# CHE 173: MECHANISTIC ORGANIC CHEMISTRY II
## Winter, 2002

**Dr. Matthew R. Dintzner**
**O'Connell 440, 446 (Lincoln Park Campus)**
**(773) 325-4726, office (773) 325-4725, lab**
http://www.depaul.edu/~mdintzne

**Office Hours:** Mondays 3:00-5:00 p.m., Tuesdays 9:30-11:30 a.m., or by appointment.

**Course Description:** This is the second in a sequence of courses designed to investigate what organic chemistry is and how it works, by emphasizing the relationship between structure and function of organic molecules. Our primary objective for CHE 173 is to expand on the foundation established last quarter and continue to build on our knowledge of organic chemistry. Everything about this subject is comprehensive, and so it is very important that you not fall behind with the material. Unlike other courses, it is very difficult to "cram" for organic chemistry at the end of the quarter. The best strategy for success in this course is to stay on top of the material. The schedule is outlined below and we will stick to this as closely as possible. Please read the assigned sections of the text before you come to class. Problems from the book will be assigned at the end of each class for you to do at your own pace; they will not be collected or graded, but it is in your best interest to work through the problems.

**Texts:** *Organic Chemistry (3rd ed.)* by Paula Yurkanis Bruice, with *Study Guide and Solutions Manual*.

**Quizzes:**

- Quizzes will be given during quiz section on Tuesdays throughout the quarter. Missing a quiz will result in a grade of zero, unless an official medical excuse (from a doctor) is provided.
- The lowest quiz grade will be dropped, but in order for the quiz grade to be dropped, you have to have taken the quiz (i.e., missed quizzes that result in a grade of zero are not eligible for omission).
- The format for quizzes will be: 4 short-answer questions or problems (40 %, or 10 pts each) and10 multiple choice questions (60 %, or 6 pts each).

**Final Exam:** Thursday, March 21 (11:45-2:00 p.m.); it will be cumulative. The final exam will consist of 25 questions, each worth 5 points, and you must complete 20 of the 25 (your choice). There will be a mix of short-answer and multiple choice questions.

**Grades:** Final grades will be based on the scale and distribution shown below. If the overall class average is NOT between 77 and 82, final grades will be curved accordingly so that the average grade is between a B- and a C+.

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|---|---|---|---|
| **93 – 100, A** | **83 – 86, B** | **73 – 76, C** | **60 – 66, D** |
| **90 – 92, A-** | **80 – 82, B-** | **70 – 72, C-** | **< 60, F** |
| **87 – 89, B+** | **77 – 79, C+** | **67 – 69, D+** | |

**Quizzes = 50 %**
**Final Exam = 25 %**
**Lab = 25 %**

**Schedule and Objectives:** The following is an outline of the material we will cover throughout the quarter and the specific learning objectives for each class period (bulleted). This schedule is subject to change as a function of class-performance and understanding of the individual topics (we will spend additional time on some topics if necessary).

| DATE | READING ASSIGNMENTS (please read ahead) | SPECIFIC LEARNING OBJECTIVES AND LABS | ✓ |
|---|---|---|---|
| M 1/7 | Bruice 12.1-12.5 | We will briefly review the final exam from Fall quarter and learn about Mass Spectrometry (MS):<br>▪ what it is<br>▪ how it works<br>▪ how to use MS to determine molecular formulas | |
| T 1/8 | Bruice 12.6-12.15 | We will discuss Infrared Spectroscopy (IR):<br>▪ what it is<br>▪ how it works<br>▪ how to interpret an IR spectrum (recognize characteristic absorption bands) | |
| W 1/9 | Bruice 12.16-12.19 | We will finish discussing MS and IR and introduce Ultraviolet (UV) and Visible spectroscopy:<br>▪ practical uses<br>▪ colors | |
| F 1/11 | Bruice 13.1-13.8 | NMR Spectroscopy<br>▪ Proton ($^1$H) NMR<br>▪ Chemical Shift<br>▪ Integration | |

