Advanced Organic Chemistry I
Physical Organic Chemistry
Chemistry 411/511

This course will examine the tools -- both theoretical and experimental -- that the modern organic chemist has at his or her disposal for elucidating mechanisms.

Instructor

Professor J. K. Lee
Office: Room 382 Wright-Rieman Laboratories

Meetings

Lectures: Tues Thurs 1 pm
Office hours: before class/by appointment

Required Texts

•"Modern Physical Organic Chemistry,"; Eric V. Anslyn and Dennis A. Dougherty (Textbook AND Solutions manual)
•"Perspectives on Structure and Mechanism in Organic Chemistry"; F. A. Carroll (2nd Ed.)

Additional Useful References, Not Required

•"Advanced Organic Chemistry," 4th Edition; F. A. Carey and R. J. Sundberg
•"Mechanism and Theory in Organic Chemistry", 3rd Edition; T. H. Lowry and K. S. Richardson
•"Theoretical and Physical Principles of Organic Reactivity"; A. Pross
•"The Physical Basis of Organic Chemistry"; H. Maskill
•"Physical Organic Chemistry"; N. S. Isaacs
•"March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure", 4th Edition; J. March
•"Reactive Intermediate Chemistry", R. A. Moss, M. S. Platz, and M. Jones

My Expectations

• A working knowledge of undergraduate Organic Chemistry is expected.
• You should also have taken two semesters of physical chemistry (quantum mechanics and statistics)
• This class is not about memorization; it is about developing analytical thinking.
• By the end of the semester, for a particular reaction you should be able to a) write a reasonable arrow-pushing mechanism and b) use the tools you have learned to explain the observed reactivity, and c) evaluate the validity/plausibility of others' explanations.

Course Requirements

• Three exams. • "Homework" problems will be primarily from Anslyn; solutions are in the solutions manual accompanying each text.
• A copy of this syllabus and problem sets are available on sakai.rutgers.edu, Chem 411_511 F20 Announcements will also be posted here.

Resources for practice problems in arrow pushing:
https://www.organicchemproblems.com/
https://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Questions/problems.htm

Detailed outline

Introduction and arrow-pushing

chemical bonding and structure (counting electrons, hybridization)
conventions, drawing
arrow-pushing strategies
typical reactivity patterns for various reactive intermediates

Thermochemistry

types of energy
stability (overused and often poorly defined)
reference states
isodesmic and homodesmotic reactions
kinetic versus thermodynamic stability
estimating heats of reaction
group additivity (Benson's rules) - relate to molecular modeling
application to organic mechanism

Acid base chemistry

Bronsted
Properties in different media (solvents, active sites, gas phase)
controlling factors
Lewis
Hard/soft acid base theory

Kinetics

Basics

terminology (rate determining step, microscopic reversibility)
intro to chemical kinetics: reaction order, molecularity, corresponding rate laws

Interpretation of rate constants and applications:

Arrhenius
Eyring (activated complex theory derivation)
Curtin Hammett
kinetic versus thermodynamic control of product distributions

Kinetic isotope effects and related topics

definition
intuitive derivation for first order
more mathematical derivation with Eyring
why aren't all KIEs maximum? (how does TS contribute)
secondary KIEs - qualitative and quantitative
natural abundance KIEs
kinetic exceptions: tunneling, dynamic effects (Carpenter, Singleton)

Solvolysis

kinetics application
intimate ion pairs, solvent separated ion pairs
common ion rate depression, salt effect, special salt effect
mechanistic example

Hammond Postulate, Marcus Theory

how they relate
explain and derive Marcus equations
diffusion control, Marcus inverted region

Linear free energy relationships

Molecular orbital theory

- Schroedinger equation
- LCAO to MOs
- HMO theory
- orbitals interacting
- FMO theory
- Pericyclic reactions - predicting allowedness (symmetry)