

# CHEM-769 PHYSICAL ORGANIC CHEMISTRY

## Course Outline Winter Semester 2018

Physical organic chemistry, including a discussion of reactive intermediates, substituent effects, pericyclic reactions, radical chemistry and a basic theoretical description of the bonding in organic molecules.

**Instructor:** Professor Adrian L. Schwan, Office: MacN 336, Guelph Campus. 824-4120 X58781; E-mail: schwan@uoguelph.ca FAX: 1-519-766-1499

**Text:** Modern Physical Organic Chemistry, E.V. Anslyn and D.A Dougherty....suggested

The text is a useful reference for most of the topics to be covered in the lectures. Further references will be given where appropriate. Supplemental information in the form of class notes are provided. These will be presented to you in some form in advance of lectures.

**Method of Presentation:** One 2 1/2 hour lecture per week, Thurs. nights starting at 7:00 pm in the main link room. First lecture is Thurs. Jan. 11, 2018. There will be no lectures during reading week (Feb. 22) or on Feb. 8.

**Method of Evaluation:** The course grade will be based on a final examination, some problem assignments and an essay of one research group's recent efforts in physical organic or related chemistry. The final examination will be given in April. Regular problem sets will be comprised of a few questions. Several practice problems will be part of the course notes. The absolute final due date for the essay is March 30, 2018.

The final grade will be calculated as follows:

research essay	30%
problem assignments	35%
final examination	35%

Should you wish to drop one of your in-term efforts (once you have completed it and seen your grade) and make the final exam worth the difference, that option is available and should be requested in writing before you write the final.

Audits: Please understand that an audit is an official entry on your transcript and there are certain course requirements to achieve this. Audit does not mean "sitting-in". Professor Schwan generally does not recommend the audit or 'sitting in' process, since 1. your graduate career will be assessed primarily by the quality of your thesis and 2. a graduate degree means that you can learn things for yourself. It follows that your time should be spent on your research project.

## CONTENT OUTLINE

1. Kinetics and Mechanism
  - (a) Transition state theory
  - (b) Energy profiles
2. Substituent Effects on Organic Rates and Equilibria
  - (a) Qualitative description of substituent effects
  - (b) Linear free energy relationship: the Hammett equation
  - (c) Acid and Base catalysis
3. The Hückel Molecular Orbital Method -- a tool for appreciating molecular orbitals
  - (a) Description of the method
  - (b) Regularities in Hückel Molecular Orbitals
  - (c) The concept of aromaticity
4. Aromaticity
  - (a) NMR analysis of aromaticity
  - (b) Homoaromaticity
  - (c) Heterocyclic aromaticity
5. Orbital Symmetry Control of Concerted Reactions
  - (a) FMO analysis of pericyclic reactions
  - (b) Introduction to 1,3-dipoles
  - (c) Other reactive species in pericyclic reactions
6. Radical Reactions
  - (a) Concepts and BDE's
  - (b) Prevalence
  - (c) Rearrangements
7. Evaluation of Some Research Publications  
-to take place throughout the year as a class discussion

### Library Reserve List

-due to lack of use in the past, there are no books on reserve in the libraries.

Several useful general texts:

Anslyn and Dougherty as noted above

Felix A. Carroll Perspectives on Structure and Mechanism in Organic Chemistry

F.A. Carey and R.J. Sundberg Advanced Organic Chemistry Part A: Structure and Mechanisms. 5th Ed.

Neil Isaacs Physical Organic Chemistry, 2nd Ed.

T.H. Lowry and K.S. Richardson Mechanism and Theory in Organic Chemistry

## **For University of Waterloo Students**

**Academic Integrity:** *In order to maintain a culture of academic integrity, members of the University of Waterloo community are expected to promote honesty, trust, fairness, respect and responsibility.*

**Grievance:** *A student who believes that a decision affecting some aspect of his/her university life has been unfair or unreasonable may have grounds for initiating a grievance. Read Policy #70, Student Petitions and Grievances, Section 4. <http://www.adm.uwaterloo.ca/infosec/Policies/policy70.htm>*

**Discipline:** *A student is expected to know what constitutes academic integrity, to avoid committing academic offenses, and to take responsibility for his/her actions. A student who is unsure whether an action constitutes an offense, or who needs help in learning how to avoid offenses (e.g., plagiarism, cheating) or about “rules” for group work/collaboration should seek guidance from the course professor, academic advisor, or the Undergraduate Associate Dean. For information on categories of offenses and types of penalties, students should refer to Policy #71, Student Discipline, <http://www.adm.uwaterloo.ca/infosec/Policies/policy71.htm>*

**Appeals:** *Concerning a decision made under Policy #70 (Student Petitions and Grievances) (other than petitions) or Policy #71 (Student Discipline) a student may appeal the finding, the penalty, or both. A student who believes he/she has a ground for an appeal should refer to Policy #72 (Student Appeals) <http://www.adm.uwaterloo.ca/infosec/Policies/policy72.htm>*