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| **LAB 1** | Handout | SPECTROSCOPY TUTORIAL | |
| M 1/14 | Bruice 13.9-13.21 | NMR Spectroscopy<br>▪ Splitting of Resonance Signals<br>▪ Carbon ($^{13}C$) NMR | |
| T 1/15 | **QUIZ** | **1** | |
| W 1/16 | Bruice 7.1-7.3 | Dienes, Nomenclature, Isomers and Stability<br>▪ Nomenclature<br>▪ Isomers<br>▪ Relative stabilities | |
| F 1/18 | Bruice 7.4-7.8 | Electrophilic Addition<br>▪ MO, Reactivity<br>▪ Electrophilic addition reactions<br>▪ Thermodynamics vs. Kinetics | |
| M 1/21 | Bruice 7.9 | Diels-Alder Reaction<br>▪ Dienes, dienophiles<br>▪ Stereochemistry<br>▪ Predicting products (regiochemistry) | |
| **LAB 2** | G/M 12.1, 12.2, 12.3 B & C2<br>*miniscale* | THE DIELS-ALDER REACTION: REACTION OF 1,3-CYCLOPENTADIENE AND MALEIC ANHYDRIDE; HYDROLYSIS OF ANHYDRIDES | |
| T 1/22 | **QUIZ** | **2** | |
| W 1/23 | Bruice 8.1-8.3 | Reactions of Alkanes with Halogens<br>▪ Reactivity<br>▪ Free radical reaction mechanism<br>▪ Product distribution | |
| F 1/25 | Bruice 8.5 | Reactivity-selectivity , Radical Substitution of Benzylic and Allylic Protons<br>▪ Relative stability of free radicals<br>▪ NBS | |
| M 1/28 | Bruice 8.6-8.9 | Stereochemistry of Radical Reactions<br>▪ The radical intermediate ($sp^2$ hybridized)<br>▪ Reactions with cyclic compounds<br>▪ Radicals in biological systems | |
| **LAB 3** | G/M 9.1, 9.2<br>*miniscale* | ALKANES: FREE-RADICAL CHAIN CHLORINATION OF 1-CHLOROBUTANE | |
| T 1/29 | **QUIZ** | **3** | |
| W 1/30 | Bruice 9.1-9.4 | Substitution Reactions of Alkyl Halides, $S_N2$ Reactions<br>▪ Reactivity<br>▪ $S_N2$ mechanism<br>▪ "Leaving groups"<br>▪ Reversibility (Le Châtelier's princip.e) | |
| F 2/1 | Bruice 9.5-9.6 | $S_N1$ Reactions<br>▪ $S_N1$ mechanism<br>▪ Relative reactivities of alkyl halides | |
| M 2/4 | Bruice 9.7-9.11 | Stereochemistry of $S_N2$ and $S_N1$ Reactions<br>▪ Inversion, retention | |

