

DAT Organic Chemistry Rapid Learning Series – Course GuideBook



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Chemistry : Biology : Physics : Math

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## COURSE FEATURES

This tutorial series is a carefully selected collection of core concept topics that cover the essential concepts. It consists of three parts:

1. Concept Tutorials – 24 essential topics
2. Problem-Solving Drills – 24 practice sets
3. Super Condense Cheat Sheets – 24 super review sheets

### **Core Tutorials**

- + Self-contained tutorials...not an outline of information which would need to be supplemented by an instructor.
- + Concept map showing inter-connections of new concepts in this tutorial and those previously introduced.
- + Definition slides introduce terms as they are needed.
- + Visual representation of concepts.
- + Conceptual explanation of important properties and problem solving techniques
- + Animated examples of processes and cycles in human physiology.
- + A concise summary is given at the conclusion of the tutorial.

### **Problem Solving Drills**

Each tutorial has an accompanying Problem Set with 10 problems covering the material presented in the tutorial. The problem set affords the opportunity to practice what has been learned.

### **Condensed Cheat Sheet**

Each tutorial has a one-page cheat sheet that summarizes the key concepts and vocabularies and structures presented in the tutorial. Use the cheat sheet as a study guide after completing the tutorial to re-enforce concepts and again before an exam.

## Chapter by Chapter Detailed Content Descriptions

## 01: Introduction to DAT Organic Chemistry

## Chapter Summary

In this first tutorial, we will give you the introduction to the test you are about to take. In particular, you will learn more about this DAT Organic Chemistry course and get ready for the extensive coverage on required knowledge in the chemistry section of biological survey subtest. The DAT and CBT are defined and the scope of the organic chemistry section is introduced. The test-prep and test-taking strategies are also discussed. Finally, the tips in how to solve chemistry problems are described.

## Tutorial Features

- Concept map showing inter-connections of concepts.
- Definition slides introduce terms as they are needed.
- Examples given throughout to illustrate how the concepts apply.
- A concise summary is given at the conclusion of the tutorial.

## Key Concepts

Dental Admissions Test  
Computer based test format of the DAT  
The DAT Natural Sciences focus areas  
DAT Organic Chemistry comprehension areas  
Test-preparation strategies  
Test-taking strategies  
How to attack and solve Organic Chemistry problems

## Chapter Review

**DAT** - The DAT is the Dental College Admissions Test by American Dental Association (ADA). Its computer based test is a standardized exam that most US and Canadian dental schools require in order to consider a student for admission.

**DAT Organic Chemistry** - The science section of the DAT consists of 100 items that includes questions about: General Chemistry, Organic Chemistry and Biology. Organic Chemistry usually consists of about 30 items broken down as shown with the numbers representing the number of items usually tested within each focus area.

**Test -Prep Strategies:** (1) Smart Time Management (2) Key Concept Mastery (3) Practice-Practice-Practice (4) Systematic Review

**Test-Taking Strategies:** (1) Know the Test (2) Plan Your Attack (3) Build Focus (4) Zoom In On The Answer (5) Guess The Right Way

**Organic Chemistry Problem Solving:** (1) Think of the answer before scanning the answer choices (2) Beware of the familiar (3) Aware of the Absolute (4) Deal with the

Similar and Opposites (5) Know about the elimination and answer selection (6) Make educated guesses.

## 02: Chemistry Review – Structure and Bonding

### Chapter Summary

Organic chemistry is the study of carbon compounds. In order to learn more about carbon compounds, and the reactions they undergo, one must understand some basic, underlying principles of chemistry first. It is essential to have a firm grasp of concepts like atomic structure, molecular orbitals, intra- and intermolecular interactions, and resonance. With these basic concepts as the foundation, learning about organic compounds and how they react will be much easier.

### Tutorial Features

- Definition slides introduce terms as they are needed.
- Color coded atoms in examples to enable the reader to better follow the action.
- Visual representation of concepts.
- Examples given throughout to illustrate how the concepts apply.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

#### Atomic and Molecular Structure

- Atomic structure
- Electronic configuration
- Valence electrons
- Isotopes, ions and radicals
- Lewis structures
- Formal charges

#### Molecular Shape

- VSEPR (valence shell electron pair repulsion) theory
- Predicting molecular shape
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#### Types of Carbon Molecules

- Stable, neutral molecules
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#### Intramolecular Bond Interactions

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- Hybridization

#### Resonance

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Intermolecular Forces  
London Dispersion forces  
Dipole-dipole forces  
Hydrogen bonding

## Chapter Review

### Atomic Number

The number of protons in an atom.