## ***For University of Guelph Students***

**Accessibility:** The University of Guelph is committed to creating a barrier-free environment. Providing services for students is a shared responsibility among students, faculty and administrators. This relationship is based on respect of individual rights, the dignity of the individual and the University community's shared commitment to an open and supportive learning environment. Students requiring service or accommodation, whether due to an identified, ongoing disability or a short-term disability should contact the Centre for Students with Disabilities as soon as possible. For more information, contact CSD at 519-824-4120 ext. 56208 or email [csd@uoguelph.ca](mailto:csd@uoguelph.ca) or see the website: <http://www.csd.uoguelph.ca/csd/>

**E-mail Communication:** As per university regulations, all students are required to check their <uoguelph.ca> e-mail account regularly: e-mail is the official route of communication between the University and its students.

**When You Cannot Meet a Course Requirement:** When you find yourself unable to meet an in-course requirement because of illness or compassionate reasons, please advise the course in writing, with your name, id#, and e-mail contact. See the graduate calendar for information on regulations and procedures for Academic Consideration:

[http://www.uoguelph.ca/registrar/calendars/graduate/current/genreg/sec\\_d0e1400.shtml](http://www.uoguelph.ca/registrar/calendars/graduate/current/genreg/sec_d0e1400.shtml)

**Drop Date:** The last date to drop one-semester courses, without academic penalty, is DATE HERE. Two-semester courses must be dropped by the last day of the add period in the second semester. Refer to the Graduate Calendar for the schedule of dates:

<http://www.uoguelph.ca/registrar/calendars/graduate/current/sched/sched-dates-f10.shtml>

**Academic Misconduct:** The University of Guelph is committed to upholding the highest standards of academic integrity and it is the responsibility of all members of the University community – faculty, staff, and students – to be aware of what constitutes academic misconduct and to do as much as possible to prevent academic offences from occurring. University of Guelph students have the responsibility of abiding by the University's policy on academic misconduct regardless of their location of study; faculty, staff and students have the responsibility of supporting an environment that discourages misconduct. Students need to remain aware that instructors have access to and the right to use electronic and other means of detection. The Academic Misconduct Policy is detailed in the Graduate Calendar:

[http://www.uoguelph.ca/registrar/calendars/graduate/current/genreg/sec\\_d0e1687.shtml](http://www.uoguelph.ca/registrar/calendars/graduate/current/genreg/sec_d0e1687.shtml)

**Recording of Materials:** Presentations which are made in relation to course work—including lectures—cannot be recorded in any electronic media without the permission of the presenter, whether the instructor, a classmate or guest lecturer.

**Resources:** The Graduate Calendar is the source of information about the University of Guelph's procedures, policies and regulations which apply to graduate programs:

<http://www.uoguelph.ca/registrar/calendars/graduate/current/>

## Course learning objectives:

Chapter 1: To be able to:

- understand, interpret and draw potential energy reaction profiles
- know and understand theories related to such reaction profiles
- understand and apply activation parameters

Chapter 2: To be able to:

- look at the structure of molecules and outline factors affecting the acidity of hydrogens
- understand and apply common parameters associated with free energy relationships, particularly relating to substituents
- interpret the significance of outcomes of physical organic studies and apply those towards assigning structure of transition states and intermediates

Chapter 3: To be able to:

- appreciate the fundamental origins and assumptions of the Huckel Molecular Orbital method for determining MO's and their energy levels
- performing simple math processes to establish the MO energy levels for small conjugated molecules
- use a simple computer program to establish MO's and their energy levels, given the molecule
- recognize and utilize symmetry-based shortcuts to establish specific and important feature about MO's

Chapter 4: To be able to:

- accurately recognize the presence and geometry of occupied and empty p/ $\pi$  orbitals in cyclic molecules as a means to assess aromaticity and antiaromaticity
- understand the significance of selected aromaticity parameters such as NICS

Chapter 5: To be able to:

- envision and utilize MO's within molecules to understand allowed and disallowed pericyclic processes
- solve problems of stereochemistry and structural preferences for pericyclic transformation
- resolve the sequences of pericyclic reactions that can be multistep transformations.
- understand reactivity and regioselectivity patterns in pericyclic reactions using MO's and their energy levels
- to be able to recognize the sets of reactive entities in pericyclic and related reactions

Chapter 6: To be able to:

- to be able to envision and draw out radical chain reaction mechanisms
- to understand parameters involved in radical reactions and appreciate the differences from ionic reactions.

Overall: To be able to:

- understand key and fundamental aspects of the analysis of various organic reaction mechanisms.
- recognize and apply substituent effects and MO's of simple molecules for predicting or understanding reactivity
- recognize parameters and tools that can be called upon to assist in the assessment and rationalization of observed chemistry