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| | | ▪ Reactions conditions<br>▪ Benzylic, allylic, vinylic and aryl halides<br>▪ $S_N2$ vs. $S_N1$<br>▪ Solvent effects | |
| **LAB 4** | G/M 14.1-14.4<br>*miniscale* | NUCLEOPHILIC ALIPHATIC SUBSTITUTION: PREPARATION OF 1-BROMOBUTANE | |
| T 2/5 | **QUIZ** | **4** | |
| W 2/6 | Bruice 10.1-10.4 | Elimination Reactions<br>▪ E2 Reaction<br>▪ Zaitsev's rule<br>▪ E1 Reaction<br>▪ E2 vs. E1, competition | |
| F 2/8 | Bruice 10.5-10.6 | Stereochemistry of E2 and E1 Reactions<br>▪ Syn-periplanar vs. Anti-periplanar mechanisms<br>▪ E2 and E1 with cyclic compounds | |
| M 2/11 | Bruice 10.8-10.12 | Competition between Substitution and Elimination<br>▪ $S_N2$/E2 conditions<br>▪ $S_N1$/E1 conditions<br>▪ Williamson ether synthesis<br>▪ Intermolecular vs. intramolecular reactions | |
| **LAB 5** | G/M 10.1,<br>10.2A *miniscale*<br>10.3A *miniscale* | ALKENES: ELIMINATION WITH ALCOHOLIC POTASSIUMM HYDROXIDE; DEHYDRATION OF 4-METHYL-2-PENTANOL | |
| T 2/12 | **QUIZ** | **5** | |
| W 2/13 | Bruice 11.1-11.3 | Substitution Reactions of Alcohols<br>▪ $S_N1$, $S_N2$ reactions<br>▪ R-OH → R-X → R-Nu<br>▪ Sulfonate esters | |
| F 2/15 | Bruice 11.4-11.6 | Dehydration of Alcohols and Reactions of Ethers<br>▪ Relative rates<br>▪ Substitution reactions of ethers<br>▪ Eppoxides | |
| M 2/18 | Bruice 11.8 | Organometallic Compounds<br>▪ Grignard reactions<br>▪ Organolithium and organocuprate reagents | |
| **LAB 6** | G/M 19.4 A & B<br>*miniscale* | ORGANOMETALLIC CHEMISTRY: PREPARATION OF GRIGNARD REAGENTS; PREPARATION OF TRIPHENYLMETHANOL | |
| T 2/19 | **QUIZ** | **6** | |
| W 2/20 | Bruice 14.1-14.5 | Aromaticity<br>▪ Criteria (Hückel's rule)<br>▪ Cyclic and heterocyclic compounds<br>▪ Chemical consequences of aromaticity<br>▪ Antiaromaticity | |
| F 2/22 | Bruice 14.7-14.9 | Electrophilic Aromatic Substitution Reactions | |

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| | | ▪ Mechanism<br>▪ Halogenation of benzene | |
| M 2/25 | Bruice 14.10-14.13 | Other reactions<br>▪ Nitration<br>▪ Sulfonation<br>▪ Friedel-Crafts acylation<br>▪ Friedel-Crafts alkylation | |
| **LAB 7** | G/M 15.4<br>*miniscale* | NITRATION OF BROMOBENZENE | |
| T 2/26 | **QUIZ** | **7** | |
| W 2/27 | Bruice 15.1-15.5 | Nomenclature and Reactions of Substituted Benzenes<br>▪ Disubstituted, polysubstituted benzene derivatives<br>▪ Reactions<br>▪ Electron donation and electron withdrawl<br>▪ Resonance<br>▪ Effect of substituents on reactivity and $pK_a$ | |
| F 3/1 | Bruice 15.6-15.11 | Substituent Effects, Synthesis of Substituted Benzenes<br>▪ Ortho/para ratio<br>▪ Additional considerations<br>▪ Synthesis<br>▪ Arenediazonium salts | |
| M 3/4 | Bruice 15.13-15.14 | Nucleophilic Aromatic Substitution<br>▪ Mechanism<br>▪ Benzyne | |
| **LAB 8** | Handout | PERPARING ISOPENTYL ACETATE | |
| T 3/5 | **QUIZ** | **8** | |
| W 3/6 | Bruice 16.1-16.5 | Carbonyl Compounds, Nomenclature, Properties and Reactivity<br>▪ Carboxylic acids, acyl halides, anhydrides, esters, amides and nitriles<br>▪ Structure of the carbonyl group<br>▪ Relative reactivities | |
| F 3/8 | Bruice 16.6-16.11 | Acyl Substitution Reactions, Hydrolysis of Esters<br>▪ General mechanism<br>▪ Acid- and base-catalysis mechanisms | |
| M 3/11 | Bruice 16.12-16.19 | Reactions of Carboxylic Acids and Amides, Hydrolysis of Amines and Nitriles<br>▪ Fischer esterification reaction<br>▪ Gabriel synthesis<br>▪ Activation of carboxylic acids | |
| T 3/12 | **QUIZ** | **9** | |
| W 3/13 | **REVIEW** | **SESSION** | |
| F 3/15 | **REVIEW** | **SESSON** | |
| Th 3/21 | **FINAL** | **EXAM** | |

# CHE 172L: MECHANISTIC ORGANIC CHEMISTRY LAB II
# Winter, 2002

**Objectives:**
In addition to good laboratory techniques and the methods of carrying out basic laboratory procedures, other things you will also learn from this laboratory course are: (1) how to take data carefully; (2) how to record relevant observations; (3) how to use your time effectively; (4) how to assess the efficiency of your experimental method; (5) how to plan for the isolation and purification of the substance you prepare; (6) how to work safely; (7) how to solve problems and think like a chemist.

