Chemistry 432 Organic Chemistry – Fall 2022 Sections 26091 – 26097

COURSE INFORMATION

Class Days: M/W/F Class Times: 11:00 – 11:50 AM Class Location: HT-140

Review sessions dates and times will be announced in class. These will be given by Zoom only: Instructor: Prof Thomas Cole tcole@sdsu.edu (preferred)

(619) 594-5579 Office Hours Location: CSL-210A (no visitors) Office Hours Times (and by appointment): M 12:00 – 1:00 PM <u>https://SDSU.zoom.us/j/83878506078</u> and Wed 8:00 - 9:00 AM <u>https://SDSU.zoom.us/j/83958481533</u>

https://SDSU.zoom.us/j/353907903

Prerequisites

The prerequisites for those enrolling in Chem 432 is Chem 232 with a grade of C (2.0) or better and credit or concurrent registration in Chem 432L.

Enrollment Information

Please include information about enrollment for the course including, but not limited to:

- Students in this class are expected to have covered material found in Chem 232 and Chem 232L
- Drop deadline: 9/2/2022 at 19:59 (7:59 PM)

Concepts and Scope

Course Objectives:

This second semester class in organic chemistry covers reactions of carbonyl compounds; at the carbonyl carbon, at the α -carbon to a carbonyl group and the β -carbon for conjugate additions, aromatic compounds, amines and metal catalyzed bond forming reactions.

The purpose and scope of the course including, but not limited to:

- Develop the foundations for use in other classes, such as biochemistry and advanced organic chemistry.
- This classes covers the following topics in the Solomons, Fryhle and Snyder 13th ed text:
- Chapter 12 Alcohols from Carbonyl Compounds. Oxidation-Reduction and Organometallic Compounds
- Chapter 13 Conjugated Unsaturated Systems
- Chapter 14 Aromatic Compounds

- Exam #1 9/24/22 SHW-011, 10:00 AM 12:00 noon
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- Chapter 15 Reactions of Aromatic Compounds
- **Chapter 16** Aldehydes and Ketones. Nucleophilic Addition to the Carbonyl Group
- Exam #2 10/22/21 GMCS-333, 10:00 AM 12:00 noon.
- **Chapter 17** Carboxylic Acids and their Derivatives. Nucleophilic Addition-Elimination at the Acyl Carbon
- **Chapter 18** Reactions at the α -Carbon of Carbonyl Compounds. Enols and Enolates.
- Chapter 19 Condensation and Conjugate Addition Reactions of Carbonyl Compounds. More Chemistry of Enolates
- Exam #3 11/19/22 SHW-011, 10:00 AM 12:00 noon
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- Chapter 20 Amines (Second half of chapter)
- Chapter 21 Transition Metal Complexes. Promoters of Key Bond-Forming Reactions
- Left-overs and review
- Final Saturday, December 17, 2022. 14:30 16:30 (2:30 4:30) Room to be announced later.
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Student Learning Outcomes:

- 1. Students will be able to use various reducing agents to selectively prepare alcohol products as well as use the different oxidizing reagents to prepare carbonyl compounds. In a similar fashion, they will also be able to use organometallic reagents to alkylate carbonyl compounds to form new carbon-carbon bonds. Students will be able to use draw resonance structures. allowing them to determine the relative stability of reactive intermediates, such as radicals and carbocations, especially those seen in 1,2 and 1,4-additions in conjugated diene systems. All students in this class will be able to recognize aromatic, heteroaromatic (carbocations and carbanions) from anti-aromatic and non-aromatic compounds. They will be able to predict reactivities in aromatic electrophilic additions, formation of the electrophile, and identify the factors that control the regioselectivity. In addition to the electrophilic aromatic substitution, one also needs to be able to identify conditions that favor nucleophilic addition/elimination and the benzyne route (elimination/addition) for substitution. Students will be familiar with aromatic side-chain modifications and be able to effectively plan synthesis of aromatic based compounds. Students in this class will be familiar with the major routes to prepare aldehydes and ketones and their conversions to hemiacetals, acetals, imines, enamines. Cyanohydrins, Wittig reaction as well as the oxidation of aldehydes and Baeyer-Villiger oxidation. Student will be able to predict products and write mechanisms for the interconversion of carboxylic acids and their derivatives as well as their use as synthetic intermediates.
- 6. The reactions at α -carbonyl carbons are important for the formation of enol and enolates. Everyone in this class will be able to recognize the reaction conditions and write the

mechanism that lead to these essential intermediates used in carbon-carbon bond forming reactions.

