

GRANDE PRAIRIE REGIONAL COLLEGE

Department of Science

Discipline of Chemistry

Thirty-Ninth Session 2004 - 2005

CHEMISTRY 1610 A3: Organic Chemistry I

PREREQUISITE: Chemistry 30 or equivalent

INSTRUCTOR: Dr. John P. Sloan
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LECTURE: CH1610 A3 T, R 1:00 - 2:20 in J229

ALBERTA TRANSFER CREDIT for CH1610 plus CH1630:

U of Alberta:	CHEM 161/163	6 credits
U of Calgary:	CHEM 351/353	6 credits
U of Lethbridge:	CHEM 2100/2200	6 credits
Athabasca U:	CHEM 2xx/2xx	6 credits
Augustana U Col:	CHE 1xx/1xx	6 credits
Concordia Col:	CH 161/163	6 credits
The King's U Col:	CHEM 2xx/2xx	6 credits
Canadian Univ. C:	CHEM 1xx/1xx	8 credits

COURSE OUTLINE:

Lecture Component:

A study of the fundamental principles of the chemistry of carbon compounds. The study is based on a reaction mechanism approach to the functional group chemistry of alkanes, alkenes, alkynes, cycloalkanes, alkyl halides, alcohols and ethers. Topics include: structure and bonding; physical properties; acidity and basicity; conformations of molecules; stereochemistry; addition, elimination and substitution reactions; structure-reactivity relationships; and introduction to methods for structure determination.

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

Laboratory Component:

Laboratory 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 tests/assignments will be given and marked.

Notes:

1. Lectures, Time and Place
CH1610 A3 T, R 1:00 - 2:20 in J229
2. Laboratory Component, Time and Place
CH1610 L1 M, 14:30 - 17:20 in J119
3. Tutorial Component, Time and Place
CH1610 S1 F, 11:30/12:00 – 12:50 in L123

TEXT BOOKS AND LABORATORY ITEMS:

The following books are required:

1. Solomons, T.W.G., and C.B. Fryhle, *Organic Chemistry*, 8th Edition, Wiley, 2004;
2. A Three Ring Binder to Hold: Sloan, J.P., *Organic Chemistry Experiments, Chemistry 1610/1630*, Grande Prairie Regional College, 2004/2005.

The following is highly recommended:

3. Molecular Model Set for Organic Chemistry, Prentice Hall.

The following is a supplementary item:

1. Fernandez, J.E., and Solomons, T.W.G., *Study Guide and Solutions Manual to Organic Chemistry*, 8th Edition, 2004;

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.

LABORATORY FEE:

A laboratory Fee in the amount of \$30.00 is payable to the cashiers office prior to commencement of the first organic chemistry lab. The fee is levied as an initial payment to cover the replacement cost of glassware and equipment items broken by the student. In the event of replacement costs of broken items being less than \$30.00, the balance of the deposit will be returnable to the student. In the event of breakage costs being greater than \$30.00, an equitable surcharge will be assessed and levied on the student.

EVALUATION:

Examination Schedule and Composition of the Final Grade:

- | | | | |
|----|---|-------|------|
| 1. | Midterm Exam, Friday October 29 | ----- | 25% |
| 2. | Final Exam to be scheduled between December 13 - 21 | ----- | 40% |
| 3. | Laboratory | ----- | 25% |
| 4. | Tutorial Grading Component | ----- | 10% |
| | | | 100% |

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

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

Notes:

- The Mid-Term exam will be of 2 hours duration and the Final Exam will be of 3 hours duration.
- Between 5 and 15% of exam content will be taken directly from weekly Tests/Assignments.

3. A pass grade is essential for the Laboratory Component.
4. The Tutorial Grading Component consists of tests/assignments and will contribute towards 10% of the final grade. A 10 question test/assignment will normally be given each week. To encourage general discussion and active student participation, test/assignment questions may be answered within "paired teams". Tests/assignments not completed during the tutorial period are due within 24 hours without penalty, or later at the discretion of the Instructor.
The marking scheme is:
 - 4.1 1 mark per correct answer with full details;
 - 4.2 ½ mark per correct answer with incomplete details;
 - 4.3 20% shall be deducted from the mark for each college business day that a test is overdue.
5. Regular attendance in Lecture, Laboratory, and Tutorial Components is a Course Requirement.

Grande Prairie Regional College Calendar 2004 - 2005: Course Description (p 165).

CH1610 3(3-1-3)UT, 105 Hours, Organic Chemistry I

A study of the fundamental principles of the chemistry of carbon compounds based on a reaction mechanism approach to the functional group chemistry of alkanes, alkenes, alkynes, cycloalkanes, alkyl halides, alcohols and ethers. Topics include structure and bonding; physical properties; acidity and basicity; conformations of molecules; stereochemistry; addition, elimination and substitution reactions; structure-reactivity relationships; and introduction to methods of structure determination. Examples of organic molecules found in agricultural, biological, environmental, industrial, medical and pharmaceutical applications of organic chemistry will be discussed., e.g., molecules found in agrochemicals, fibres, food, perfumes, polymers, and prescription drugs.

