School of Chemistry

Aims and Objectives: Session 2023-2024, Semester 1

Module CH3615: Mechanism in Organic Chemistry

Duration: 15 hours

Lecturers: Dr N. S. Keddie and Professor A. D. Smith*

(*Module Convenor)

Aims: The aim of this course is to provide the student with a basic understanding of the physical aspects of organic chemistry. A problem-solving approach will be used in order to develop the ability to elucidate information, both qualitative and quantitative, concerning reaction mechanisms from experimental data. The use of frontier orbital models of chemical reactivity will be introduced again with an emphasis on problem-solving and practical applications.

Objectives:

1. The basis of conformational analysis in simple acyclic and cyclic molecules, and be able to predict the preferred three-dimensional shapes (conformations) of these molecules.

2. Conformational analysis of six-membered ring systems (chair and boat conformers, locking groups, decalins) and how the spatial arrangement of substituents in these systems impacts upon stereoisomerism and chemical reactivity.

3. The electronic basis of stereoelectronic effects. The influence of stereoelectronic effects upon conformation and reactivity (such as anomeric effects, the gauche effect, conformation and acidity effects upon esters and lactones).

4. The influence of stereoelectronic effects upon reactivity and their particular application to Baldwin's rules, substitution reactions (intramolecular, reactivity of allyl/benzyl/α-carbonyl systems), addition reactions, elimination reactions and neighbouring group participation (all with particular reference to conformational analysis and the stereoselectivity of reactions).

5. How the alignment of orbitals controls the reactivity of rearrangement and fragmentation reactions with particular emphasis upon the reaction outcome of such processes upon six-membered ring systems.

6. To appreciate the implications of the Arrhenius equation, transition state theory, potential energy surfaces and reaction coordinates.

7. To be able to analyse reaction coordinates by application of the Hammond postulate, transition state structure and appreciate the effect of substituents on the transition state.

8. To be able to map organic chemical reactivity using experimental methods including linear free energy relationships and kinetic isotope effects.

9. To understand the factors governing the interactions between molecules.

10. To identify and apply orbital interactions in reactions and the importance of symmetry in orbital interactions.

11. To understand and apply the concept of frontier orbitals and perturbation theory of reactivity.

12. To be able to estimate chemical reactivity, factors affecting reactivity and control of reactions.

13. To understand and apply the concepts of Hard and Soft Acids and Bases (HSAB Theory).

14. To understand and explain the reactivity of ambident nucleophiles, such as the cyanide ion and enolate anions.

15. To explain electrophilic aromatic substitution in terms of product development control and an FMO picture of benzene.

16. To be able to construct orbital manifolds and identify the role of orbital control.