- 7. Condensation reactions involving enol or enolates with carbonyl compounds as well as those leading to conjugate addition reactions are very important. Students will learn how to identify these reactions, write an acceptable mechanism and predict the products formed in these types of reactions.
- 8. Students will be able to explain the basic reactions of amines, predict their relative basicity and write acceptable mechanisms of amine and their formation.
- 9. All students in this class with be able to understand the basic reaction steps in catalytic carbon-carbon bond forming reactions as well as developing a basic understanding of organometallic bonding and prediction of stable and reactive intermediates.
- **Real Life Relevance:** This course prepares students for working in industry or academic research involving synthesis or identification of organic compounds. This course is also critical for students doing synthetic work as part of their research project.
- **Relation to Other Courses:** This class is a continuation of material covered in lower division classes such as Chem 232, and prepares students for upper-level organic chemistry, 530, 531, 532, 534, 536 in addition to the biochemistry classes, 365, 562, 563 and 564.

Course Materials

- "Organic Chemistry" Thirteenth Edition, by T. W. Solomons, C. B. Fryhle and S. A. Snyder.
- A "Student Study Guide & Solution Manual for Organic Chemistry" 13th Edition of Solomons, Fryhle and Snyder is also available at the bookstore. Another study guide that is recommended is "Success in Organic Chemistry: A Problems Book" by Andrew Ternay or the Schaum's outline for "Organic Chemistry." There are a number of alternative organic textbooks. Many of these use a slightly different approach to understanding the class material.
- A set of molecular models is **very** useful to visualize the three dimensions of compounds. There are several sets of molecular models available. You can order an inexpensive set from Andrus Education Supplies (see Canvas page for details). Alternatively, a computer based molecular modeling kit is also available. These models are optional but recommended.

Course Conduct

- Attendance and participation in lectures are most strongly recommended in aiding in mastery of organic chemistry.
- It is also highly recommended that you work the suggested problems to gauge your progress and reinforce fundamentals.
- Review sessions will be held in advanced of the midterm exams to help answer your questions.

Exams

Examinations:

Midterm Exam #1	9/24/22	100 pts
Midterm Exam #2	10/22/22	100 pts
Midterm Exam #3	11/19/22	100 pts
Final Exam	12/17/22	150 pts

All Midterm exams are given Saturday mornings, 10:00 AM - 12:00 noon. The rooms are listed in this syllabus. Students participating in official university events and activities must present to me a memorandum indicating reasons and dates of absences within the first two weeks of the semester. If you have a conflict between the midterm exams and one of your regularly scheduled classes, you may take the midterm exams at another time. However, you must contact me at least one week in advance of each of the midterm exams. You will need to bring a copy of class schedule and times that you can take the makeup exam. This will be the day before the midterm or the following Monday or Wednesday. I will attempt to find one common time for these make-up exams. If you do not contact me the week before to the exam, you will not have a choice when these make-ups are given. If you are ill or have a family emergency, you MUST contact as soon as possible, preferably before the exam begins by either emailing me (preferred). You will need to present documentation to your illness or family emergency. Conflicts with other activities, such as interviews, vacations, and weddings are not acceptable excuses. The keys to the exams are posted at the Canvas web page along with supplemental information, handout information, and addendum's to the notes. I strongly recommend that you check your exams after they are returned. You can submit an exam for a re-grade up to one week after the posting of the key. In your request for a regrades you need to attach a paper giving your basis for a regrade for each question. Do not write on your answer. After one week, I will not make any changes in your exam scores, except mathematical errors.

Chemistry 432 is a continuation of Chemistry 232. By the nature of this material, all exams are accumulative. In this course we will cover the properties and chemical reactivities of carbonyl (aldehydes, ketones and carboxylic acids), aromatics, amines and conjugated dienes. In addition, we will continue to examine the principles of spectroscopic identification of organic compounds adding the fundamentals of UV-Vis spectroscopy to that of NMR, and IR. This course is essential to the understanding of biochemistry, advanced organic chemistry and molecular biology.

Attendance is HIGHLY recommended, since additional material will be presented in lecture that is not found in the text. Frequently, alternative explanations of class material will be presented as well as approaches to the solution of problems. As a rule, lack of attendance strongly correlates to a low course grade. I strongly recommend that you also form a study group. You can learn a lot helping someone else. Another opportunity to master this material is attending the help sessions. I will be offering help sessions the week before the midterm exams. However, if attendance falls below a present level, I will cancel the remaining help sessions for the semester. Students are strongly encouraged to turn-off phones and lap top computers. Recent studies show paper and pencil notes are far more effective than electronic means. Finally, come to lecture anticipating what will be covered at day. If you miss lecture, email me for access to those lectures and I will give you access to the MediaSite recordings.