Prerequisite: Chemistry 30 or equivalent.

Note: Students with credit in CH 1010 and 1020 normally will proceed to CH2610. Such students may enrol in CH1610 only in consultation with an advisor and with written consent of the department chairperson.

Transfer: UA, UC, UL, UA*, CU, CUC, KUC*, AUC*

CHEMISTRY 1610
READING, STUDYING, AND PRACTICE PROBLEMS

All references are to T.W.G. Solomons and C.B. Fryhle, *Organic Chemistry*, 8th Edition Upgrade, Wiley, 2004.

FALL SEMESTER

Weeks of

Jan 3 & 10: CARBON COMPOUNDS AND CHEMICAL BONDS.

Sect #	Page #	Read and Study Chapter 1 "We are Star Dust"
	1	Life is Organic Chemistry
1.1	2	Introduction
1.2	3	The Development of Organic Chemistry as a Science
1.3	4	The Structural Theory of Organic Chemistry
1.4	6	Chemical Bonds and the Octet Rule
1.5	8	Writing Lewis Structures
1.6	10	Exceptions to the Octet Rule
1.7	12	Formal Charge
1.8	14	Resonance Theory
1.8A	16	Summary of Rules for Resonance
1.9	19	Quantum Mechanics
1.10	20	Atomic Orbitals of Electron Probability Densities: the Aufbau Principle; the Pauli Exclusion Principle; Hund's Rule
1.11	22	Molecular Orbitals: Bonding and Antibonding
1.12	25	The Structure of Methane and Ethane: sp^3 Hybridization;
1.12A	25	The Structure of Methane
1.12B	28	The Structure of Ethane
1.13	28	The Structure of Ethene (Ethylene): sp^2 Hybridization
1.13A	32	Restricted Rotation and the Double Bond
1.13B	33	Cis-Trans Isomers
1.14	34	The Structure of Ethyne (Acetylene): sp Hybridization
1.14A	35	Bond Lengths of Ethyne, Ethene, and Ethane
1.15	36	A Summary of Important Concepts that Come from Quantum Mechanics
1.16	38	Molecular Geometry: The Valence Shell Electron-Pair Repulsion (VSEPR) Model.
1.16A-F	38	Molecular Geometry: VSEPR Models for Methane, Ammonia, Water, Boron Trifluoride, Beryllium Hydride and Carbon Dioxide
1.17	41	Representation of Structural Formulas: Dash; Condensed; Cyclic Molecules; Bond Line; and the Three Dimensional Wedge, Dash, Line Representation
	46	Key Terms and Concepts
	47	Concept Map

Practice Problems: You are encouraged to work all of the in-chapter problems, and you are required to work all of the assigned weekly test problems. 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.”

Problems:	In-Chapter	1.1 to 1.16
48	End of Chapter	1.17 to 1.39
51	Learning Group Problem	

Week of Jan 17: REPRESENTATIVE CARBON COMPOUNDS: Functional Groups, Intermolecular Forces, and Infrared (IR) Spectroscopy

		Read and Study Chapter 2
	52	Structure and Function: Organic Chemistry, Nanotechnology, and Bioengineering
2.1	53	Carbon-Carbon Covalent Bonds
2.2	53	Hydrocarbons: Representative, Alkanes, Alkenes, Alkynes, and Aromatic Compounds
2.3	56	Polar Covalent Bonds
2.4	59	Polar and Nonpolar Molecules
2.4A	61	Dipole Moments in Alkenes
2.5	61	Functional Groups
2.5A	62	Alkyl Groups and the Symbol R
2.5B	62	Phenyl and benzyl Groups
2.6	63	Alkyl Halides or Haloalkanes
2.7	63	Alcohols, including Classification as Primary, Secondary and Tertiary (1E, 2E, 3E)
2.8	65	Ethers
2.9	66	Amines, including classification as Primary, Secondary and Tertiary
2.10	67	Aldehydes and Ketones
2.11	68	Carboxylic Acids, Esters, and Amides
2.12	69	Nitriles
2.13	70	Summary of Important Families of Organic Compounds
2.14	70	Physical Properties and Molecular Structure with emphasis on Intermolecular Interactions, namely
2.14A	71	Ion-Ion Forces in ionic compounds, e.g. sodium acetate, sodium chloride
2.14B	72	Dipole-Dipole Forces resulting from permanent dipoles, e.g. acetone, chloromethane
2.14C	73	Hydrogen Bonds
2.14D	74	van der Waals Forces, or London forces or dispersion forces, e.g. methane

2.14E	76	Solubilities
2.14F	77	Guidelines for Water Solubility
2.14G	77	Intermolecular Forces in Biochemistry, and Organic templates Engineered to Mimic Bone Growth
2.15	78	Summary of Attractive Electrical Forces
2.16	79	Infrared Spectroscopy: An Instrumental Method for Detecting Functional Groups
2.16A	84	Hydrocarbons
2.16B	86	Other Functional Groups, including Carbonyl Functional Groups of Aldehydes, Ketones, Esters, Carboxylic Acids and Amides, plus Alcohols, Phenols and Amines
	88	Key Terms and Concepts
	89	Concept Map
Problems:	In-Chapter	2.1 to 2.19
	90	End of Chapter 2.20 to 2.48
	93	Learning Group Problem