**Lab Text:** *Experimental Organic Chemistry*, by Gilbert and Martin (Saunders College Publishing).

**Teaching Assistants**: Kristen McColough (Tuesday), Gil Villaseñor (Wednesday), Debbie Coligado (Thursday, a.m.), Andrea Toth (Thursday, p.m.), Tom Lynch (Friday).

**General Rules:**
- Safety goggles are to be worn at all times when in the laboratory; wear gloves when necessary.
- No shorts, sandals or rollerblades are to be worn in the laboratory.
- Please read and be familiar with the University's Chemical Hygiene Plan.
- Please respect the laboratory space and your classmates by cleaning up after yourself.
- Please come to lab prepared by reading over the experiment prior to your laboratory period.

***** Prepare your notebook AHEAD OF TIME. You will NOT be allowed to bring your textbook into the lab, so you'll rely solely on your notebook to get you through the experiment. Be sure that you can read your notes and that they make sense to you.*****

**Lab Grades:**
Your notebook is your "ticket" into the lab, and will be checked by your T.A. as you enter. This is not meant to be a scare tactic-- you'll find that the better prepared you are for lab, the quicker you'll finish the experiment and the better will be your results... it just makes sense. Your T.A. will also be responsible for grading your lab reports and

observing your lab technique. The overall lab grade is based on the following distribution:

| | |
|---|---|
| **Notebook** | **25%** |
| **Lab Reports** | **60%** |
| **Technique** | **10%** |
| **Cleanliness** | **5%** |

**Schedule and Reading Assignments:**

| Week of | Reading | Experiment |
|---|---|---|
| 1/14 | Hand-out | SPECTROSCOPY TUTORIAL (DRY LAB) |
| 1/21 | G/M 12.1, 12.2, 12.3 B & C2 *miniscale* | THE DIELS-ALDER REACTION: REACTION OF 1,3-CYCLOPENTADIENE AND MALEIC ANHYDRIDE; HYDROLYSIS OF ANHYDRIDES |
| 1/28 | G/M 9.1, 9.2 *miniscale* | ALKANES: FREE-RADICAL CHAIN CHLORINATION OF 1-CHLOROBUTANE |
| 2/4 | G/M 14.1-14.4 *miniscale* | NUCLEOPHILIC ALIPHATIC SUBSTITUTION: PREPARATION OF 1-BROMOBUTANE |
| 2/11 | G/M 10.1, 10.2A *miniscale* 10.3A *miniscale* | ALKENES: ELIMINATION WITH ALCOHOLIC POTASSIUMM HYDROXIDE; DEHYDRATION OF 4-METHYL-2-PENTANOL |
| 2/18 | G/M 19.4 A & B *miniscale* | ORGANOMETALLIC CHEMISTRY: PREPARATION OF GRIGNARD REAGENTS; PREPARATION OF TRIPHENYLMETHANOL |
| 2/25 | G/M 15.4 *miniscale* | NITRATION OF BROMOBENZENE |
| 3/4 | Hand-out | PERPARING ISOPENTYL ACETATE |

**Notebooks:**
Prepare your notebook AHEAD OF TIME according to the guidelines below. You will NOT be allowed to bring your textbook into the lab, so you'll rely solely on your notebook to get you through the experiment.

*Key Components of a Laboratory Experiment Write-up Notebook:*

(1) Date experiment was conducted; (2) Title of experiment and reference for it; (3) Purpose for running the reaction; (4) Reaction scheme, a balanced equation (if applicable); (5) Table of reagents and product with data on the compounds' names, physical constants like MF, mp, bp (literature and experimental values), density, volume, weight and moles, theoretical and percent yield (where applicable), safety information related to exposure and toxicity from the Material Safety Data Sheets (MSDS); (6) Details of procedure and set-up used and all changes from procedure from the lab manual; (7) Characteristics of the products; (8) Analytical and spectral data.

