Reaction Mechanisms

Schedule:

Week 1: Repetitive survey of VB and LCAO-MO methods; electron shift phenomena; effects of substituents; reactive intermediates; Hammond postulate; interactions between particles; solvent properties and effects.

Week 2: Perturbation theory of chemical reactions; Klopman–Salem equation; stereoelectronic effects; Baldwin's rules; principle of least motion.

Week 3: Substitution on tetrahedral carbon atoms: SN2 and SN1 mechanisms, kinetics and stereochemistry; ion-pairs; neighbouring group effects; Walden inversion; effects of nucleophile, solvent and substrate; ambident and α-effect nucleophiles.

Week 4: Eliminations: α-, β-, 1,n-eliminations; E2 and E1 mechanisms, kinetics and stereochemistry; substrate, base and leaving-group effects; substitution/elimination ratio.

Week 5: Substitutions on trigonal carbon atoms: acyl substitution; reactivity of carboxylic acid derivatives; tetrahedral mechanism; stereoelectronic control; activation and catalysis; ring-closures on acyl carbons.

Week 6: Additions: electrophilic additions on C=C bonds; stereochemistry and intermediates; nucleophilic additions on carbonyl groups and C=C bonds; regioselectivity; 1,2- vs. 1,4-addition; ring closures.

Week 7: Pericyclic reactions: concepts and explanatory methods; electrocyclic reactions; cycloadditions including normal and inverse demand Diels–Alder; Lewis acid catalysis; position- and periselectivity.

Week 8: 1,3-Dipolar cycloadditions; cheletropic reactions; sigmatropic rearrangements; solvent effects in pericyclic reactions.

Week 9: Pericyclic reactions in biological systems and their applications in bioorthogonal labelling.

Week 10: Explanation of pericyclic reactions through aromatic transition states; comparison of explanatory models.

Week 11: Free radicals: generation, initiators, structures and elementary reactions; chain and non-chain mechanisms; thermodynamic and kinetic stability; substituent effects.

Week 12: Radical abstraction reactions: thermochemical, polar, stereoelectronic and steric factors; radical addition reactions and their determining factors.

Week 13: Radical fragmentations and rearrangements; in situ generation; synthetic applications; comparison with ionic mechanisms; SET processes; determining radical character.