### Electronic Configuration

The arrangement of an atom or ion's electrons into atomic orbitals. There are four types of atomic orbitals: s orbitals (maximum of 2 electrons), p orbitals (maximum of 6 electrons), d orbitals (maximum of 10 electrons), and f orbitals (maximum of 14 electrons).

### Valence Electrons

The electrons that comprise the outer shell of an atom and are typically the electrons involved in bonding.

### Isotope

An atom having the same number of protons in its nucleus as other varieties of the element but has a different number of neutrons.

### Ion

An atom or group of atoms that has either lost or gain an electron(s) resulting in a charged species.

### Radical

An atomic or molecular species with an unpaired electron.

### Formal Charge

The charge that an atom would have if the bonding electrons in every bond to it were equally shared. Formal charges are useful for accounting for the electrons in a molecule, but they do not have any intrinsic physical meaning. The equation used to determine the formal charge of an atom(s) is below:

$$\text{Formal charge} = [\text{number of valence electrons}] - [\text{nonbonding electrons}] - \frac{1}{2}[\text{bonding electrons}]$$

### Lewis Structures

Diagrams that show the bonding between atoms of a covalently bonded molecule and any lone pairs of electrons that may exist in the molecule. Lewis structures are drawn using only the valence electrons.

### VSEPR Theory

Valence shell electron pair repulsion theory (VSEPR) is a model in chemistry that attempts to predict the shape of a molecule based on the valence electrons of a molecule. The theory states that the areas of electron density in a molecule will repel each other, and in doing so, adopt regular, predictable shapes.

### Carbanion



A molecule that contains a carbon which has gained a pair of electrons and is negatively charged.

**Carbocation**

A molecule that contains a carbon which has lost a pair of electrons and is positively charged.

**Carbon Radical**

A carbon that is neutral and possesses a single, unpaired electron.

**Stable, Neutral Carbon Compound**

A compound that has not lost or gained any electrons.

**Electronegativity**

The ability of an atom to attract electrons.

**Dipole**

The separation of charge between two covalently bonded atoms.

**Intramolecular Bond Interactions**

Bonding interactions within a molecule.

**Ionic Bonding**

Type of intramolecular bonding interaction that involves the actual transfer of electrons from one atom to another.

**Covalent Bonding**

Type of intramolecular bonding interaction that involves the sharing of electrons between atoms. The difference in electronegativity, as well as other factors, between atoms in a bond can affect the extent to which the electrons are shared.

**Polar Covalent Bonding**

Type of covalent bonding where the atoms participating in a bond differ in electronegativity so the electrons in the bond are shared unequally.

**Nonpolar Covalent Bonding**

Type of covalent bonding where the atoms in a bond have the same electronegativity and share the electrons in the bond equally.

**Homolytic Bond Cleavage**

Process in which each atom involved in a bond obtains one electron forming radicals.

**Heterolytic Bond Cleavage**

Process in which one atom involved in bond obtains both electrons while the other atom gets no electrons. Ions are formed as a result.

**Molecular Orbitals**

Orbitals obtained by combining atomic orbitals in a molecule together.

**Sigma Bonds**

Bonds formed by the overlapping of orbitals in such a way that the electron density of the bond is located between the nuclei of the two atoms involved in the bond. Single bonds

obtained by one of three ways: two s orbitals overlapping, one s overlapping with an end of one p orbital, or two p orbitals overlapping end-on-end.

**Pi Bonds**

Bonds formed by the overlapping of orbitals in such a way that the electron density of the bond is located both above and below the plane of the nuclei involved in the bond. Pi bonds can be obtained by the side-to-side overlap of two p orbitals.

**Hybrid Orbitals**

The combination of two or more atomic orbitals to form a new orbital.

**Resonance**

A tool used in organic chemistry to describe molecules that can be drawn in more than one way.