**Week of Jan 24: AN INTRODUCTION TO ORGANIC REACTIONS:
ACIDS AND BASES IN ORGANIC CHEMISTRY**

		Read and Study Chapter 3
	94	Shuttling the Protons, or, from the Lewis and Sloan perspective, Shuttling the Electrons
3.1	95	Reactions and their Mechanisms - Substitution, Addition, Elimination and Rearrangement Reactions
3.1A	96	Homolysis and Heterolysis of Covalent Bonds, and Introduction to the Use of Curved Arrows
3.2	97	Acids and Bases
3.2A	97	The Brønsted-Lowry Definition of Acids and Bases
3.2B	99	The Lewis Definition of Acids and Bases
3.2C	100	Opposite Charges Attract
	101	The Chemistry of ... HOMOs and LUMOs in Reactions
3.3	101	Heterolysis of Bonds to Carbon - Carbocations and Carbanions
3.4	102	The Use of Curved Arrows in Illustrating Reactions
3.5	104	The Strength of Acids and Bases, K_a and pK_a
3.5A	104	The Acidity Constant, K_a
3.5B	104	Acidity and pK_a
	105	Table 3.1: Relative Strength of Selected Acids and Their Conjugate Bases
3.5C	106	Predicting the Strength of Bases the Stronger the Acid, the Weaker the Conjugate Base
3.6	107	Predicting the Outcome of Acid-Base Reactions
3.6A	108	Water Solubility as a Result of Salt Formation

3.7	109	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;
		2. Electronegativity Effect, acidity increases from left to right in the Periodic Table, H-F is a stronger acid than CH ₄ .
3.7A	111	3. The Effect of Hybridization, more s-character means the anion has lower energy, is more stable, and is a weaker base
3.7B	112	4. Inductive Effects, from polarization by electron attracting and electron withdrawing groups
3.8	113	Energy Changes; higher potential and kinetic energy implies less stable, lower energy implies more stable
3.8A	114	Potential Energy and Covalent Bonds, exothermic reactions give out heat, endothermic reactions absorb heat
3.9	114	The Relationship Between the Equilibrium Constant and the Standard Free-Energy Change, ΔG° ; a negative value favours products at equilibrium
3.10	115	The Acidity of Carboxylic Acids, with explanations arising from Resonance Effects and Inductive Effects
3.10A	116	5. An Explanation based on Resonance Effects, due to resonance stabilization of the carboxylate anion
3.10B	117	An Explanation based on Inductive Effects, due to inductive withdrawal of electronic charge by -O and -C=O in carboxylate anions
3.10C	119	Inductive Effects of Other Groups
3.11	120	The Effect of Solvent on Acidity - Protic Solvents
3.12	121	Organic Compounds as Bases
3.13	122	A Mechanism for an Organic Reaction
	124	The Chemistry of carbonic Anhydrase
3.14	124	Acid and Base in Nonaqueous Solutions
3.15	126	Acid-Base Reactions, and Synthesis of Deuterium- and Tritium-Labelled Compounds
	127	Key Terms and Concepts
	128	Concept Map
Problems:	In-Chapter	3.1 to 3.14
	129	End of Chapter 3.15 to 3.42
	132	Learning Group Problem

Week of Jan 31: ALKANES AND CYCLOALKANES: Nomenclature, Conformational Analysis, and an Introduction to Synthesis

Read and Study Chapter 4

	134	To be Flexible or Inflexible - Molecular Structure Makes the Difference
4.1	135	Introduction to Alkanes and Cycloalkanes

4.1A	135	Sources of Alkanes: Petroleum
4.1B	135	Petroleum Refining
4.1C	136	Cracking
	136	Table 4.1: Typical Fractions Obtained by Distillation of Petroleum
4.2	137	Shapes of Alkanes
	139	Tables 4.1: Physical Constants of Hexane Isomers
	139	Table 4.2: Number of Alkane Isomers
4.3	139	IUPAC Nomenclature of Alkanes, Alkyl Halides and Alcohols
4.3A	141	Nomenclature of Unbranched Alkyl Groups
4.3B	141	Nomenclature of Branched Chain Alkanes
4.3C	143	Nomenclature of Branched Alkyl Groups
4.3D	145	Classification of Hydrogen Atoms, as Primary (1°), Secondary (2°), and Tertiary (3°)
4.3E	145	Nomenclature of Alkyl Halides
4.3F	146	Nomenclature of Alcohols
4.4	147	Nomenclature of Cycloalkanes
4.4A	147	Monocyclic Compounds
4.4B	148	Bicyclic Compounds
4.5	150	Nomenclature of Alkenes and Cycloalkenes
4.6	152	Nomenclature of Alkynes
4.7	152	Physical Properties of Alkanes and Cycloalkanes
4.8	154	Sigma (Φ) Bonds and Bond Rotation
4.9	157	Conformational Analysis of Butane
4.10	159	The Relative Stability of Cycloalkanes: Ring Strain
4.10A	159	Heats of Combustion
4.10B	160	Heats of Combustion of Cycloalkanes
	161	Table 4.6: Heats of Combustion and Ring Strain of Cycloalkanes
4.11	162	The origin of Ring Strain in Cyclopropane and Cyclobutane: Angle Strain and Torsional Strain
4.11A	163	Cyclopentane
4.12	163	Conformations of Cyclohexane
4.12A	165	Conformations of Higher Cycloalkanes
	166	The Chemistry of Motors and Molecular Switches
4.13	167	Substituted Cyclohexanes, Axial and Equatorial Hydrogen Atoms
4.14	171	Disubstituted Cyclohexanes, Cis-Trans Isomerism
4.14A	172	Cis-Trans Isomerism and Conformational Structures
4.15	175	Bicyclic and Polycyclic Alkanes
	177	The Chemistry of Pheromones: Communication by Means of Chemicals
4.16	177	Chemical Reactions of Alkanes
4.17	178	Synthesis of Alkanes and Cycloalkanes
4.17A	178	Hydrogenation of Alkenes and Alkynes
4.17B	179	Reduction of Alkyl Halides
4.17C	179	Alkylation of Terminal Alkynes
4.18	180	Some General Principles of Structure and Reactivity: A Look Towards Synthesis, Introduction to the Terms Nucleophile and Electrophile
4.19	181	An Introduction to Organic Synthesis