Grading

Your grade will be determined only at the end of the semester. Do not ask me what your grade is, I don't know. This class is graded on a curve. The grades are assigned based on clusters of points, where everyone in a cluster are within no more than 4-5 points different to the closest students in that cluster. The minimum difference between clusters are typically 6-7 points or greater. Clusters at the high or low end are generally larger, with separations of 15-20 points. About $10\%, \pm 3\%$ of the classes will earn an A. The class average is usually within the C+ grade. Better than average classes have the average grade in the B- cluster or higher in a few cases. Experience has shown that less than 40%

scores will be given less than a C grade. Also, the sizes of the clusters are larger near the class average.

Grading: Your course grade will be based on 450 points maximum.

In summary; Midterm Exam #1	100 points	22%
Midterm Exam #2	100 points	22%
Midterm Exam #3	100 points	22%
Final Exam	150 points	33%
Total	450 points	100%

University Policies

Student Privacy and Intellectual Property: The <u>Family Educational Rights and Privacy Act</u> (FERPA) mandates the protection of student information, including contact information, grades, and graded assignments. I will use Blackboard to communicate with you, and I will not post grades or leave graded assignments in public places. Students will be notified at the time of an assignment if copies of student work will be retained beyond the end of the semester or used as examples for future students or the wider public. Students maintain intellectual property rights to work products they create as part of this course unless they are formally notified otherwise.

Religious observances: According to the University Policy File, students should notify the instructors of affected courses of planned absences for religious observances by the end of the second week of classes.

Students with Disabilities

If you are a student with a disability and believe you will need accommodations for this class, it is your responsibility to contact Student Ability Success Center at sasc@sdsu.edu. To avoid any delay in the receipt of your accommodations, you should contact Student Ability Success Center as soon as possible. Please note that accommodations are not retroactive, and that accommodations based upon disability cannot be provided until you have presented your instructor with an accommodation letter from Student Ability Success Center. Your cooperation is appreciated.

Academic Honesty

The University adheres to a strict <u>policy regarding cheating and plagiarism</u>. These activities will not be tolerated in this class. Become familiar with the policy (http://www.sa.sdsu.edu/srr/conduct1.html). Any cheating or plagiarism will result in failing this class and a disciplinary review by Student Affairs. Do not expect a warning!

Examples of Plagiarism include but are not limited to:

- copying, in part or in whole, from another's test or other examination;
- obtaining copies of a test, an examination, or other course material without the permission of the instructor;
- collaborating with another or others in work to be presented without the permission of the instructor;

- falsifying records, laboratory work, or other course data;
- submitting work previously presented in another course, if contrary to the rules of the course;
- altering or interfering with grading procedures;
- assisting another student in any of the above;
- using sources verbatim or paraphrasing without giving proper attribution (this can include phrases, sentences, paragraphs and/or pages of work);
- copying and pasting work from an online or offline source directly and calling it your own;
- replacing words or phrases from another source and inserting your own using information you find from an online or offline source without giving the author credit;
- replacing words or phrases from another source and inserting your own words or phrases.

If you have questions on what is plagiarism, please consult the <u>policy</u> (http://www.sa.sdsu.edu/srr/conduct1.html) and this <u>helpful guide from the Library</u>: (http://infodome.sdsu.edu/infolit/exploratorium/Standard_5/plagiarism.pdf)

The California State University system requires instructors to report all instances of academic misconduct to the Center for Student Rights and Responsibilities. Academic dishonesty will result in disciplinary review by the University and may lead to probation, suspension, or expulsion. Instructors may also, at their discretion, penalize student grades on any assignment or assessment discovered to have been produced in an academically dishonest manner.

Resources for students: A complete list of all academic support services-including the <u>Writing Center</u> and <u>Math Learning Center</u>--is available on the Student Affairs' <u>Academic Success</u> website. <u>Counseling</u> and <u>Psychological Services</u> (619-594-5220) offers confidential counseling services by licensed therapists; you can Live Chat with a counselor at <u>http://go.sdsu.edu/student affairs/cps/therapist-consultation.aspx</u> between 4:00pm and 10:00pm, or call San Diego Access and Crisis 24-hour Hotline at (888) 724-7240.

Classroom Conduct Standards: SDSU students are expected to abide by the terms of the Student Conduct Code in classrooms and other instructional settings. Prohibited conduct includes:

- • Willful, material and substantial disruption or obstruction of a University-related activity, or any on-campus activity.
- • Participating in an activity that substantially and materially disrupts the normal operations of the University, or infringes on the rights of members of the University community.
- Unauthorized recording, dissemination, or publication (including on websites or social media) of lectures or other course materials.
- Conduct that threatens or endangers the health or safety of any person within or related to the University community, including
 - 1. physical abuse, threats, intimidation, or harassment.
 - 2. sexual misconduct.

