GRANDE PRAIRIE REGIONAL COLLEGE DEPARTMENT OF SCIENCE: CHEMISTRY

FORTY-FOURTH SESSION 2009 – 2010

COURSE OUTLINE: ORGANIC CHEMISTRY

CH2630 A3

CHEMISTRY 2630 A3: Organic Chemistry II

PREREQUISITE: CH1610 or CH2610

INSTRUCTOR: Dr. John P. Sloan Office # J207 Phone # 539-2004 E-mail <u>SLOAN@GPRC.AB.CA</u>

LECTURE: CH2630 A3 M,W 8:30 – 9:50 in J201

ALBERTA TRANSFER CREDIT

(Ref: 2009-2010 Guide to Transfer Credit at Alberta Post-Secondary Institutions)

GPRC:	CH 2610 (3)	CH 2630	(3)
U of Alberta:	CHEM 261 (3)	CHEM 263	(3) or AUCHE 252 3
U of Calgary:	CHEM 351 (3)	CHEM 353	(3)
U of Lethbridge:	CHEM 2500 (3)	CHEM 2600	(3)
Athabasca U:	CHEM 350 (3)	CHEM 360	(3)
Canadian UC:	CHEM 241 (4)	CHEM 242	(4)
Concordia UC:	CHEM 261 (3)	CHEM 263	(3)
King's UC:		CHEM 351	(3)

COURSE OUTLINE:

Lecture Component:

A continuation of the study of the fundamental principles of the chemistry of carbon compounds as commenced in Chemistry 2610. The study is based on a reaction mechanism approach to the functional group chemistry of arenes, aldehydes, ketones, carboxylic acids, esters, amides, amino acids and carbohydrates. Topics include: structure and bonding; physical properties; acidity and basicity; conformations of molecules; stereochemistry; addition, elimination and substitution reactions; structure-reactivity relationships; aromaticity and aromatic substitution; and spectroscopic methods for structure determination.

A representative selection of molecules found in agricultural, biological, environmental, industrial, medical, and pharmatheutical applications of organic chemistry will be discussed, e.g., molecules found in agrochemicals, fibres, food additives, perfumes, polymers, and prescription drugs.

Laboratory Component:

Techniques in organic chemistry; preparation of some organic compounds, and; methods of qualitative organic analysis.

Tutorial Component:

Problem solving and discussion sessions with weekly problem sets. Regular assignments will be given and marked.

Notes:

- 1. Lectures: Days, Time and Place CH2630 A3 T,R 8:30 9:50 in J201
- 2. Laboratory Component: Day, Time and Place CH2630 L1 W 14:30 - 17:20 in J116
- 3. Tutorial Component: Day, Time and Place CH2630 S1 F 11:30 - 12:20 in J204

TEXT BOOKS AND LABORATORY ITEMS:

The following text book is required:

CH2610

Solomons, T.W.G., and C.B. Fryhle, Organic Chemistry, 9th Edition, Wiley, 2008

And

A Three Ring Binder to Hold: Sloan, J.P., *Organic Chemistry Experiments, Chemistry 2610/2630*, Grande Prairie Regional College, 2009/2010.

Molecular Models are highly recommended, namely:

Molecular Model Set for Organic Chemistry, Prentice Hall.

Study Guides, Solutions Manuals, and Wiley Plus are supplementary items, namely:

- 1. Fernandez, J.E., and Solomons, T.W.G., *Study Guide and Solutions Manual to Organic Chemistry*, 9th Edition, 2008;
- 2. Wiley Plus.

Note:

1. All required and supplementary books, molecular structure model sets, safety glasses, and lab coats are available at the College Bookstore. *Organic Chemistry Experiments*, by J.P. Sloan, will be given as handouts in advance of each lab period. These are to be inserted in a three ring binder.

EVALUATION:

Examination Schedule and Composition of the Final Grade:

1.	Midterm Exam # 1, Friday February 12 15	5%
2.	Midterm Exam # 2, Friday March 19 20	0%
2.	Final Exam to be scheduled between April 17 – 29 39	30%
3.	Laboratory 23	25%
4.	Tutorial Grading Component <u>10</u>	0%
	10	00%

The Grades are based on the alpha grading system. The Registrar's Office will convert alpha grades to fourpoint equivalence for the calculation of grade point averages. Alpha grades, 4-point equivalence, and grade descriptors are as follows:

Alpha	4-Point Equivalence	Descriptor
Grade		
A+	4.0	Excellent
А	4.0	
A-	3.7	First Class Standing
B+	3.3	
В	3.0	Good
B-	2.7	
C+	2.3	Satisfactory
С	2.0	
C-	1.7	
D+	1.3	Poor
D	1.0	Minimal Pass
F	0.0	Failure

* Other post secondary institutions may not award transfer credit for grades of D and D+. Notes:

- 1. The Mid-Term exams will be of 1.5 hours duration and the Final Exam will be of 3 hours duration.
- 2. Between 5 and 15% of exam content will be taken directly from weekly assignments.
- 3. A pass grade is essential for the Laboratory Component.
- 4. The Tutorial Grading Component consists of assignments and will contribute towards 10% of the final grade. A 10 question assignment will normally be given each week.
- 5. Assistance with assignments will be given upon request.
- 6. Regular attendance in Lecture, Laboratory, and Tutorial Components is a Course Requirement.

Grande Prairie Regional College Calendar 2009 - 2010: Course Description (page 185).