4.19A	182	Retrosynthetic Analysis – Planning an Organic Synthesis
4.19B	183	Identifying Precursors
	185	The Chemistry of --- From the Inorganic to the Organic
4.19C	185	Raison d’Etre --- solving synthetic puzzles by application of retroactive synthesis is one of the joys of learning organic chemistry
	185	Key Terms and Concepts
	187/188	Concept Maps
Problems:	In-Chapter	4.1 to 4.18
	186	End of Chapter 4.19 to 4.56
	192	Learning Group Problems

Week of Feb 7: STEREOCHEMISTRY: CHIRAL MOLECULES

Read and Study Chapter 5

	193	The Handedness of Life
5.1	194	The Biological Significance of Chirality
5.2	195	Isomerism, Constitutional Isomers and Stereoisomers
5.3	196	Enantiomers and Chiral Molecules
5.4	200	More about the Biological Importance of Chirality
5.5	201	The Historical Origin of Stereochemistry
5.6	202	Tests for Chirality, Planes of Symmetry and Points of Symmetry
5.7	203	Nomenclature of Enantiomers, the R-S System
5.8	208	Properties of Enantiomers, Optical Activity
5.8A	209	Plane-Polarized Light
5.8B	209	The Polarimeter
5.8C	210	Specific Rotation
5.9	212	The Origin of Optical Activity
5.9A	213	Racemic Forms
5.9B	214	Racemic Forms and Enantiomeric Excess
5.10	215	The Synthesis of Chiral Molecules
5.10A	215	Racemic Forms
5.10B	216	Stereoselective Synthesis
5.11	217	Chiral Drugs
	218	The Chemistry of ... Selective Binding of Drug Enantiomers to Left- and Right-Hand Coiled DNA
5.12	219	Molecules with More Than One Stereocentre
5.12A	220	Meso Compounds
5.12B	222	Naming Compounds with More than One Stereogenic Carbon
5.13	223	Fischer Projection Formulas
5.14	224	Stereoisomerism of Cyclic Compounds
5.14A	225	Cyclohexane Derivatives
5.15	227	Relating Configurations Through Reactions in Which No Bonds to the Stereogenic are Broken

5.15A	228	Relative and Absolute Configurations
5.16	230	Separation of Enantiomers: Resolution
5.16A	230	Pasteur's Method for Separating Enantiomers
5.16B	231	Current Methods for Resolution of Enantiomers
5.17	231	Compounds with Stereogenic Centres Other than Carbon
5.18	231	Chiral Molecules that do not Possess a Tetrahedral Atom with Four Different Groups
	233	Key Terms and Concepts
	234	Concept Map

Problems:	In-Chapter	5.1 to 5.29
	235	End of Chapter 5.30 to 5.45
	237	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 14: IONIC REACTIONS: NUCLEOPHILIC SUBSTITUTION AND ELIMINATION REACTIONS of ALKYL HALIDES

Read and Study Chapter 6

	238	Breaking Bacteria Cell Walls With Organic Chemistry
6.1	239	Introduction
	239	Table 6.1: Carbon-Halogen Bond lengths and Bond Strengths
6.1A	240	Physical Properties of Organic Halides
	240	Table 6.2: Organic Halides
6.2	241	Nucleophilic Substitution Reactions
6.3	241	Nucleophiles
6.4	242	Leaving Groups
6.5	243	Kinetics of a Nucleophilic Substitution Reaction - a Substitution Nucleophilic Bimolecular, S_N2 , Reaction
6.6	244	A Mechanism for the S_N2 Reaction
6.7	245	Transition State Theory - Free-Energy Diagrams
6.8	249	The Stereochemistry of S_N2 Reactions
6.9	251	The Reaction of Tert-Butyl Chloride with Hydroxide Ion - an S_N1 Reaction
6.9A	252	Multistep Reactions and the Rate determining Step
6.10	252	A Mechanism for the S_N1 Reaction
6.11	254	Carbocations
6.11A	254	The Structure of Carbocations
6.11B	255	The Relative Stabilities of Carbocations
6.12	256	The Stereochemistry of S_N1 Reactions
6.12A	256	Reactions That Involve Racemization
6.12B	257	Solvolysis – Cleavage of the Solvent by the Nucleophile

