

SYLLABUS

CHEM 311 **Mechanistic Organic Chemistry** Fall, 2020

Instructor: Prof. Graeme Howe

Instructor Contact Information:

Chernoff Hall, Rm 512, Ph: (613) 533-6089, email: graeme.howe@queensu.ca

Office Hours: Monday 3PM-4PM EST; Wednesday 9:30AM-10:30AM EST; Friday 4PM-5PM EST; or by appointment (see onQ course website for Zoom Meeting info)

TA: Carolyn Kimball

TA Contact Information: email: carolyn.kimball@queensu.ca

Tutorials: Monday 6:30PM-7:30PM EST; Tuesday 9:30AM-10:30AM EST

Office Hours: by appointment

By the end of this course, students will be able to:

1. Apply models of molecular orbitals and hybridization to predict the structures and properties of chemicals.
2. Apply models of conjugated systems and aromaticity to predict the products of pericyclic reactions.
3. Correlate changes in chemical structure with changes in transition states using one- and two-dimensional reaction coordinates.
4. Use kinetic isotope effects, solvent effects, and linear free energy relationships as tools to evaluate mechanisms of organic reactions.
5. Predict the reactivity of non-classical carbocations and various ion pairs.
6. Rationalize the regiochemistry, stereochemistry, and reactivity of various classes of reactions.
7. Apply general chemical principles to predict or understand the structure and reactivity of molecules.

Required Text: *Modern Physical Organic Chemistry* by Anslyn and Dougherty.

Supplemental Text: *Advanced Organic Chemistry* by Carey and Sundberg. An electronic version of this text is freely available through the Queen's Library.

Course Outline:

Recommended readings from Anslyn & Dougherty are given in parentheses. Recommended readings from Carey and Sundberg are noted with "C&S")

- **Structure and models of bonding (1.1)** - Basics of bonding, VSEPR and hybridization, valence bond theory, hybridization indices
- **Thermochemistry of stable molecules and reactive intermediates (2.1, 2.2)** - Thermodynamics, thermochemistry of reactive intermediates, carbanions, carbocations, radicals
- **Hückel molecular orbital theory (14.2-14.3, 14.5; C&S: 1.2.1)** - Hückel MO theory, Frost circles, aromaticity/antiaromaticity, Semiempirical MO methods
- **Thermal pericyclic reactions (15.2-15.5)** - Cycloaddition reactions, electrocyclic reactions, sigmatropic reactions
- **Reactivity, kinetics, and mechanisms (7.3, 7.8)** - Transition state theory, kinetic postulates, More O'Ferrall-Jencks plots

- **Experiments related to thermodynamics and kinetics (8.1-8.5, 8.8)** - experimental considerations, isotope effects, linear free energy relationships, substituent effects, Hammett plots, Taft equation, Swain-Scott parameters, Grunwald-Winstein relationship, solvent effects
- **Catalysis (9.1-9.3)** - General principles, forms of catalysis, acid-base catalysis, Brønsted relationship
- **Organic reaction mechanisms - Substitutions (10.18, 10.19, 11.5)** - Aliphatic substitution, structure-function correlations, carbocation rearrangements, anchimeric assistance, non-classical carbocations, electrophilic aromatic substitution, nucleophilic aromatic substitution
- **Organic reaction mechanisms - Eliminations (10.12-10.13)** - Elimination vs. substitution, E1cB mechanisms, structure-function correlations, regiochemical considerations, carbonyl-forming reactions
- **Organic reaction mechanisms - Carbonyl chemistry (10.8, 10.17, 11.1, C&S: 6.5.2, 7.1-7.5, 7.7)** - Keto-enol tautomerism, enols and enolates, nucleophilic carbonyl additions, acyl transfer reactions, substitution reactions of acid derivatives, intramolecular catalysis
- **Photochemistry (16.1-16.3; time permitting)** - Jablonski diagrams, fluorescence, phosphorescence, bimolecular photophysical processes, photochemical reactions

Grading Scheme:

- 2 Midterms: 50% collectively (higher graded midterm: 30%; lower graded midterm: 20%)
 - Midterm 1: Wednesday, October 7th, 6PM - 9PM
 - Midterm 2: Monday, November 9th, 2:30PM - 5:30PM
- Final Exam: 45%
- Tutorial Quizzes: 5%

Assessments:

Midterms and the final exam will be released via onQ at a set time and date and must be turned in prior to the **strict** deadline. TurnItIn will be used to check all materials for plagiarism prior to grading. All assessed work must be entirely your own, and a zero-tolerance policy will be enforced for academic dishonesty.

Tutorials:

Tutorials are held synchronously via Microsoft Teams (see course website for Teams Meeting info). Attendance will be logged and will make Students must log into the tutorial on time, as the Teams Meeting will be locked to new attendees 15 minutes after the scheduled start time.