CH 2630 3(3-1-3)UT 105 Hours Organic Chemistry II

Continuation of the study of structural and chemical properties of the basic functional groups of organic compounds including aromatic compounds, aldehydes, ketones, carboxylic acids and their derivatives and amines. Illustration of these functional groups in natural products such as carbohydrates, amino acids and proteins, nucleic acids and lipids and discussion of the application of spectroscopic methods for structure determination in simple organic molecules.

Prerequisites: CH1610 or CH 2610

Notes: Credit will be granted for only one of CH1630 or CH2630.

Engineering students who take this course will receive 4.5 credits of transfer to UofA. Transfer: UA, UC, UL, AU, AF, CU, CUC, KUC

CHEMISTRY 2610: READING, STUDYING, AND PRACTICE PROBLEMS

All references are to T.W.G. Solomons and C.B. Fryhle, Organic Chemistry, 9th Edition, Wiley, 2008.

FALL SEMESTER

Weeks of

Jan 5 & 11: THE BASICS: Bonding and Molecular Structure

Molecular Graphic: Glycine, an organic molecule found in space

- Sect # Page # Read and Study Chapter 1 "We are Star Dust"
- 1.1 2 Organic Chemistry and Life
- 1.2 3 The Structural Theory of Organic Chemistry
- 1.3 4 Isomers: The Importance of Structural Formulas
- 1.4 5 Chemical Bonds: The Octet Rule
- 1.5 7 Writing Lewis Structures
- 1.6 9 Exceptions to the Octet Rule
- 1.7 10 Formal Charge
- 1.8 13 Resonance Theory
- 1.8A 15 Summary of Rules for Resonance
- 1.9 18 Quantum Mechanics and Atomic Structure
- 1.10 20 Atomic Orbitals and Electron Configuration:
- 1.10A 21 Aufbau Principle; the Pauli Exclusion Principle; Hund's Rule
- 1.11 21 Molecular Orbitals: Bonding and Antibonding
- 1.12 24 The Structure of Methane and Ethane: sp^3 Hybridization;
- 1.12A 24 The Structure of Methane
- 1.12B 27 The Structure of Ethane
- 1.13 28 The Structure of Ethene (Ethylene): sp^2 Hybridization
- 1.13A 31 Restricted Rotation and the Double Bond
- 1.13B 32 Cis-Trans Isomers
- 1.14 33 The Structure of Ethyne (Acetylene): sp Hybridization
- 1.14A 34 Bond Lengths of Ethyne, Ethene, and Ethane
- 1.15 35 A Summary of Important Concepts that Come from Quantum Mechanics
- 1.16 36 Molecular Geometry: The Valence Shell Electron-Pair Repulsion (VSEPR) Model.
- 1.16A-F 37 Molecular Geometry: VSEPR Models for Methane, Ammonia, Water, Boron Trifluoride, Berylium Hydride and Carbon Dioxide
- 1.17 39 Representation of Structural Formulas: Dash; Condensed; Bond Line; and the Three Dimensional Wedge, Dash, Line Representation
- 1.18 44 Applications of Basic Principles: Opposite Charges Attract; Like Charges repel; Nature Tends Towards States of Lower Potential Energy; Orbital Overlap Stabilizes Molecules
 - 45 Key Terms and Concepts
 - 46 Concept Map

Practice Problems: You are encouraged to work all of the in-chapter problems, and you are required to complete the assignments given in-seminar-class and from Wiley Plus. Routinely doing problems in organic chemistry leads to understanding of the theory, and good grades in organic chemistry.

In the words of Solomons and Fryhle:

"One way to check your progress is to work each of the in-chapter problems when you come to it. These problems have been written just for this purpose and are designed to help you decide whether or not you understand the material that has just been explained."

And, in the words of Wade:

"It's easy to fool yourself into thinking you understand organic chemistry when you actually do not. As you read through this book, all the facts and ideas may make sense, yet you have not learned to combine and use those facts and ideas. An examination is a painful time to learn that you do not really understand the material.

The best way to understand organic chemistry is to use it. You will certainly need to read and reread all the material in the chapter, but this level of understanding is just the beginning. Problems are provided so you can work with the ideas, applying them to new compounds and new reactions that you have never seen before. By working problems, you force yourself to use the material and fill in the gaps in your understanding. You also increase your level of self-confidence and your ability to do well on exams".

Problems:	In-Chapter	1.1 to 1.15
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- 47 End of Chapter 1.16 to 1.38
 - 50 Learning Group Problem

Week of Jan 18: REPRESENTATIVE CARBON COMPOUNDS: Functional Groups, Intermolecular Forces, and Infrared (IR) Spectroscopy

- 51 Structure and Function: Organic Chemistry, Nanotechnology, and Bioengineering
- 2.1 52 Carbon-Carbon Covalent Bonds
- 2.2 52 Hydrocarbons: Representative, Alkanes, Alkenes, Alkynes, and Aromatic Compounds
- 2.3 55 Polar Covalent Bonds
- 2.4 56 Polar and Nonpolar Molecules
- 2.4A 58 Dipole Moments in Alkenes
- 2.5 59 Functional Groups
- 2.5A 59 Alkyl Groups and the Symbol R
- 2.5B 60 Phenyl and Benzyl Groups
- 2.6 60 Alkyl Halides or Haloalkanes
- 2.7 61 Alcohols, including Classification as Primary, Secondary and Tertiary (1E, 2E, 3E)
- 2.8 63 Ethers
- 2.9 63 Amines, including Classification as Primary, Secondary and Tertiary
- 2.10 65 Aldehydes and Ketones
- 2.11 65 Carboxylic Acids, Esters, and Amides
- 2.12 67 Nitriles
- 2.13 68 Summary of Important Families of Organic Compounds
- 2.14 68 Physical Properties and Molecular Structure with emphasis on Intermolecular Interactions, namely:
- 2.14A 69 Ion-Ion Forces in ionic compounds, e.g. sodium acetate, sodium chloride
- 2.14B 70 Dipole-Dipole Forces resulting from permanent dipoles, e.g. acetone, chloromethane