Violation of these standards will result in referral to appropriate campus authorities.

Medical-related absences: Students are instructed to contact their professor/instructor/coach in the event they need to miss class, etc. due to an illness, injury or emergency. All decisions about the impact of an absence, as well as any arrangements for making up work, rest with the instructors. <u>Student Health Services</u> (SHS) does not provide medical excuses for short-term absences due to illness or injury. When a medical-related absence persists beyond five days, SHS will work with students to provide appropriate documentation. When a student is hospitalized or has a serious, ongoing illness or injury, SHS will, at the student's request and with the student's consent, communicate

with the student's instructors via the Vice President for Student Affairs and may communicate with the student's Assistant Dean and/or the <u>Student Ability Success Center</u>. If you are unable to be in person for lecture, please contact the instructor. You **may** be asked to give documentation to your absence. I will give you access to the MediaSite video of the lecture(s) that you have missed. This video may only available for a few days, generally 2-3 weekdays.

SDSU Economic Crisis Response Team: If you or a friend are experiencing food or housing insecurity, or any unforeseen financial crisis, visit <u>sdsu.edu/ecrt</u>, email <u>ecrt@sdsu.edu</u>, or walk-in to Well-being & Health Promotion on the 3rd floor of Calpulli Center.

Other Help. This semester supplemental instruction is available. More details will be found on the Canvas page. Private tutoring, or other academic support resources may be available.

Texts and materials

Land Acknowledgment

For millennia, the Kumeyaay people have been a part of this land. This land has nourished, healed, protected and embraced them for many generations in a relationship of balance and harmony. As members of the San Diego State University community, we acknowledge this legacy. We promote this balance and harmony. We find inspiration from this land, the land of the Kumeyaay.

Inclusion in this Course

The science that we will be discussing is blissfully independent of geography or era, remaining valid (we believe) on planets halfway across the universe as much as here and for billions of years behind us and yet to come. However, the concepts that we will be spending most of our time on in physical chemistry were formulated and recorded primarily in rather specific places and times, in the US and Western Europe over the last 200 years. But it matters that the science itself exceeds these narrow boundaries, and people of all backgrounds and cultures have contributed to the early development of the science we use today, and will contribute to its continued growth in the future.

As scientists, we must all pay attention to the biases that may cause us to misinterpret data, to dismiss potentially valid alternatives, to see from only one perspective. It is our obligation to overcome these biases as much as possible to examine nature with an unfiltered eye. Part of that obligation is appreciating that everyone in the classroom, even the instructor, has a history that has shaped our perspective such that our experience is necessarily limited, and we broaden our ability to understand the world by each of us bringing our perspective to the classroom. Please feel free to ask questions and challenge assertions, but always with respect for others and the understanding that we are all there to learn from one another.

The Important Concepts of Organic Chemistry

For Chemistry 432

Note - not in any particular order of importance

Electronegativity and the periodic table – predictions of reactivity (nucleophilicity/electrophilicity), role of hybridizations.

 pk_a – Know the basic and important compounds and the trends due to substituents. Phenols, carboxylic acids, amines pK_b , aliphatic compounds and roles of resonance. Also, be able to relate conjugate acid and base strengths.

The octet rule and the basic structure of organic compounds.

Reaction mechanisms

- 1. Nucleophilic additions to carbonyl compounds (strong and weak nucleophiles)
- 2. Electrophilc attack
- 3. Aromatic electrophilic substitution
- 4. Free radical substitution
- 5. Pericylic reactions (decarboxylation, Diels-Alder, Claisen and Cope rearrangements, etc.
- 6. Nucleophilic substitutions, S_N1 , S_N2 and S_NAr and factors that allows one to predict differences between.

Stabilities of carbocations and free radicals. Carbanions have an approximate inverse order of stability.

Stability of alkenes

Kinetic versus Thermodynamic Control of reactions

Aromaticity and antiaromaticity. Hückel's rule and application to compounds

Resonances, structures and stability

Principle of microscopic reversibility

Truisms

Don't make strong acids in basic reaction conditions and don't make strong bases in acid reaction conditions. Acidity and basicity are all relative.

The higher the reactivity the lower the selectivity and the lower the reactivity the higher the selectivity.