Always record your data in ink. If a mistake is made, make a neat line through the word or words so they remain legible. Write and organize your work so that someone else could come into the laboratory and repeat the experiment using your directions without confusion and uncertainty. Completeness and legibility are key factors. **Make sure your notebook is signed by the TA at the end of each lab period. (**This does not mean that the TA has approved your method of taking data).

**Lab Reports:**
The purpose of the laboratory report is to give a complete and concise description of the experiment. **All lab reports must be turned in to your TA one week after the experiment is completed.** Turning in lab reports after the due date will result in a loss of 10 points, minus 5 points for each day after the due date. No lab reports will be accepted after March 18$^{th}$.

Formal laboratory reports should be typed (no more than 3-5 pages, double-spaced with figures, illustrations, etc.) according to the guidelines below.

*Lab Report Format:*

(The headings printed in bold-face below should appear in your lab report)

- Lab #_____ **Date of Experiment**:
- Experiment # and Title (from textbook), **Date of Report**:

- **References:** (lab manual, handbooks, etc.)
- **Purpose:** One or two sentences telling the objective of the experiment.

*Failure to include the above information can lose you 5 points.*

- Equation and reactions: (5 points) Write a balanced equation, if the experiment involves a synthesis.
- **Procedure:** (10 points) You may reference your lab textbook and note only those reagents, steps, and equipment that have been changed.
- **Results:** (25 points) Data include all observations and numbers as transcribed from your lab notebook. The should be neatly written in tabular form when appropriate. Units must be shown. The calculation for the limiting reagent (when appropriate) and the theoretical yield should be included.
- **Discussion:** (30 points) Discuss your data and observations as they relate to the reactions and the experiment in a logical manner. You must talk about your results in a way that describes how your results support your lab objective. Exclude those points that are not relevant to your experiment.
- **Conclusion:** (10 points) This section sums up the lab. It re-tells your lab's objectives and says how the results helped you to achieve these objectives or not. This section does not simply say if your lab was a success or not. We will be the judges of that.
- Answers to Questions at the end of the experiment; check with your TA (15 points).

**General Guidelines for the Organic Chemistry Laboratory:**

- Study the experiment and the reasons for each operation before you come to lab. Study, do not just read about the experiment before lab period. Although the techniques employed in the laboratory are not particularly difficult to acquire, they do demand a significant amount of attention. For you to reach a successful and happy conclusion, you cannot afford to have the focus of your concentration broken by having to constantly refer to the text during the experiment (this is why the texts are not allowed in the lab). Disaster is ever present for the unprepared.
- ALWAYS work with clean equipment. You must take time to scrupulously clean your equipment before you start any experiment. Contaminated glassware will ultimately cost you additional time, and you will face the frustrations of experiencing inconsistent results and lower yields.
- CAFEFULLY measure the quantities of materials to be used in the experiments. A little extra time at the beginning of the laboratory can speed you on your way at the end of the session. Many organic reactions are very sensitive to relative quantities of reagents. Do not be hurried or careless at the balance.

- Clean means DRY. Water or cleaning solution can be as detrimental to the success of a reaction as dirt or sludge in the system.
- ALWAYS work on a clean laboratory bench surface.
- ALWAYS place reaction vials or flasks in a clean beaker when standing them on the laboratory bench.
- ALWAYS think through the next step you are going to perform before starting it. Once you have added the wrong reagent, it is back to square one.
- ALWAYS save everything you have generated in an experiment until it is successfully completed. You can retrieve a mislabeled chromatographic fraction from your locker but not from the waste container.
- ALWAYS keep a permanent record of all lab work in a bound notebook.

## ACADEMIC DISHONESTY

**ANY VIOLATION OF THE ACADEMIC HONESTY POLICY IN THE CLASSROOM, DURING QUIZ SECTION, OR IN THE LABORATORY IS EXTREMELY SERIOUS. READ THE APPROPRIATE SECTIONS OF THE STUDENT HANDBOOK FOR THE POLICY.**