2.14C 70 Hydrogen Bonds 2.14D 71 van der Waals Forces, or London forces or dispersion forces, e.g. methane 2.14E 73 **Solubilities** 2.14F 74 Guidelines for Water Solubility 2.14G 74 Intermolecular Forces in Biochemistry, and Organic Templates Engineered to Mimic Bone Growth 2.15 75 Summary of Attractive Electric Forces Infrared Spectroscopy: An Instrumental Method for Detecting Functional Groups 2.16 76 2.16A 80 Infrared Spectra of Hydrocarbons IR Spectra of Some Functional Groups Containing Heteroatoms including Carbonyl Functional 2.16B 82 Groups of Aldehydes, Ketones, Esters, Carboxylic Acids and Amides, plus Alcohols, Phenols and Amines 2.17 Applications of Basic principles: Polar Bonds are Caused by Electronegativity Differences; 84 **Opposite Charges Attract; Molecular Structure Determines Properties** Key Terms and Concepts 85 Concept Map 86

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Problems:	In-Chapter	2.1 to 2.19	
87	End of Chapter	2.20 to 2.48	

90 Learning Group Problem

Week of Jan 25: AN INTRODUCTION TO ORGANIC REACTIONS: ACIDS AND BASES IN ORGANIC CHEMISTRY

- 91 Diamox, a drug that prevents altitude sickness
- 91 Shuttling the Protons, or, from the Lewis and Sloan perspective, Shuttling the Electrons
- 3.1 92 Reactions and their Mechanisms Substitution, Addition, Elimination and Rearrangement Reactions
- 3.1A 92 Homolysis and Heterolysis of Covalent Bonds, and Introduction to the Use of Curved Arrows
- 3.2 94 Acids and Bases
- 3.2A 94 The BrNnsted-Lowry Definition of Acids and Bases
- 3.2B 95 The Lewis Definition of Acids and Bases
- 3.2C 96 Opposite Charges Attract
- 97 The Chemistry of ... HOMOs and LUMOs in Reactions
- 3.3 97 Heterolysis of Bonds to Carbon Carbocations and Carbanions
- 3.4 98 The Use of Curved Arrows in Illustrating Reactions
- 3.5 100 The Strength of Acids and Bases, K_a and pK_a
- 3.5A 100 The Acidity Constant, K_a
- 3.5B 100 Acidity and pK_a
 - 101 Table 3.1: Relative Strength of Selected Acids and Their Conjugate Bases
- 3.5C 102 Predicting the Strength of Bases
 - the Stronger the Acid, the Weaker the Conjugate Base
- 3.6 103 Predicting the Outcome of Acid-Base Reactions
- 3.6A 104 Water Solubility as a Result of Salt Formation
- 3.7 105 The Relationship between Structure and Acidity, i.e. Structural Effects on Acidity and Basicity, namely:
 - 1. Size Effect, acidity increases upon descending a column in the Periodic Table,

		H-I is a stronger acid than H-F; the acidity order is: $H-I > H-Br > H-Cl > H-F$
		2. Electronegativity Effect, acidity increases from left to right in the Periodic Table, H-F is a stronger acid than CH_4 ; the acidity order is: $HF > H_2O > NH_3 > CH_4$
3.7A	107	3. The Effect of Hybridization, more s-character means the anion has lower energy, is
		more stable, and is a weaker base
3.7B	108	4. Inductive Effects, from polarization by electron attracting and electron withdrawing
		groups
3.8	108	Energy Changes; higher potential and kinetic energy implies less stable, lower energy implies more stable
3.8A	109	Potential Energy and Covalent Bonds, exothermic reactions give out heat, endothermic
		reactions absorb heat
3.9	110	The Relationship Between the Equilibrium Constant and the Standard Free-Energy Change,
		ΔG° ; a negative value favours products at equilibrium
3.10	111	The Acidity of Carboxylic Acids, with explanations arising from Resonance Effects and
		Inductive Effects
3.10A	. 112	The Effect of Delocalization: An Explanation based on Resonance Effects, due to resonance
2 100	110	stabilization of the carboxylate anion
3.10B	113	An Explanation based on Inductive Effects, due to inductive withdrawal of electronic charge by –O and -C=O in carboxylate anions
3.10C	114	Summary of a Comparison of Conjugate Acid-Base Strengths
3.10C		Inductive Effects of Other Groups
3.11	115	The Effect of Solvent on Acidity - Protic Solvents
3.12	116	Organic Compounds as Bases
3.13	117	A Mechanism for an Organic Reaction
	118	The Chemistry of carbonic Anhydrase
3.14	119	Acid and Base in Nonaqueous Solutions
3.15	120	Acid-Base Reactions, and Synthesis of Deuterium- and Tritium-Labelled Compounds
3.16	121	Applications of Basic Principles: Electronegativity Differences Polarize Bonds; Polarized
		Bonds Underlie Inductive Effects; Opposite Charges Attract; Nature Prefers States of Lower
		Potential Energy; Resonance Effects Can Stabilize Molecules and Ions
	122	Key Terms and Concepts
	123	Concept Map
Proble	ems:	In-Chapter 3.1 to 3.14
	124	End of Chapter 3.15 to 3.42

