Chemistry II (Organic): Introduction to Stereoelectronics

Overview (2006-7)

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Aims
To introduce orbital interactions and the importance of stereoelectronic effects in controlling the conformation of molecules and the outcome of reactions.

Building Upon: Year 1 ‘Stereochemistry’ (ACS); several year 2 courses.

Looking forward to: Year 3 ‘Advanced Stereochemistry’ (DC)

Summary
Molecular shape and conformation in the 'ground state' (i.e. structure) will be examined and then 'transition state' stereoelectronic effects which influence reactivity will be explored. This 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:

• Understand the factors which make good donor and acceptor orbitals
• Draw energy diagrams for a given stereoelectronic interaction
• Discuss the factors that affect orbital overlap and lead to important (stabilising) interactions
• Recognise anti-periplanar relationships between reacting bonds in synthetic transformations
• Appreciate the influence of orbital control in ionic reactions, particularly in carbonyl chemistry
• Rationalise the stereochemical outcome of synthetically important rearrangements and fragmentations

Course delivery (5 lectures)

Lecture 1: will examine the basic requirements for effective orbital interactions.
Lecture 2: will explore the importance of stereoelectronic and steric interactions in the conformation of hydrocarbons.
Lecture 3: will explore the importance of stereoelectronic interactions in the conformation of selected functional groups (including e.g. anomeric and gauche effects).
Lecture 4: will look at stereoelectronic influences in reactions (i.e. on transition states); thermodynamic vs. kinetic control; Curtin-Hammett, nucleophilic addition to carbonyls (Burgi-Dunitz angle) and deprotonation α to carbonyls.
Lecture 5: will look at neighbouring group participation (NGP); ionic 1,2-rearrangements (Wagner-Meerwein) & fragmentations (Eschenmoser).

Reference material
The following texts all contain information pertinent to the course content.