An Introduction to Reaction Stereoelectronics

Overview

Prof Alan Spivey; Office: 835 C1; e-mail: a.c.spivey@imperial.ac.uk; Tel.: 45841

Aims
To demonstrate the role of orbital interactions and the importance of stereoelectronic effects in controlling the conformation of molecules and in influencing the reactivity of molecules and the outcome of reactions. Familiar reactions as well as new reactions will be used to illustrate the ideas.

Building Upon: Year 2 ‘Pericyclic Reactions’ course.
Looking forward to: Year 4 ‘Advanced Stereochemistry, Synthesis and Biosynthesis’ course.

Summary
Building upon the concepts introduced in the ‘Pericyclic Reactions’ course regarding the importance of orbital interactions in influencing reactions, this course explains how orbital interactions influence molecular shape and conformation in the ‘ground state’ (i.e. structure) and explores ‘transition state’ stereoelectronic effects which influence reactivity. The course will concentrate on ‘ionic’ reactions (i.e. those involving electrophiles/nucleophiles, carbanions/carbocations etc.) since these constitute the majority of synthetically useful transformations.

Objectives:
On completion of this course you will be able to:

- Recognise anti-periplanar relationships between reacting bonds in synthetic transformations
- Draw orbital representations and energy diagrams for several stereoelectronic interactions
- Discuss the factors that affect orbital overlap and lead to important (stabilising) interactions
- Explain the role of stereoelectronic interactions in determining the conformations of functional groups
- Appreciate the influence of orbital control in ionic reactions, particularly in carbonyl chemistry, substitution reactions and ring opening/closure reactions
- Rationalise the stereochemical outcome of synthetically important rearrangements and fragmentations

Course delivery (6 lectures + 1 problem class)

Lecture 1: Recap on key stereoelectronic principles.
Lecture 2: Conformational analysis of selected functional groups. The anomeric effect.
Lecture 4: Reactions of the carbonyl group – Burgi-Dunitz nucleophilic attack, Felkin-Ahn diastereoselectivity, α-deprotonation to give enolates – control of stereochemistry.
Lecture 6: Other ionic 1,2-rearrangements (pinacol, semi-pinacol, Baeyer-Villiger & Beckmann). Ionic fragmentations (Grob, Eschenmoser ring-expansion).

Problem class: Revision of the whole module and exam-style questions.
Reference material
The following texts all contain information pertinent to the course content.