127 Learning Group Problem

Week of Feb 1: NOMENCLATURE AND CONFORMATIONS OF ALKANES AND CYCLOALKANES

- 129 To be Flexible or Inflexible Molecular Structure Makes the Difference
- 4.1 130 Introduction to Alkanes and Cycloalkanes
- 4.1A 130 Sources of Alkanes: Petroleum
 - 130 The Chemistry of Petroleum Refining
 - 131 Typical Fractions Obtained by Distillation of Petroleum
- 4.2 132 Shapes of Alkanes

	133	Tables 4.1: Physical Constants of Hexane Isomers
	134	Table 4.2: Number of Alkane Isomers
	135	Table 4.3: The Unbranched Alkanes
4.3	134	IUPAC Nomenclature of Alkanes, Alkyl Halides and Alcohols
4.3A	135	Nomenclature of Unbranched Alkyl Groups
4.3B	135	Nomenclature of Branched-Chain Alkanes
4.3C	137	Nomenclature of Branched Alkyl Groups
4.3D	138	Classification of Hydrogen Atoms,
		as Primary (1°) , Secondary (2°) , and Tertiary (3°)
4.3E	139	Nomenclature of Alkyl Halides
4.3F	139	Nomenclature of Alcohols
4.4	141	Nomenclature of Cycloalkanes
4.4A	141	Monocyclic Compounds
4.4B	142	Bicyclic Compounds
4.5	143	Nomenclature of Alkenes and Cycloalkenes
4.6	145	Nomenclature of Alkynes
4.7	146	Physical Properties of Alkanes and Cycloalkanes
	148	The Chemistry of Pheromones: Communication by Means of Chemicals
4.8	148	Sigma (Φ) Bonds and Bond Rotation
4.9	151	Conformational Analysis of Butane
4.10	153	The Relative Stability of Cycloalkanes: Ring Strain
4.10A	153	Heats of Combustion
4.10B	154	Heats of Combustion of Cycloalkanes
	154	Table 4.5: Heats of Combustion and Ring Strain of Cycloalkanes
4.11	155	The origin of Ring Stain in Cyclopropane and Cyclobutane: Angle Strain and Torsional Strain
4.11A	155	Cyclopropane
4.11B	156	Cyclobutane
4.11C	156	Cyclopentane
4.12	156	Conformations of Cyclohexane
4.12A	158	Conformations of Higher Cycloalkanes
	159	The Chemistry of Nanoscale Motors and Molecular Switches
4.13	160	Substituted Cyclohexanes, Axial and Equatorial Hydrogen Atoms
4.14	163	Disubstituted Cyclohexanes, Cis-Trans Isomerism
4.14A	164	Cis-Trans Isomerism and Conformational Structures
4.15	166	Bicyclic and Polycyclic Alkanes
	167	The Chemistry of Elemental Carbon
4.16	168	Chemical Reactions of Alkanes
4.17	168	Synthesis of Alkanes and Cycloalkanes
4.17A	168	Hydrogenation of Alkenes and Alkynes
4.18	169	Structural Information from Molecular Formulas and the Index of Hydrogen Deficiency
4.18A	170	Compounds Containing Halogens, Oxygen, or Nitrogen
4.19	171	¹³ C NMR Spectroscopy- A Practical Introduction
4.19A	172	One Signal for each Unique Carbon
4.19B	173	Chemical Shift – Location of the Signal Depends on Electronic Environment
4.19C	174	Using ¹³ C NMR to Elucidate Structure
4.20	175	Application of Basic Principles: Nature Prefers States of Lower Energy;
	176	Key Terms and Concepts
	177	Concept Maps

Problems: In-Chapter 4.1 to 4.21

- 178 End of Chapter 4.22 to 4.54
- 180 Learning Group Problems

Week of Feb 8: STEREOCHEMISTRY: CHIRAL MOLECULES

- 181 The Handedness of Life 5.1 182 The Biological Significance of Chirality 5.2 183 Isomerism, Constitutional Isomers and Stereoisomers **Enantiomers and Chiral Molecules** 5.3 184 5.4 187 More about the Biological Importance of Chirality The Historical Origin of Stereochemistry 5.5 188 5.6 189 Tests for Chirality, Planes of Symmetry and Points of Symmetry Nomenclature of Enantiomers: The R-S System 190 5.7 Properties of Enantiomers, Optical Activity 5.8 194 5.8A 195 Plane-Polarized Light 5.8B 195 The Polarimeter 5.8C 195 **Specific Rotation** The Origin of Optical Activity 5.9 198 **Racemic Forms** 5.9A 199 5.9B 199 **Racemic Forms and Enantiomeric Excess** 5.10 200 The Synthesis of Chiral Molecules 5.10A 200 **Racemic Forms** Stereoselective Synthesis 5.10B 201 5.11 202 Chiral Drugs 203 The Chemistry of: Selective Binding of Drug Enantiomers to Left- and Right-Hand Coiled DNA 5.12 203 Molecules with More Than One Chirality Centree 5.12A 205 Meso Compounds 5.12B 206 Naming Compounds with More than One Chirality Centre 207 **Fischer Projection Formulas** 5.13 Stereoisomerism of Cyclic Compounds 5.14 209 **Cyclohexane Derivatives** 5.14A 209 Relating Configurations Through Reactions in Which No Bonds to the Chirality Centre are 5.15 211 Broken 5.15A 212 **Relative and Absolute Configurations** Separation of Enantiomers: Resolution 5.16 213 5.16A 214 Pasteur's Method for Separating Enantiomers Current Methods for Resolution of Enantiomers 5.16B 214 5.17 214 Compounds with Chirality Centres Other than Carbon 5.18 215 Chiral Molecules that do not Possess a Chirality Centre (a Tetrahedral Atom with Four **Different Groups Attached**) Key Terms and Concepts 216 217 Concept Map Problems: In-Chapter 5.1 to 5.29 218 End of Chapter 5.30 to 5.44
 - 220 Learning Group Problems

