Subject Code : P8CH10

CORE COURSE X - ORGANIC CHEMISTRY II

UNIT – I

Nucleophilic Substitution Reactions

Aliphatic Nucleophilic substitution – Mechanisms – Effect of structure - Stereochemical factors – Neighbouring group participation, substitutions at allylic and vinylic carbons. Correlation of structure with reactivity – Solvent effects.Rearrangements involving Carbocations - Wagner Meerwein and Dienone – phenol rearrangements.

Aromatic Nucleophilic substitution – SN1 SNAr ,Benzyne mechanism – reactivity orientation – Ullman,Sandmeyer and Chichibabin reaction.Rearrangements involving nucleoplilic substitution – Stevens – sommelet Hauser and Von – Richter rearrangements.

UNIT - II

Electrophilic Substitution Reactions

Aromatic electrophilic substitution reaction - Orientation, reactivity and mechanisms based on transition state theory with suitable reactions, substitutions in Thiophene, Pyridine and Pyridine-N-Oxide. Quantitative treatment of the structural effects on reactivity. Substituents effects – Origins of Hammett equation – Principles of Hammett correlation – Effect of structure on reaction mechanisms Hammett parameters; σ and ρ, modified forms of Hammett equation. Taft Equation.

Aliphatic Electrophilic Substitution: SE^2,SE^i and SE^1mechanisms ,Diazonium coupling reactions. Metals as electrophile in substitution reactions and decomposition of diazonium salts.

UNIT – III

Addition and Elimination Reactions

Addition to carbon – carbon multiple bonds: Electrophilic, nucleophilic and free radical additions – Orientation of the addition – Stereochemical factors influencing the addition of bromine and hydrogen bromide, hydroxylation, hydroboration leading to formation of alcohols. Addition to carbonyl and conjugated carbonyl systems - Mechanism – Grignard reagents – 1,2 and 1,4-additions (dimethyllithiumcuprate),Benzoin , Knovenagel, Stobbe and Darzen's glycidic ester condensation and Reformatsky reactions.

Elimination Reactions: Mechanisms; E1,E2, E1cB – Stereochemistry of elimination, Hofmann and Saytzeff rules – Competition between elimination and substitution - Pyrolytic cis elimination, Chugaev reaction – Examples such as dehydration, dehydrohalogenatio, Hofmann degradation, Cope elimination – Bredt's rule with examples.

UNIT – IV

Pericyclic Reactions and Rearrangements

Concerted reactions – stereochemistry-orbital symmetry and concerted symmetry and correlation diagram –Frontier molecular orbital approach – Woodward and Hoffmann rules – Electrocylcic reactions – cycloaddition reactions – sigmatropic rearrangements – selection rules and examples with simple molecules – 1,3 and 1,5 hydrogen shifts –Cope and Claisen rearrangements. Other molecular rearrangements Wolff – Lossen – Schmidt – Favorski – Pummmerer and Hofman Freytas reagents

UNIT V

Reagents in Organic Synthesis

Reduction: Catalytic hydrogenation – Wilkinson Catalyst, dehydrogenation, reduction with LAH, $NaBH_4$, tertiarybutoxy aluminum hydride, $NaCNBH_3$, tributyltin hydride, alkali metals for reduction, reductions involving hydrazines,Wolf Kishner reduction.

Oxidation: Osmium tetroxide, Sharpless asymmetric epoxidation, Chromyl chloride, Ozone, DDQ, Dioxiranes, Lead tetraacetate, Selenium dioxide, DMSO with either Ac_2O or Oxalyl chloride, Dess-Martin reagent. Synthesis involving phase transfer catalysis (PTC),use of crown ethers, Merrifield resin, Baker's yeast

References

1. S.H. Pine, J.B. Hendrickson, D.J. Cram and G.S. Hammond, Organic chemistry, McGraw Hill, 4th ed., 1980.
2. T.H. Lowry and K.S. Richardson, Mechanism and Theory in Organic Chemistry,Harper and Row, 1976.
3. J. March, Advanced Organic Chemistry; Reactions, Mechanisms and Structure, 5th Ed., Willey, 2000.
4. R.K. Bansal, Reaction Mechanism in Organic Chemistry, Tata McGraw Hill, 1990.
5. F.A. Carey and R.J. Sundberg, Advanced Organic Chemistry, Parts A & B, Plenum, 2002.