6.13	258	Factor's Affecting the Rates of S_N1 and S_N2 Reactions
6.13A	258	The Effect of the Structure of the Substrate
	259	Table 6.4: Relative Rates of Reactions of Alkyl Halides in S_N2 Reactions
	260	S_N1 Reactions and the Hammond-Leffler Postulate
6.13B	261	The Effect of the Concentration and the Strength of the Nucleophile
	262	Nucleophilicity versus Basicity
6.13C	262	Solvent Effects on S_N2 Reactions: Polar Protic and Aprotic Solvents
6.13D	264	Solvent Effects on S_N1 Reactions: The Ionizing Ability of the Solvent
	265	Table 6.5: Dielectric Constants of Common Solvents
6.13E	265	The Nature of the Leaving Group
6.13F	267	Summary: S_N1 versus S_N2
	267	Table 6.6: Factors Favouring S_N1 versus S_N2 Reactions
6.14	267	Organic Synthesis - Functional Group Transformations Using S_N2 Reactions
	268	The Chemistry of ... Biological Methylation: A Biological Nucleophilic Substitution Reaction
6.14A	270	The Unreactivity of Vinylic and Phenyl Halides
6.15	271	Elimination Reactions of Alkyl Halides
6.15A	271	Dehydrohalogenation (loss of H-X)
6.15B	272	Bases Used in Dehydrohalogenation
6.15C	273	Mechanisms in Dehydrohalogenation: E2 and E1 Mechanisms
6.16	273	The Elimination-Bimolecular, E2, Reaction
6.17	274	The Elimination-Unimolecular, E1, Reaction
6.18	275	Substitution versus Elimination
6.18A	275	S_N2 versus E2
6.18B	277	Tertiary Halides: S_N1 versus E1
6.19	278	Overall Summary
	278	Table 6.7: Overall Summary of S_N1 , S_N2 , E1 and E2 Reactions
	279	Summary and Review Tools
	280	Key Terms and Concepts
Problems:		In-Chapter 6.1 to 6.12
	280	End of Chapter 6.13 to 6.49
	286	Learning Group Problems

**Week of Feb 28: ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS.
Elimination Reactions of Alkyl Halides**

Read and Study Chapter 7

	287	Cell Membrane Fluidity
7.1	288	Introduction
7.1A	288	Physical Properties of Alkenes and Alkynes
7.2	288	The (E) - (Z) System for Designating Alkene Diastereomers
7.3	290	Relative Stabilities of Alkenes

7.3A	290	Heat of Reaction
	290	Figure 7.2: Order of Stability of Alkenes from Heats of Hydrogenation
7.3B	291	Overall Relative Stabilities of Alkenes
7.4	292	Cycloalkenes
7.5	292	Synthesis of Alkenes via Elimination Reactions
7.6	293	Dehydrohalogenation of Alkyl Halides
7.6A	293	Zaitsev's Rule: Formation of the Most Substituted Alkene is Favoured with a Small Base
7.6B	295	Formation of the least Substituted Alkene Using a Bulky Base
7.6C	296	The Stereochemistry of E2 Reactions: The Orientation of Groups in the Transition State
7.7	298	Acid-Catalyzed Dehydration of Alcohols
7.7A	299	Mechanism for Dehydration of Secondary and Tertiary Alcohols: An E1 Reaction
7.7B	300	Carbocation Stability and the Transition State
7.7C	302	A Mechanism for Dehydration of Primary Alcohols: An E2 Reaction
7.8	303	Carbocation Stability and the Occurrence of Molecular Rearrangements
7.8A	303	Rearrangements During Dehydration of Secondary Alcohols
7.8B	305	Rearrangement after Dehydration of a Primary Alcohol
7.9	307	Synthesis of Alkynes by Elimination Reactions: Dehydrohalogenation of vic-Dibromides
7.10	308	The Acidity of Terminal Alkynes
7.11	309	Replacement of the Acetylenic Hydrogen Atom of Terminal Alkynes
7.12	310	Hydrogenation of Alkenes
	311	The Chemistry of --- Hydrogenation in the Food Industry
7.13	312	Hydrogenation: The Function of the Catalyst
7.13A	313	Syn and Anti Additions
	313	The Chemistry of --- Homogeneous Asymmetric Catalytic Hydrogenation: Examples Involving L-DOPA, (S)-Naproxen, and Aspartame
7.14	315	Hydrogenation of Alkynes
7.14A	315	Syn Addition of Hydrogen: Synthesis of cis-Alkenes
7.14B	316	Anti Addition of Hydrogen: Synthesis of trans-Alkenes
7.15	317	Structural Information from Molecular Formulas and the, Index of Hydrogen Deficiency
7.15A	317	Unsaturated and Cyclic Compounds
7.15B	318	Compounds Containing Halogens, Oxygen, or Nitrogen
	320	Summary and Review Tools
	321	Summary of Methods for the Preparation of Alkenes and Alkynes ;
		1. Dehydrohalogenation of Alkyl Halides (Section 7.6, p 293)
		2. Dehydration of Alcohols (Sections 7.7 and 7.8, p 298)
		3. Hydrogenation of Alkynes (Section 7.14, p 315)
		(4. Dehydrohalogenation of vic-Dihalides x 2 (Section 7.9, p 307))
	322	Summary and Review Tools
	323	Key Terms and Concepts
Problems:	In-Chapter	7.1 to 7.17