Additional Problems - The CD accompanying the text book includes a set of computer molecular model stereochemistry exercises that are keyed to the text

Weeks of Feb 15: IONIC REACTIONS: Nucleophilic Substitution and Elimination Reactions of Alkyl Halides

	221	Breaking Bacteria Cell Walls With Organic Chemistry
6.1	222	Organic Halides
	222	Table 6.1: Carbon-Halogen Bond lengths and Bond Strengths
6.1A	223	Physical Properties of Organic Halides
	223	Table 6.2: Organic Halides
6.2	224	Nucleophilic Substitution Reactions
6.3	224	Nucleophiles
6.4	225	Leaving Groups
6.5	226	Kinetics of a Nucleophilic Substitution Reaction -
		a Substitution Nucleophilic Bimolecular (S _N 2) Reaction
6.6	227	A Mechanism for the S _N 2 Reaction
6.7	228	Transition State Theory: Free-Energy Diagrams
6.8	229	The Stereochemistry of S _N 2 Reactions
6.9	235	The Reaction of Tert-Butyl Chloride with Hydroxide Ion: An S _N 1 Reaction
6.9A	235	Multistep Reactions and the Rate-Determining Step
6.10	236	A Mechanism for the S _N 1 Reaction
6.11	237	Carbocations
6.11A	237	The Structure of Carbocations
6.11B	238	The Relative Stabilities of Carbocations
6.12	239	The Stereochemistry of S _N 1 Reactions
6.12A	239	Reactions That Involve Racemization
6.12B	240	Solvolysis – Cleavage of the Solvent by the Nucleophile
6.13	241	Factor's Affecting the Rates of S _N 1 and S _N 2 Reactions
6.13A	241	The Effect of the Structure of the Substrate
	241	Table 6.4: Relative Rates of Reactions of Alkyl Halides in S _N 2 Reactions
	243	S _N 1 Reactions and the Hammond-Leffler Postulate
6.13B	244	The Effect of the Concentration and the Strength of the Nucleophile
	244	Nucleophilicity versus Basicity
6.13C	245	Solvent Effects on S _N 2 Reactions: Polar Protic and Aprotic Solvents
6.13D	247	Solvent Effects on S _N 1 Reactions: The Ionizing Ability of the Solvent
	247	Table 6.5: Dielectric Constants of Common Solvents
6.13E	247	The Nature of the Leaving Group
	249	Summary of $S_N 1$ versus $S_N 2$
	249	Table 6.6: Factors Favouring S _N 1 versus S _N 2 Reactions
6.14	250	Organic Synthesis - Functional Group Transformations Using S _N 2 Reactions
	251	The Chemistry of Biological Methylation: A Biological Nucleophilic Substitution Reaction
6.14A	252	The Unreactivity of Vinylic and Phenyl Halides
6.15	253	Elimination Reactions of Alkyl Halides
6.15A	253	Dehydrohalogenation (loss of H-X)
6.15B	254	Bases Used in Dehydrohalogenation
6.15C	255	Mechanisms of Dehydrohalogenation: E2 and E1 Mechanisms

6.16	255	The Elimination-Bimolecular (E2) Reaction
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- 6.17 256 The Elimination-Unimolecular (E1) Reaction
- 6.18 257 Substitution versus Elimination
- 6.18A 257 S_N2 versus E2
- 6.18B 259 Tertiary Halides: S_N1 versus E1
- 6.19 260 Overall Summary
 - 260 Table 6.7: Overall Summary of $S_N 1$, $S_N 2$, E1 and E2 Reactions
 - 261 Summary and Review Tools
 - 262 Key Terms and Concepts

Problems:	In-Chapter	6.1 to 6.12
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- 252 End of Chapter 6.13 to 6.48
- 268 Learning Group Problems

Week of Feb 22: ALKENES AND ALKYNES I: Properties and Synthesis. Elimination Reactions of Alkyl Halides

	269	Cell Membrane Fluidity
7.1	270	Introduction
7.1A	270	Physical Properties of Alkenes and Alkynes
7.2	270	The (E) - (Z) System for Designating Alkene Diastereomers
7.3	272	Relative Stabilities of Alkenes
7.3A	272	Heat of Reaction
	272	Figure 7.2: Order of Stability of Alkenes from Heats of Hydrogenation
7.3B	273	Overall Relative Stabilities of Alkenes
7.4	274	Cycloalkenes
7.5	274	Synthesis of Alkenes via Elimination Reactions
7.6	275	Dehydrohalogenation of Alkyl Halides
7.6A	275	Zaitsev's Rule: Formation of the Most Substituted Alkene is Favoured with a Small Base
7.6B	277	Formation of the Less Substituted Alkene Using a Bulky Base
7.6C	278	The Stereochemistry of E2 Reactions: The Orientation of Groups in the Transition State
7.7	280	Acid-Catalyzed Dehydration of Alcohols
7.7A	281	Mechanism for Dehydration of Secondary and Tertiary Alcohols: An E1 Reaction
7.7B	282	Carbocation Stability and the Transition State
7.7C	284	A Mechanism for Dehydration of Primary Alcohols: An E2 Reaction
7.8	285	Carbocation Stability and the Occurrence of Molecular Rearrangements
7.8A	285	Rearrangements During Dehydration of Secondary Alcohols
7.8B	287	Rearrangement after Dehydration of a Primary Alcohol
7.9	288	Synthesis of Alkynes by Elimination Reactions:
		Dehydrohalogenation of vic-Dibromides
7.10	290	The Acidity of Terminal Alkynes
7.11	290	Replacement of the Acetylenic Hydrogen Atom of Terminal Alkynes
7.12	292	Alkylation of Alkynide Anions: Some General Principles of Structure and Reactivity Illustrated
7.13	292	Hydrogenation of Alkenes
	293	The Chemistry of Hydrogenation in the Food Industry
7.14	294	Hydrogenation: The Function of the Catalyst
7.14A	295	Syn and Anti Additions