Comments and Recommended Problems for "Organic Chemistry" 12<u>th</u> Ed. T. W. Graham Solomons, Craig B. Fryhle and Scott A. Snyder **General Notes.** First, you need to realize that Organic Chemistry isn't all that hard. It may be complex but there is only fairly small set of fundamental concepts that you need to know. Look as the list of Important Concepts for this class on Blackboard. Second, in order to get a satisfactory grade in this course it is very important to study daily. Actually the amount of time need only be short periods of time (5-10 min max) and several times a day. If you do this, you will find that the problems are far easier to do and you will spend less time doing them. Work as many of the problems as possible. If you find that the problems are easy, move onto the more difficulty ones. Because there is so much material it is imperative that you keep up with the reading, studying and doing problem sets. If you have questions or problems - get help as soon as possible. Help is available during my office hour, with your laboratory TA or if necessary hire a tutor (there is a list of tutors on the bulletin board outside the Chemistry Office GMCS-209 as well as advertisements around campus for other tutors). I strongly suggest you form study groups, work together on problems. Tutoring someone else will usually help you more that the student your help.

Read for General Interest (RGI) and background

Chapter 12

Alcohols from Carbonyl Compounds. Oxidation – Reduction and Organometallic Compounds

Problems: 12.1; 12.3; 12.5; 12.6; 12.8; 12.12; 12.16; 12.20, 12.25; 12.28.

Chapter 13

Conjugated Saturated Systems

Problems: 13.3; 13.4; 13.10; 13.16; 13.25; 13.29; 123.39; 13.40; 13.42.

Chapter 14

Aromatic Compounds

- Section 14.8A Know structures and names for napthalene and anthracenes compounds.
- 14.7A Read for General Interest on Relative Energies of Monocylic Systems
- pg 648 Read for General Interest on Sunscreens
- Problems 14.5; 14.10; 14.11; 14.12; 14.14; 14.18; 14.20; 14.25; 14.27; 14.30.

Chapter 15

Reactions of Aromatic Compounds

- Table 15.10GThis is a very important table. You must know which groups are ortho, meta and
para directing. You should also know which are strong, moderate and weak. Also,
you must know the limitations of the Friedel-Crafts alkylation and acylation
reactions.
- Problems 15.2; 15.5; 15.7; 15.12; 15.13; 15.17; 15.18; 15.22, 15.24; 15.33; 15.34; 15.36; 15.40; 15.47.

Chapter 16

Aldehydes and Ketones I. Nucleophilic Addition to the Carbonly Group

- Section 16.5 Include to your list of methods for the preparation of ketones, ozonalysis of alkenes, Friedel Crafts Acylations, oxidation of secondary alcohols, hydration of alkynes and Grignard reagent addition to nitriles
- Section 16.7A Hydrates of aldehydes and ketones have little synthetic value.
- Section 16.10 A very important section.
- Problems 16.2; 16.4(a, c-f); 16.6, 16.8; 16.9; 16.11; 16.13; 16.14; 16.16; 16.17; 16.18; 16.19(a-g, j-n); 16.25; 16.26; 16.29.

Chapter 17

Carboxylic Acids and Their Derivatives. Nucleophilic Additions at the Acyl Carbon

- Section 17.2J Briefly go over the spectroscopy of the acyl compounds for general information.
- Section 17.4 Nucleophilic substitution, an important subject. Known the mechanism!
- Sections 17.7 Esters, know the mechanism of formation and hydrolysis.
- Problems 17.1; 17.2; 17.4; 17.6; 17.8; 17.9; 17.11; 17.20; 17.21; 17.24; 17.28; 17.29; 17.30; 17.32; 17.43.

Chapter 18

Reactions at the -Carbon of Carbonyl Compounds. Enols and Enolates

Problems

18.1; 18.2; 18.3; 18.7; 18.8; 18.12; 18.14; 18.19; 18.20; 18.21; 18.27; 18.29; 18.33; 18.35.

Chapter 19

Condensation and Conjugate Addition Reactions of Carbonyl Compounds.

More Chemistry of Enolates

- Section 19.12 RGI
- Problems 19.3; 19.6; 19.9; 19.12; 19.15; 19.17; 19.21; 19.24; 19.29; 19.34; 19.35; 19.36; 19.41; 19.43; 19.46; 19.47.

Chapter 20

Amines

Section 20.6A, 20.6C RGI

Problems 20.1; 20.2; 20.4; 20.6; 20.7; 20.13; 20.22; 20.25; 20.31(a, d, f, h, m); 20.33; 20.48.

Chapter 21

Transition Metal Complexes: Promoters of Key Bond-Forming Reactions

Problems 21.1; 21.3; 21.5; 21.6; 21.8; 21.10; 21.11; 21.12; 21.13; 21.16; 21.17; 21.20.