- 323 End of Chapter 7.18 to 7.46
 326 Learning Group Problems

Week of Mar 7: ALKENES AND ALKYNES II: ADDITION REACTIONS.

Read and Study Chapter 8.

- 328 The Sea: A Treasure of Biologically Active Natural Products
 8.1 329 Introduction: Addition to Alkenes
 8.2 331 Addition of Hydrogen Halides to Alkenes: Markovnikov's Rule
 8.2A 333 Theoretical Explanation of Markovnikov's Rule
 8.2B 335 Modern Statement of Markovnikov's Rule
 8.2C 336 Regioselective Reactions
 8.2D 336 An Exception to Markovnikov's Rule
 8.3 336 Stereochemistry of the Ionic Addition to an Alkene
 8.4 337 Addition of Sulfuric Acid to Alkenes
 8.4A 337 Alcohols from Alkyl Hydrogen Sulfates
 8.5 338 Addition of Water to Alkenes, Acid Catalyzed Hydration
 8.6 340 Alcohols from Alkenes through Oxymercuration-Demercuration:
 Markovnikov Addition
 8.7 343 Alcohols from Alkenes through Hydroboration-Oxidation:
 Anti-Markovnikov Syn Hydration
 8.8 343 Hydroboration: Synthesis of Alkylboranes
 8.8A 344 Mechanism of Hydroboration
 8.9 346 Oxidation and Hydrolysis of Alkyl Boranes
 8.9A 347 Regiochemistry and Stereochemistry of Alkyl Boranes:
 Oxidation and Hydrolysis
 8.10 348 Summary of Alkene Hydration Methods
 8.11 348 Propanolysis of Alkyl Boranes
 8.12 349 Addition of Bromine and Chlorine to Alkenes
 8.12A 350 Mechanism of Halogen Addition
 8.13 351 Stereochemistry of the Addition of Halogens to Alkenes
 8.13A 352 Stereospecific Reactions
 8.14 354 Halohydrin Formation
 355 Chemistry of --- Regiospecificity in Unsymmetrically Substituted
 Bromonium Ions: Bromonium Ions of Ethene, Propene, and 2-
 Methylpropene
 8.15 357 Divalent Carbon Compounds: Carbenes
 8.15A 358 Structure and Reactions of Methylene
 8.15B 358 Reactions of Other Carbenes: Dihalocarbenes
 8.15C 359 Carbenoids: The Simmons-Smith Cyclopropane Synthesis
 8.16 359 Oxidation of Alkenes: Syn 1,2-Dihydroxylation
 8.16A 360 Mechanisms for Syn Dihydroxylations of Alkenes
 361 The Chemistry of --- Catalytic Asymmetric Dihydroxylations
 8.17A 364 Ozonolysis of Alkenes

8.18	365	Addition of Bromine and Chlorine to Alkynes
8.19	366	Addition of Hydrogen Halides to Alkynes
8.20	367	Oxidative Cleavage of Alkynes
8.21	367	Synthetic Strategies Revisited, including:
		1. Construction of the Carbon Skeleton
		2. Functional Group Interconversions
		3. Control of Regiochemistry and
		4. Control of Stereochemistry
	370	The Chemistry of ... Cholesterol Biosynthesis: Elegant and Familiar Reactions in Nature
	374	Summary and Review Tools: Mechanism Review: Summary of Alkene Addition Reactions
	375	Summary and Review Tools: Synthetic Connections of Alkynes and Alkenes: II
	376	Key Terms and Concepts
Problems:	In-Chapter	8.1 to 8.26
	376	End of Chapter 8.21 to 8.68
	381	Learning Group Problems.

Week of Mar 14: RADICAL REACTIONS

Read and Study Chapter 10

	447	Calicheamicin gamma ₁ ¹ : A Radical Device for Slicing the Backbone of DNA
10.1	449	Introduction
10.1A	449	Production of Radicals
10.1B	449	Reactions of Radicals
	450	The Chemistry of ... Radicals in Biology, Medicine, and Industry.
10.2	450	Homolytic Bond Dissociation Energies
10.2A	451	Homolytic Bond Dissociation Energies and Heats of Reaction
	452	Table 10.1 Single-Bond Homolytic Dissociation Energies DH° at 25° C
10.2B	453	Homolytic Bond Dissociation Energies and the Relative Stabilities of Radicals
10.3	454	The Reactions of Alkanes with Halogens
10.3A	455	Multiple Substitution Reactions versus Selectivity
10.4	456	Chlorination of Methane: Mechanism of Reaction
		1. Chain Initiation
		2. Chain Propagation
		3. Chain Termination
10.5	459	Chlorination of Methane: Energy Changes
10.5A	460	The Overall Free-Energy Change
10.5B	461	Activation Energies
10.5C	464	Reaction of Methane with other Halogens