- 7.15 297 Hydrogenation of Alkynes
- 7.15A 297 Syn Addition of Hydrogen: Synthesis of cis-Alkenes
- 7.15B 297 Anti Addition of Hydrogen: Synthesis of trans-Alkenes
- 7.16 298 An Introduction to organic Synthesis
- 7.16A 298 Why do Organic Synthesis?
- 7.16B 299 Retrosynthetic Analysis Planning an Organic Synthesis
- 7.16C 300 Identifying Precursors
- 302 The Chemistry of From the Inorganic to the Organic
- 7.16D 302 Raison d'Etre
 - 303 Summary and Review Tools
 - 304 Summary of Methods for the Preparation of Alkenes and Alkynes ;
 - 1. Dehydrohalogenation of Alkyl Halides (Section 7.6, p 275)
 - 2. Dehydration of Alcohols (Sections 7.7 & 7.8, p 280)
 - 3. Hydrogenation of Alkynes (Section 7.15, p 297)
 - (4. Dehydrohalogenation of vic-Dihalides x 2 (Section 7.9, p 288))
 - 305 Summary and Review Tools
 - 306 Key Terms and Concepts

Problems:	In-Chapter	7.1 to 7.17
306	End of Chapter	7.18 to 7.46
310	Learning Group Problems	

Week of Mar 1: ALKENES AND ALKYNES II: Addition Reactions.

- 311 The Sea: A Treasure of Biologically Active Natural Products
- 8.1 312 Introduction: Addition to Alkenes
- 8.1A 313 Understanding Additions to Alkenes
- 8.2 314 Electrophilic Addition of Hydrogen Halides to Alkenes:
- Mechanism and Markovnikov's Rule
- 8.2A 316 Theoretical Explanation of Markovnikov's Rule
- 8.2B 318 Modern Statement of Markovnokov's Rule
- 8.2C 319 Regioselective Reactions
- 8.2D 319 An Exception to Markovnikov's Rule
- 8.3 319 Stereochemistry of the Ionic Addition to an Alkene
- 8.4 320 Addition of Sulfuric Acid to Alkenes
- 8.4A 320 Alcohols from Alkyl Hydrogen Sulfates
- 8.5 321 Addition of Water to Alkenes: Acid Catalyzed Hydration
- 8.5A 321 Mechanism for Acid-Catalyzed Hydration
- 8.5B 322 Rearrangements
- 8.6 323 Alcohols from Alkenes through Oxymercuration-Demercuration: Markovnikov Addition
- 8.6A 323 Regioselectivity of Oxymercuration-Demercuration
- 8.6B 324 Rearrangements Seldom Occur in Oxymeercuration-Demercuration
- 8.6C 324 Mechanisms of Oxymercuration
- 8.7 326 Alcohols from Alkenes through Hydroboration-Oxidation: Anti-Markovnikov Syn Hydration

8.8	326	Hydroboration: Synthesis of Alkylboranes
8.8A	327	Mechanism of Hydroboration
8.8B	328	Stereochemistry of Hydroboration
8.9	329	Oxidation and Hydrolysis of Alkyl Boranes
8.9A	330	Regiochemistry and Stereochemistry of Alkyl Boranes:
		Oxidation and Hydrolysis
8.10	331	Summary of Alkene Hydration Methods
8.11	331	Proponolysis of Alkyl Boranes
8.12	332	Addition of Bromine and Chlorine to Alkenes
8.12A	333	Mechanism of Halogen Addition
8.13	334	Stereochemistry of the Addition of Halogens to Alkenes
8.13A	335	Stereospecific Reactions
8.14	337	Halohydrin Formation
8.15	338	Divalent Carbon Compounds: Carbenes
8.15A	339	Structure and Reactions of Methylene
8.15B	339	Reactions of Other Carbenes: Dihalocarbenes
8.15C	340	Carbenoids: The Simmons-Smith Cyclopropane Synthesis
8.16	340	Oxidation of Alkenes: Syn 1,2-Dihydroxylation
8.16A	341	Mechanisms for Syn Dihydroxylations of Alkenes
	342	The Chemistry of Catalytic Asymmetric Dihydroxylations
8.17	343	Oxidative Cleavage of Alkenes
8.17A	343	Cleavage with Hot Basic Potassium Permanganate
8.17B	344	Cleavage with Ozone
8.18	345	Addition of Bromine and Chlorine to Alkynes
8.19	346	Addition of Hydrogen Halides to Alkynes
8.20	347	Oxidative Cleavage of Alkynes
8.21	347	Synthetic Strategies Revisited, including:
		1. Construction of the Carbon Skeleton
		2. Functional Group Interconversions
		3. Control of Regiochemistry and
		4. Control of Stereochemistry
8.21A	347	Retroactive Analysis
8.21B	348	Disconnections, Synthons, and Synthetic Equivalents
8.21C	349	Stereochemical Considerations
	350	The Chemistry of Cholesterol Biosynthesis: Elegant and Familiar Reactions in Nature
	354	Summary and Review Tools:
	354	Mechanism Review: Summary of Alkene Addition Reactions
	355	Synthetic Connections of Alkynes and Alkenes: II
	356	Key Terms and Concepts
Proble	ms:	In-Chapter 8.1 to 8.26
	356	End of Chapter 8.27 to 8.68

