar SN_1 - mechanism
 - (i) Salient features
 - (ii) Evidences supporting Ar SN_1 mechanism
- Benzyne mechanism
 - (i) Salient features
 - (ii) Evidences supporting benzyne mechanism
- Orientation of nucleophile through benzyne intermediate
- SRN_1 - mechanism
 - (i) Salient features
 - (ii) Evidences supporting the mechanism
- Factors influencing reactivity of aromatic nucleophilic substitution.
 - (i) Effect of structure of the substrate
 - (ii) Effect of leaving group
 - (iii) Effect of attacking nucleophile
- Von-Richter rearrangement
- Sommelet-Hauser rearrangement
- Smiles rearrangement
- Some possible questions.

CHAPTER – 14

FREE RADICAL SUBSTITUTION REACTION

- Free radical
- Free radical reactions
- Characteristics of free radical reactions
- Mechanism of free radical reactions.
- Mechanism of free radical substitution
 - (i) Aliphatic substitution
 - (ii) Aromatic substitution
- Neighbouring group assistance in free radical reactions
- Factors influencing free radical reactions.
 - (i) Nature of aliphatic substrate
 - (ii) Nature of aromatic substrate
- (iii) Nature of attacking radical
- (iv) Nature of the solvent
- Free radical substitution at bridge head
- Allylic halogenation
- Oxidation of aldehydes to carboxylic acid
- Autoxidation
- Coupling of alkynes
- Arylation of aromatic compounds by diazonium salt
- Sandmeyer reaction
- Hunsdiecker reaction
- Kochi reaction
- Some possible questions.

CHAPTER – 15

ADDITION TO CARBON - CARBON MULTIPLE BOND

- Electrophilic addition mechanism
 - (i) Syn addition
 - (ii) Anti addition
- Nucleophilic addition mechanism
- Free radical addition mechanism
- Addition to conjugated system.
- Reactivity of the substrate
- Orientation
 - (i) Electrophilic addition (Markownikoff's rule)
 - (ii) Nucleophilic addition
 - (iii) Free radical addition
- (iv) Addition to conjugated diene
- (v) Addition to allene system
- Addition of halogen
- Addition of hydrogen halide
- Acid-catalysed addition of water
- Addition involving metal ion
- Hydroboration
- Hydroxylation of alkene
- Epoxidation
- Sharpless asymmetric epoxidation
- Michael addition
- Some possible questions

CHAPTER – 16

ELIMINATION REACTION

- Introduction
- The E₂-mechanism
 - (i) Salient features
 - (ii) Elimination involving more than one β-carbon
- (iii) Evidences supporting E₂ - mechanism
- (iv) Stereochemistry of E₂ - reactions
- Consecutive E₂-elimination

- The E_1 -mechanism
 - (i) Salient features
 - (ii) Evidences supporting E_1 -mechanism
 - (iii) Elimination involving more than one β -carbon
- The E_{1CB} mechanism
 - (i) Salient features
 - (ii) Evidences supporting E_{1CB} -mechanism
- Comparison in between E_1 , E_2 and E_{1CB} - mechanism
- Factors influencing elimination mechanism
 - (i) Effect of substrate structure
 - (ii) Effect of attacking base
 - (iii) Effect of leaving group
 - (iv) Effect of reaction medium
- Pyrolytic elimination (E_i -mechanism)
 - (i) Salient features
 - (ii) Evidences supporting E_i - mechanism
- Dehydration of alcohols
- Dehalogenation of vicinal dihalides
- Peterson elimination reaction
- Hydroalkoxy elimination
- Some possible questions

CHAPTER – 17

OXIDATION

- Introduction
- Oxidative processes
- Aromatization of cyclohexane
- Oxidation of alcohols
- Oxidation of α , β -diols
- Oxidation of allylic or benzylic alcohol
- Oxidation of aldehyde
- Oxidation of ketone
- Oxidation of carboxylic acid
- Oxidation of amines
- Oxidation of hydrocarbon :
 - (i) Oxidation of active methylene group
 - (ii) Oxidation of aryl methane
- Oxidation of double bonded compounds
 - (i) Oxidation of alkene
 - (ii) Ozonolysis
 - (iii) Oxidation of aromatic hydrocarbon
- Some possible questions

CHAPTER-18

REDUCTION

- Introduction
- Different reductive processes
- Reduction of alkene
- Reduction of alkyne
- Reduction of aromatic rings
- Reduction of cyclopropane
- Reduction of carbonyl compounds
 - (i) Reductive deoxygenation
 - (ii) Reduction through hydride transfer
- Reduction of carboxylic acid
- Reduction of ester
- Reduction of acid halide
- Reduction of amide
- Reduction of nitro compounds
- Hydrogenolysis
- Some possible questions

CHAPTER – 19

SOME SELECTED ORGANIC NAME REACTIONS

- Aldol condensation
 - Arndt - Eistert reaction
 - Baeyer - Villiger reaction
 - Claisen condensation
 - Chichibabin reaction
 - Claisen - Schmidt reaction
 - Dieckmann condensation
 - Hofmann reaction
 - Knoevenagel reaction
 - Mannich reaction
 - Michael reaction
 - Perkin reaction
 - Reformatsky reaction
 - Reimer - Tiemann reaction
 - Shapiro reaction
 - Stobbe condensation
 - Wittig reaction
 - Some possible questions
-

CHAPTER – 20

MOLECULAR REARRANGEMENT

- Introduction
 - Beckmann rearrangement
 - Banzilic acid rearrangement
 - Claisen rearrangement
 - Curtius rearrangement
 - Dienone phenol rearrangement
 - Favorskii rearrangement
 - Fries rearrangement
 - Lossen rearrangement
 - Neber rearrangement
 - Pinacol pinacolone rearrangement
 - Stevens rearrangement
 - Tiffeneau - Demyanov rearrangement
 - Wagner - Meerwein rearrangement
 - Wolff rearrangement
 - Benzidine rearrangement
 - Some possible questions.
-

- **OBJECTIVE TYPE QUESTIONS FOR DIFFERENT COMPETITIVE EXAMINATION**
- **REFERENCES**
- **INDEX**