10.6	466	Halogenation of Higher Alkanes
10.6A	468	Selectivity of Bromine, and Selectivity versus Reactivity
10.7	469	The Geometry of Alkyl Radicals
10.8	469	Reactions that Generate Tetrahedral Stereogenic Carbons
10.8A	470	Generation of a Second Stereogenic Carbon in a Radical Halogenation
10.9	472	Radical Addition to Alkenes: The Anti-Markovnikov Addition of Hydrogen Bromide
10.9A	473	Summary of Markovnikov versus Anti-Markovnikov Addition of HBr to Alkenes
10.10	474	Radical Polymerization of Alkenes: Chain Growth Polymers
	474	Radical Polymerization of Ethene
	476	Other Common Chain-Growth Polymers
10.11	476	Other Important Radical Reactions
10.11A	476	Molecular Oxygen and Super oxide
10.11B	477	Nitric Oxide
10.11C	477	Combustion of Alkanes
10.11D	478	Autoxidation
10.11E	479	Antioxidants
10.11F	479	Ozone Depletion and Chlorofluorocarbons (CFCs)
	481	Summary and Review Tools: Concept Map: Mechanism Review of Radical Reactions
	482	Key Terms and Concepts
	485	Special Topic A: Chain-Growth Polymers
Problems:	In-Chapter	10.1 to 10.18
	482	End of Chapter 10.19 to 10.33
	484	Learning Group Problems.

Week of Nov 21: ALCOHOLS AND ETHERS.

Read and Study Chapter 11.

	492	Molecular Hosts
11.1	493	Structure and Nomenclature
11.1A	494	Nomenclature of Alcohols
11.1B	495	Nomenclature of Ethers
11.2	495	Physical Properties of Alcohols and Ethers
	496	Tables 11.1 and 11.2: Physical Properties of Ethers and Alcohols
11.3	497	Important Alcohols and Ethers
11.3A-D	497	Methanol, Ethanol, Ethylene Glycol, Diethyl Ether
11.4	499	Synthesis of Alcohols from Alkenes
		1. Acid-Catalyzed Hydration of Alkenes
		2. Oxymercuration-Demercuration
		3. Hydroboration-Oxidation
11.5	501	Reactions of Alcohols

11.6	502	Alcohols as Acids
11.7	503	Conversion of Alcohols into Alkyl Halides
11.8	503	Alkyl Halides from the Reactions of Alcohols with Hydrogen Halides
11.8A	504	Mechanisms of the Reactions of Alcohols with HX
11.9	506	Alkyl Halides from the Reactions of Alcohols with PBr ₃ or SOCl ₂
11.10	507	Tosylates, Mesylates and Triflates: Leaving Group Derivatives of Alcohols
	510	The Chemistry of --- Alkyl Phosphate
11.11	510	Synthesis of Ethers
11.11A	510	Ethers by Intermolecular Dehydration of Alcohols
11.11B	512	The Williamson Synthesis of Ethers
11.11C	513	Synthesis of Ethers by Alkoxymercuration-Demercuration
11.11D	513	tert-Butyl Ethers by Alkylation of Alcohols: Protecting Groups
11.11E	514	Silyl Ether Protecting Groups
11.12	515	Reactions of Ethers: Ether Cleavage by Strong Acids
11.13	516	Epoxides: Alkene Epoxidation
	517	The Chemistry of ... The Sharpless Asymmetric Epoxidation
11.14	519	Reactions of Epoxides: 1. Acid Catalyzed Ring Opening 2. Base Catalyzed Ring Opening
	521	The Chemistry of ... Epoxides, Carcinogens, and Biological Oxidation
11.14A	522	Polyether Formation
11.15	523	Anti 1,2-Dihydroxylation of Alkenes via Epoxides
	525	The Chemistry of --- Environmentally Friendly Alkene Oxidation Methods
11.16	526	Crown Ethers: Nucleophilic Substitution Reactions in Relatively Nonpolar Aprotic Solvents by Phase-Transfer Catalysis
11.16A	527	Crown Ethers
11.16B	529	Transport Antibiotics and Crown Ethers
11.17	529	Summary of Reactions of Alkenes, Alcohols and Ethers
11.17A	529	Alkenes in Synthesis
	530	Key Terms and Concepts.
	531	Summary and Review Tool: Some Synthetic Connections of Alkynes, Alcohols, Alkyl Halides and Ethers
Problems:	In-Chapter	11.1 to 11.24
	532	End of Chapter 11.25 to 11.51
	536	Learning Group Problems.