361 Learning Group Problems.

Week of March 15: RADICAL REACTIONS

427	Radicals in Biology, Medicine, and Industry
10.1 428	Introduction
10.1A 428	Production of Radicals
10.1B 428	Reactions of Radicals
10.2 429	Homolytic Bond Dissociation Energies
10.2A 430	Homolytic Bond Dissociation Energies and Heats of Reaction
430	Table 10.1 Single-Bond Homolytic Dissociation Energies DH ^o at 25 ^o C
10.2B 431	Homolytic Bond Dissociation Energies and the Relative Stabilities of Radicals
10.3 433	The Reactions of Alkanes with Halogens
10.3A 433	Multiple Substitution Reactions versus Selectivity
10.4 435	Chlorination of Methane: Mechanism of Reaction
	1. Chain Initiation
	2. Chain Propagation
	3. Chain Termination
10.5 437	Chlorination of Methane: Energy Changes
10.5A 438	The Overall Free-Energy Change
10.5B 439	Activation Energies
10.5C 441	Reaction of Methane with other Halogens
10.6 443	Halogenation of Higher Alkanes
10.6A 445	Selectivity of Bromine, and Selectivity versus Reactivity
10.7 446	The Geometry of Alkyl Radicals
10.8 446	Reactions that Generate Tetrahedral Chirality Centres
10.8A 447	Generation of a Second Chirality Centre in a Radical Halogenation
10.9 449	Radical Addition to Alkenes:
	The Anti-Markovnikov Addition of Hydrogen Bromide
10.9A 450	Summary of Markovnikov versus Anti-Markovnikov Addition of HBr to Alkenes
10.10 451	Radical Polymerization of Alkenes: Chain Growth Polymers
451	Radical Polymerization of Ethene
453	Other Common Chain-Growth Polymers
10.11 455	Other Important Radical Reactions
10.11A 455	Molecular Oxygen and Super Oxide
10.11B 455	Nitric Oxide
10.11C 456	Combustion of Alkanes
10.11D 457	Autoxidation
458	The Chemistry of Antioxidants
459	The Chemistry of Ozone Depletion and Chlorofluorocarbons (CFCs)
460	Concept Map: Mechanism Review of Radical Reactions
461	Key Terms and Concepts
464	Special Topic A: Chain-Growth Polymers
Problems:	In-Chapter 10.1 to 10.22

Problems:	In-Chapter	10.1 to 10.22	
461	End of Chapter	10.23 to 10.34	

463 Learning Group Problems.

Week of March 22: ALCOHOLS AND ETHERS.

	469	Molecular Hosts
11.1	470	Structure and Nomenclature
11.1A		Nomenclature of Alcohols
11.1B		Nomenclature of Ethers
11.2	472	Physical Properties of Alcohols and Ethers
	473	Tables 11.1 and 11.2: Physical Properties of Ethers and Alcohols
11.3	474	Important Alcohols and Ethers
		Methanol, Ethanol, Ethylene Glycol, Diethyl Ether
11.4	476	Synthesis of Alcohols from Alkenes
	476	1. Acid-Catalyzed Hydration of Alkenes
	477	2. Oxymercuration-Demercuration
	477	3. Hydroboration-Oxidation
11.5	478	Reactions of Alcohols
11.6	479	Alcohols as Acids
11.7	480	Conversion of Alcohols into Alkyl Halides
11.8	480	Alkyl Halides from the Reactions of Alcohols with Hydrogen Halides
11.8A	481	Mechanisms of the Reactions of Alcohols with HX
11.9	483	Alkyl Halides from the Reactions of Alcohols with PBr ₃ or SOCl ₂
11.10	484	Tosylates, Mesylates and Triflates:
		Leaving Group Derivatives of Alcohols
	487	The Chemistry of Alkyl Phosphates
11.11		Synthesis of Ethers
11.11A		Ethers by Intermolecular Dehydration of Alcohols
11.11E		The Williamson Synthesis of Ethers
11.110		Synthesis of Ethers by Alkoxymercuration-Demercuration
11.11		tert-Butyl Ethers by Alkylation of Alcohols: Protecting Groups
11.11E		Silyl Ether Protecting Groups
11.12	482	Reactions of Ethers: Ether Cleavage by Strong Acids
11.13	493	Epoxides
11.13A		Synthesis of Epoxides: Epoxidation of Alkenes
11.13E		Stereochemistry of Epoxidation
11 14	494	The Chemistry of The Sharpless Asymmetric Epoxidation
11.14	496	Reactions of Epoxides:
		1. Acid Catalyzed Ring Opening
	498	2. Base Catalyzed Ring Opening The Chemistry of Epoxides, Carcinogens, and Biological Oxidation
11.14A		Polyethers from Epoxides
11.14	500	Anti 1,2-Dihydroxylation of Alkenes via Epoxides
11.15	502	The Chemistry of Environmentally Friendly Alkene Oxidation Methods
11.16	502	Crown Ethers: Nucleophilic Substitution Reactions in Relatively Nonpolar Aprotic Solvents by
11.10	505	Phase-Transfer Catalysis
11.16A	504	Crown Ethers
11.10/ 11.16E		Transport Antibiotics and Crown Ethers
11.101		Summary of Reactions of Alkenes, Alcohols and Ethers
11.17 <i>A</i>		Alkenes in Synthesis
11.171	507	Key Terms and Concepts.
	508	Summary and Review Tool: Some Synthetic Connections of
	200	Alkynes, Alcohols, Alkyl Halides and Ethers
Proble	ms:	In-Chapter 11.1 to 11.24
	509	End of Chapter 11.25 to 11.51

Week of March 29: ALCOHOLS FROM CARBONYL COMPOUNDS: OXIDATION-REDUCTION AND ORGANOMETALLIC COMPOUNDS.

