SEMESTER-I
Paper S-1042
Organic chemistry

Time: 3 Hrs. **M.M. 75 marks**

Note: The paper will be divided into two sections.

Section-A One question with 10 parts (short answer word limit 20) spread over whole syllabus. Each part will be of 1 mark and candidate is required to attempt all the ten parts

Total 10 marks

Section-B Five questions (answer not exceeding 500 words) are from each Unit with internal choice will be asked and the candidate is required to attempt all five questions. Each question will be of 13 marks

Total 65 marks

UNIT-I

Nature of bonding in organic molecules: Delocalized chemical bonding-conjugation, cross conjugation,, bonding in fullerenes, aromaticity in benzenoid and non-benzenoid compounds, annulenes, ferrocenes and helicenes, alternant and non-alternant hydrocarbons, Huckel'sπ-molecularrule,orbitals, energyanti-aromaticity,levelϕ- o aromaticity, homo-aromaticity, PMO approach.

UNIT-II

Reaction mechanism, structure and reactivity - Kinetic and thermodynamic control, Hammond's postulate,-Hammettprinciple,Curtinpotentialenergy diagrams, transition states and intermediates, methods of determining mechanisms, iostope effects, effect of structure on reactivity-resonance and field effects, steric effect, steric inhibition to resonance, substituent and reaction constants, Taft equation.

UNIT-III

Aliphatic reaction Mechanism

(i) Nucleophilic substitution - The S_N2, S_N1, mixed S_N2 and S_N1, S_Ni and SET mechanisms, Neighbouring group participation.

Classical and nonclassical carbocations, phenonium ions, norbornyl system, common carbocation, rearrangements, neucleophilic substitution at allylic, trigonal and vinylic carbon, reactivity effects of substrate structure, attacking nucleophile, leaving group and reaction medium, ambient nucleophile, regioselectivity.

(ii) Electrophilic substitution – S_E2 and S_E1 mechanism, electrophilic substitution accompanied by double bond shift, effect of substrates, leaving group and the solvent polarity on reactivity.

UNIT-IV

Aromatic reaction Mechanism

(i) **Electrophilic substitution -** The arenium ion mechanism, orientation and reactivity, energy profile diagrams,` the ortho/para ratio, ipso attack, orientation in other ring systems, diazonium coupling, Vilsmeir - Haak reaction, Bischler-Napieralske reaction, Pechmann reaction.

(ii) **Nucleophilic substitution** - The S_NAr, S_N1, benzyne and $S_{RN}1$ mechanisms, reactivity - effect of substrate structure, leaving group and attacking nucleophile. The Von Richter, Sommetet-Hauser and Smiles rearrangements.

(iii) **Free redical reaction** - Types of free radical reactions, free radical substitution mechanism, neighboring group asistance, reactivity for aliphatic and aromatic substrate at a bridgehead, reactivity in the attacking radicals, the effect of solvents on reactivity, allylic halogenation (NBS), oxidation of aldehydes to carboxylic acids, autooxidation, coupling of alkynes and arylation of aromatic compounds by diazonium salts, Sandmeyer reaction, free radical rearrangement, Hunsdiecker reaction.

UNIT-V

Addition Reaction

Carbon-Carbon multiple bonds - Mechanistic and stereochemical aspects of addition reaction involving electrophiles, nucleophiles and free radicals, regio and chemoselectivity, orientation and reactivity, addition to cyclopropane ring, hydrogenation of double bond, triple bonds and aromatic rings, hydroboration, cyanoethylation.

Carbon-Hetero multiple bonds - Mechanism of metal hydride reduction of saturated and unsaturated carbonyl compounds, addition of Grignard reagents, organozinc and organolithium reagents to carbonyl and unsaturated carbonyl compounds, Wittig reaction, mechansim of condensation reaction involving enolates, Mannich, Benzoin, Perkin and Stobbe reactions, hydrolysis of esters and amides ammonolysis of esters.

Elimination reaction - The E2, E1, ElcB and E2cB mechanisms and their spectrum, orientation of the double bond, reactivity-effect of substrate structures, attacking base, the leaving group and the medium, stereochemistry, elimination v/s substitutions, pyrolytic eliminations.

Books Recommended :

1. Advanced Organic Chemistry-Reactions, Mechanism and Structure, Jerry March, John Wiley.
2. Advanced Organic Chemistry, F.A. Carey and R.J. Sundberg, Plenum
3. A Guide book of Mechanism in Organic Chemistry, Peter Sykes, Longman
4. Structure and Mechanism in Organic Chemistry, Peter Sykes, Longman
5. Modern Organic Reactions, H.O. House, Benjamin
6. Principles of Organic Synthesis, R.O.C. Norman and J.M. Coxon, Blackie
7. Academic & Professional
8. Reaction Mechanism in Organic Chemistry, S.M. Mukherji and S.P. Singh
9. Macmillan.
10. Stereochemistry of Organic Compounds, D. Nasipuri, New Age International.
11. Stereochemistry of Organic Compounds, P.S Kalsi, New age International
12. Organic Reaction and Their Mechanisms, P.S. Kalsi, New Age International
13. Organic Reaction Mechanism, V.K. Ahluwalia and R.K. Parshar, New Age International.

14. Stereochemistry of Organic Compounds, E.L. Eliel