**Week of Mar 28: ALCOHOLS FROM CARBONYL COMPOUNDS:
OXIDATION-REDUCTION AND ORGANOMETALLIC
COMPOUNDS.**

		Read and Study Chapter 12
	537	The Two Aspects of the Coenzyme NADH
12.1	538	Introduction

12.1A	538	Structure of the Carbonyl Group
12.1B	539	Reactions of Carbonyl Compounds with Nucleophiles
12.2	539	Oxidation-Reduction Reactions in Organic Chemistry
12.3	541	Alcohols by Reduction of Carbonyl Compounds
	544	The Chemistry of ... Alcohol Dehydrogenase
	544	The Chemistry of ... Stereoselective Reduction of Carbonyl Groups
12.4	546	Oxidation of Alcohols
12.4A	546	Oxidation of Primary Alcohols to Aldehydes: RCH_2OH to RCHO
12.4B	547	Oxidation of Primary Alcohols to Carboxylic Acids: RCH_2OH to RCO_2H
12.4C	547	Oxidation of Secondary Alcohols to Ketones: $\text{RCH}(\text{OH})\text{R}'$ to RCOR'
12.4D	547	Mechanism of Chromate Oxidations
12.4E	549	A Chemical Test for Primary and Secondary Alcohols
12.4F	550	Spectroscopic Evidence for Alcohols
12.5	550	Organometallic Compounds
12.6	551	Preparation of Organo Lithium and Organo Magnesium Compounds
12.6A	551	Organolithium Compounds
12.6B	552	Grignard Reagents
12.7	553	Reactions of Organolithium and Organomagnesium Compounds
12.7A	553	Reactions with Compounds Containing Acidic Hydrogen Atoms
12.7B	554	Reactions of Grignard Reagents with Oxiranes (Epoxides)
12.7C	555	Reactions of Grignard Reagents with Carbonyl Compounds
12.8	556	Alcohols from Grignard Reagents: Reaction of Grignard Reagents with:
		1. Formaldehyde to Give Primary Alcohols
		2. Other Aldehydes to Give Secondary Alcohols
		3. Ketones to Give Tertiary Alcohols
		4. Esters with $2 \times \text{RMgX}$ to Give Tertiary Alcohols
12.8A	557	Planning a Grignard Synthesis
12.8B	561	Restrictions on the Use of Grignard Reagents
12.8C	562	The Use of Lithium Reagents
12.8D	562	The Use of Sodium Alkynides
12.9	564	Lithium Dialkylcuprates: The Corey-Posner, Whitesides-House Synthesis
12.10	566	Protecting Groups
	567	Summary of Reactions
	567	Synthetic Connections of Alcohols and Carbonyl Compounds
	568	Key Terms and Concepts
Problems:	In-Chapter	12.1 to 12.10
	569	End of Chapter 12.11 to 12.29
	572	Learning Group Problems.
	573	First Review Problem Set 1 to 25.

Week of April 4: CONJUGATED UNSATURATED SYSTEMS.

Read and Study Chapter 13.

	577	Molecules With the Nobel Prize in Their Synthetic Lineage
13.1	578	Introduction
13.2	578	Allylic Substitution and the Allyl Radical
13.2A	579	Allylic Chlorination (High Temperature)
13.2B	581	Allylic Bromination with N-Bromosuccinimide (Low Conc. of Br ₂)
13.3	582	The Stability of the Allyl Radical
13.3A	582	Molecular Orbital Description of the Allyl Radical
13.3B	584	Resonance Description of the Allyl radical
13.4	586	The Allyl Carbocation
13.5	587	Summary of Rules for Resonance
13.5A	387	Rules for Writing Resonance Structures
13.5B	589	Estimating the Relative Stability of Resonance Structures
13.6	591	Alkadienes and Polyunsaturated Hydrocarbons
13.7	593	1,3-Butadiene: Electron Delocalization
13.7A	593	Bond Lengths of 1,3-Butadiene
13.7B	593	Conformations of 1,3-Butadiene, s-cis and s-trans
13.7C	594	Molecular Orbitals of 1,3-Butadiene
13.8	595	The Stability of Conjugated Dienes
13.9	596	Ultraviolet-Visible Spectroscopy
13.9A	597	UV-Vis Spectrophotometers
13.9B	598	Absorption Maxima for Nonconjugated and Conjugated Dienes
	600	The Chemistry of ... The Photochemistry of Vision
13.9C	603	Analytical Uses of UV-Vis Spectroscopy
13.10	604	Electrophilic Attack on Conjugated Dienes: 1,4-Electrophilic Addition
13.10A	605	Kinetic Control versus Thermodynamic Control of a Chemical Reaction
13.11	607	The Diels-Alder Reaction: 1,4-Cycloaddition of Dienes
13.11A	609	Factors Favoring the Diels-Alder Reaction
13.11B	609	Stereochemistry of the Diels-Alder Reaction
13.11C	611	Molecular Orbital Considerations That Favor an Endo Transition State
13.11D	613	Asymmetric Diels-Alder Reactions
13.11E	614	Intramolecular Diels-Alder Reactions
	615	Concept Map
	616	Key Terms and Concepts.
Problems:	In-Chapter	13.1 to 13.15
	616	End of Chapter 13.16 to 13.46
	621	Learning Group Problems.

Week of April 11: Review

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