At the end of each tutorial, there will be a short quiz. Answers must be uploaded via onQ within 15 minutes of the conclusion of the tutorial to be considered for grading. For each quiz, you will receive a 5 for getting it correct, a 3 for taking it, or a 0 for missing it. If you are not logged into the tutorial in Microsoft Teams when the tutorial ends, you will receive a 0 for the quiz.

Grading Method:

All components of this course will receive numerical percentage marks. The final grade you receive for the course will be obtained by converting your numerical course average to a letter grade according to the Queen's Official Grade Conversion Scale:

<i>Queen's Official Grade Conversion Scale</i>	
Grade	Numerical Course Average (Range)
A+	90-100

A	85-89
A-	80-84
B+	77-79
B	73-76
B-	70-72
C+	67-69
C	63-66
C-	60-62
D+	57-59
D	53-56
D-	50-52
F	49 and below

Location and Timing of Final Examinations:

The exam dates for each Term are listed on the Faculty of Arts and Science webpage under “Important Dates.” Student exam schedules for the Fall Term are posted via SOLUS immediately prior to the Thanksgiving holiday; for the Winter Term they are posted on the Friday before Reading Week, and for the Summer Term they are individually noted on the Arts and Science Online syllabi. **Students should delay finalizing any travel plans until after the examination schedule has been posted. Exams will not be moved or deferred to accommodate employment, travel/holiday plans or flight reservations.** Also, as indicated in Academic Regulation 8.3, students must write all final examinations in all on-campus courses on the Kingston campus.

Academic Integrity:

Academic Integrity is constituted by the six core fundamental values of honesty, trust, fairness, respect, responsibility and courage (see www.academicintegrity.org). These values are central to the building, nurturing and sustaining of an academic community in which all members of the community will thrive. Adherence to the values expressed through academic integrity forms a foundation for the "freedom of inquiry and exchange of ideas" essential to the intellectual life of the University (see the Senate Report on Principles and Priorities <http://www.queensu.ca/secretariat/policies/senate/report-principles-and-priorities>).

Students are responsible for familiarizing themselves with the regulations concerning academic integrity and for ensuring that their assignments conform to the principles of academic integrity. Information on academic integrity is available in the Arts and Science Calendar (see Academic Regulation <http://www.queensu.ca/artsci/academic-calendars/regulations/academic-regulations/regulation-1>), on the Arts and Science website (see <http://www.queensu.ca/artsci/academics/undergraduate/academic-integrity>), and from the instructor of this course. Departures from academic integrity include plagiarism, use of unauthorized materials, facilitation, forgery and falsification, and are antithetical to the development of an academic community at Queen's. Given the seriousness of these matters, actions which contravene the regulation on academic integrity carry sanctions that can range from a warning or the loss of grades on an assignment to the failure of a course to a requirement to withdraw from the university.

Calculator Policy:

As noted in Academic Regulation 9.2, “Calculators acceptable for use during quizzes, tests and examinations are intended to support the basic calculating functions required by most Arts and Science

courses. For this purpose, the use of the **Casio 991 series calculator** is permitted and is the only approved calculator for Arts and Science students.”

Accommodations for Disabilities:

Queen's University is committed to achieving full accessibility for people with disabilities. Part of this commitment includes arranging academic accommodations for students with disabilities to ensure they have an equitable opportunity to participate in all of their academic activities. The Senate Policy for Accommodations for Students with Disabilities was approved at Senate in November 2016 (see <https://www.queensu.ca/secretariat/sites/webpublish.queensu.ca.uslcwww/files/files/policies/senateandtrustees/ACADACCOMMPOLICY2016.pdf>). If you are a student with a disability and think you may need academic accommodations, you are strongly encouraged to contact the Queen's Student Accessibility Services (QSAS) and register as early as possible. For more information, including important deadlines, please visit the QSAS website at: <http://www.queensu.ca/studentwellness/accessibility-services/>

Academic Considerations for Students in Extenuating Circumstances [See Section 10]

Queen's University is committed to providing academic consideration to students experiencing extenuating circumstances that are beyond their control and are interfering with their ability to complete academic requirements related to a course for a short period of time, not to exceed three months. Students receiving academic consideration must meet all essential requirements of a course. The Senate Policy on Academic Consideration for Students in Extenuating Circumstances was approved at Senate in April, 2017 (see <https://www.queensu.ca/secretariat/sites/webpublish.queensu.ca.uslcwww/files/files/policies/senateandtrustees/Academic%20Considerations%20for%20Extenuating%20Circumstances%20Policy%20Final.pdf>) Each Faculty has developed a protocol to provide a consistent and equitable approach in dealing with requests for academic consideration for students facing extenuating circumstances. Arts and Science undergraduate students can find the Faculty of Arts and Science protocol and the portal where a request can be submitted at: <http://www.queensu.ca/artsci/accommodations>. Students in other Faculties and Schools who are enrolled in this course should refer to the protocol for their home Faculty.

If you need to request academic consideration for this course, you will be required to provide the name and email address of the instructor/coordinator. Please use the following:

Instructor Name: Prof. Graeme Howe

Instructor Email Address: graeme.howe@queensu.ca