Read and Study Chapter 12

- The Two Aspects of the Coenzyme NADH 513 12.1 514 Introduction 12.1A 514 Structure of the Carbonyl Group Reactions of Carbonyl Compounds with Nucleophiles 12.1B 515 12.2 515 **Oxidation-Reduction Reactions in Organic Chemistry** Oxidation States of Organic Chemistry 12.2A 516 Alcohols by Reduction of Carbonyl Compounds 12.3 517 12.3A 517 Lithium Aluminum Hydride Reductions of Carbonyl Compounds Sodium Borohydride Reductions of Carbonyl Compounds 12.3B 518 Overall Summary of LiAlH₄ and NaBH₄ Reactivity 12.3C 519 519 The Chemistry of Alcohol Dehydrogenase 520 The Chemistry of Stereoselective Reductions of Carbonyl Groups 521 12.4 **Oxidation of Alcohols** 12.4A 521 Oxidation of Primary Alcohols to Aldehydes: RCH₂OH to RCHO 12.4B 522 Oxidation of Primary Alcohols to Carboxylic Acids: RCH₂OH to RCO₂H 12.4C 522 Oxidation of Secondary Alcohols to Ketones: RCH(OH)R' to RCOR' 12.4D 523 Mechanism of Chromate Oxidations 12.4E 525 A Chemical Test for Primary and Secondary Alcohols 12.4F 525 Spectroscopic Evidence for Alcohols 12.5 526 Organometallic Compounds Preparation of Organo Lithium and Organo Magnesium Compounds 12.6 526 Organolithium Compounds 12.6A 526 **Grignard Reagents** 12.6B 527 Reactions of Organolithium and Organomagnesium Compounds 12.7 528 12.7A 528 Reactions with Compounds Containing Acidic Hydrogen Atoms 12.7B 529 Reactions of Grignard Reagents with Oxiranes (Epoxides) 12.7C 530 Reactions of Grignard Reagents with Carbonyl Compounds Alcohols from Grignard Reagents: Reaction of Grignard Reagents with: 12.8 531 Formaldehyde to Give Primary Alcohols 1. 2. Other Aldehydes to Give Secondary Alcohols 3. Ketones to Give Tertiary Alcohols Esters with 2 x RMgX to Give Tertiary Alcohols 4. 12.8A 532 Planning a Grignard Synthesis 12.8B 536 **Restrictions on the Use of Grignard Reagents** The Use of Lithium Reagents 12.8C 537 12.8D 537 The Use of Sodium Alkynides **Protecting Groups** 12.9 539 540 Summary of Reactions Synthetic Connections of Alcohols and Carbonyl Compounds 541
 - 541 Key Terms and Concepts

Problems: In-Chapter 12.1 to 12.10

- 542 End of Chapter 12.11 to 12.29
- 545 Learning Group Problems.
- 546 First Review Problem Set 1 to 25.

Week of April 5: CONJUGATED UNSATURATED SYSTEMS.

Read and Study Chapter 13.

	550	Molecules With the Nobel Prize in Their Synthetic Lineage
	551	Introduction
	551	Allylic Substitution and the Allyl Radical
13.2A	552	Allylic Chlorination (High Temperature)
13.2B	554	Allylic Bromination with N-Bromosuccinimide (Low Conc. of Br ₂)
13.3	555	The Stability of the Allyl Radical
13.3A	555	Molecular Orbital Description of the Allyl Radical
13.3B	557	Resonance Description of the Allyl radical
13.4	558	The Allyl Carbocation
13.5	559	Summary of Rules for Resonance
13.5A	560	Rules for Writing Resonance Structures
13.5B	561	Estimating the Relative Stability of Resonance Structures
13.6	563	Alkadienes and Polyunsaturated Hydrocarbons
13.7	564	1,3-Butadiene: Electron Delocalization
13.7A :	564	Bond Lengths of 1,3-Bitadiene
13.7B	565	Conformations of 1,3-Butadiene, s-cis and s-trans
13.7C	565	Molecular Orbitals of 1,3-Butadiene
13.8	566	The Stability of Conjugated Dienes
13.9	568	Ultraviolet-Visible Spectroscopy
13.9A	568	The Electromagnetic Spectrum
13.9B	569	UV-Vis Spectrophotometers
13.9C	571	Absorption Maxima for Nonconjugated and Conjugated Dienes
:	573	The Chemistry of The Photochemistry of Vision
13.9D	576	Analytical Uses of UV-Vis Spectroscopy
13.10	576	Electrophilic Attack on Conjugated Dienes: 1,4-Electrophilic Addition
13.10A	578	Kinetic Control versus Thermodynamic Control of a Chemical Reaction
13.11	580	The Diels-Alder Reaction: 1,4-Cycloaddition of Dienes
13.11A	581	Factors Favoring the Diels-Alder Reaction
13.11B	582	Stereochemistry of the Diels-Alder Reaction
13.11C	584	Molecular Orbital Considerations That Favor an Endo Transition State
	586	The Chemistry of Asymmetric and Intramolecular Diels-Alder Reactions
	588	Concept Map
	589	Key Terms and Concepts.
Problem	ns:	In-Chapter 13.1 to 13.15
:	589	End of Chapter 13.16 to 13.46
:	594	Learning Group Problems.

April 12: Review Class, e.g. review of a Practice Final Exam.

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