**Resonance Structure**

Structures that can be drawn for a given molecule that differ only by the distribution of electrons. Each structure contributes to the overall picture of a molecule.

**Resonance Hybrid**

A composite of the various contributing resonance structures that gives a better description of a molecule than a single resonance structure could by itself.

**Delocalized Electrons**

Electrons that are not associated with just one atom or bond. Delocalized electrons are thought to lead to increased molecular stability.

**Intermolecular Forces**

Attractive forces between molecules.

**London Dispersion Forces**

Forces that occur between nonpolar molecules.

**Dipole-Dipole Forces**

Forces that occur between polar molecules.

**Hydrogen Bonding**

A type of dipole-dipole force that occurs between molecules with -OH, -NH, or HF.

## 03: IUPAC Rules: Organic Nomenclature I

### Chapter Summary

Organic nomenclature, the rules for naming organic compounds, has two functions. First, the rules established in systems of nomenclature act to ensure that a person who hears or reads the name is under no ambiguity as to the compound to which it refers. One name can refer only to one chemical compound. Second, each name preferably conveys some information about the structure of a compound. In organic chemistry, the student is expected to be familiar with two systems of nomenclature: IUPAC nomenclature and common nomenclature. IUPAC nomenclature is a system of naming chemical compounds developed by the International Union of Pure and Applied Chemistry. It is a more formalized system than common nomenclature. IUPAC nomenclature uses a system of prefixes and suffixes to indicate the type of compound (what functional group is present in the molecule) present, the number of carbons in the longest, continuous chain in the molecule, and the type, number, and location of substituents on the parent chain. Common nomenclature uses prefixes to indicate the presence of certain common structural motifs in molecules. In order to fully understand the naming prefixes of common nomenclature, a discussion of the classification of carbons is also included.

### Tutorial Features

- Definition slides introduce terms as they are needed.
- Visual representation of basic concepts of nomenclature.
- Color coded atoms in examples to enable the reader to better follow the action.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

IUPAC (International Union of Pure and Applied Chemistry) Nomenclature

Parent chain

Alkyl prefixes

Substituents

Numerical prefixes

Halogen prefixes

Rules used in naming compounds

Common Nomenclature

Classification of carbons

Rules used in naming compounds

### Chapter Review

#### IUPAC Nomenclature

A system of naming chemical compounds developed by the International Union of Pure and Applied Chemistry. This system of nomenclature standardized the naming of compounds so that scientists around the world could communicate about molecules without confusion.

**Parent Chain**

The parent chain is the longest, continuous chain of carbons in a molecule.

**Alkyl Prefixes**

Prefixes that indicate the number of carbon atoms in the main chain. The table below lists the different alkyl prefixes:

Number of Carbons	Alkyl Prefix
1	Meth-
2	Eth-
3	Prop-
4	But-
5	Pent-
6	Hex-
7	Hept-
8	Oct-
9	Non-
10	Dec-

**Substituents**

Any atom or group of atoms not part of the parent chain in a molecule.

**Numerical Prefixes**

Prefixes used to indicate when more than one of a particular substituent exists in a molecule. The table below lists the numerical prefixes used for naming identical groups:

Number of Identical Group Present	Numerical Prefix
1	Mono-
2	Di-
3	Tri-
4	Tetra-
5	Penta-
6	Hexa-
7	Hepta-
8	Octa-
9	Nona-
10	Deca-

**Halogen Prefixes**

Prefixes used to indicate when a halogen (fluorine, chlorine, bromine, or iodide) is present as a substituent in a compound. The table below lists the halogen prefixes for each atom:

Halogen Atom	Halogen Prefix
Fluorine (F)	Fluoro-
Chlorine (Cl)	Chloro-
Bromine (Br)	Bromo-
Iodine (I)	Iodo-

**IUPAC Rules for Naming Compounds**

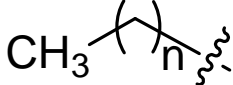
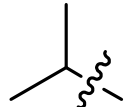
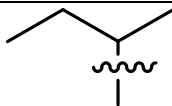
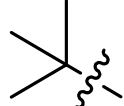
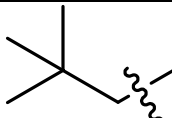
There are two parts to every organic compound name in the IUPAC system: (1) the parent and (2) the substituents. The parent conveys the number of carbon atoms present in the

longest chain through the use of an alkyl prefix and the functional group of the compound through the use of an appropriate suffix. The substituents are listed alphabetically before the parent in the name. Numerals are used to indicate their location on the main chain and numerical prefixes are used to indicate when more than one of a particular substituent exists. The following are rules used to name alkanes, alkenes, alkynes and alkyl halides:

1. Determine the longest, continuous chain of carbon atoms in the molecule. If the molecule contains an alkene or alkyne functional group, then the multiple bond(s) must be a part of the parent chain. Select the correct alkyl prefix that corresponds to the number of carbon atoms in the parent chain.
2. Determine the correct functional group suffix to use. Use the suffixes -ane for alkanes, -ene for alkenes, and -yne for alkynes. With alkyl halides, the molecules are named as alkanes with the halogens serving as substituents on the parent alkyl chain.
3. For alkanes, number the parent chain from the end that gives the lower number to the substituent encountered first.
4. For alkenes and alkynes, number the chain so that the multiple bonds have the lowest possible number. Place this location number in front of the parent name.
5. Naming substituents: For halogen substituents, use the halogen prefixes. For alkyl substituents, use the appropriate alkyl prefixes + -yl. Use numerical prefixes if more than one of a particular substituent exists in the molecule. Give the location of all substituents by placing the number of the carbon it is attached to in front of the substituent name.
6. Alphabetize the substituent groups, ignoring all numerical prefixes, in front of the parent name.
7. For alkenes, determine the relative configuration of the alkene if possible (cis versus trans). Place cis or trans in front of the substituent groups.

### Common Nomenclature

Common nomenclature uses prefixes to indicate the presence of certain common structural motifs in molecules. The table below lists the different structural motifs in common nomenclature:

Name of Structural Motif	Structure of Motif
Straight Chain/Normal (n-)	
Iso-	
Secondary (sec-)	
Tertiary (tert-)	
Neo-	

The following are rules for naming alkyl halides using common nomenclature:

1. Name the compound as an alkyl halide. Use all of the carbons in the "alkyl" name.
2. Use the prefix "n" if the structure is a straight chain with the halogen on one end.
3. Use the prefix "iso" if the structure contains two methyl groups attached to a methine (CH) carbon.
4. Use the prefix "sec" if halogen is attached to the secondary carbon of a four carbon chain.
5. Use the prefix "tert" if the halogen is attached to the tertiary carbon of a group of four or five carbons.
6. Use the prefix "neo" if the halogen is attached to a carbon attached to four other carbons.

## 04: IUPAC Rules: Organic Nomenclature II

### Chapter Summary

The theme of organic nomenclature is continued in this tutorial with the rules for naming alcohols, ethers, aldehydes, ketones, carboxylic acids, amines and carboxylic acid derivatives being the focus of study. The IUPAC rules for naming alcohols, ethers, aldehydes, ketones, carboxylic acids, amines and carboxylic acid derivatives build on those rules learned in the previous tutorial for alkanes, alkenes, alkynes, and alkyl halides. Also, the common nomenclature rules for naming alcohols, ethers, ketones, and amines will be examined.

### Tutorial Features

- Examples and practice problems in the tutorial: Naming alcohols, ethers, aldehydes, ketones, amines and carboxylic acid derivatives.
- Visual representation of basic concepts of nomenclature.
- Color coded atoms in examples to enable the reader to better follow the action.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

#### IUPAC Nomenclature

Rules for naming alcohols, ethers, aldehydes, ketones, carboxylic acids, and amines

Rules for naming carboxylic acid derivatives

#### Common Nomenclature

Rules for naming alcohols, ethers, ketones, and amines

### Chapter Review

#### Functional Group Suffixes

The functional group suffix makes up part of the parent's name and communicates the functional group of the molecule immediately upon hearing/reading the compound's name. The table below lists the suffixes for the most commonly encountered functional groups in organic chemistry:

Functional Group	Suffix
Alkane	-ane
Alkene	-ene
Alkyne	-yne
Alkyl Halide*	-ane
Ether*	-ane
Alcohol	-anol
Aldehyde	-anal
Ketone	-anone
Carboxylic Acid	-anoic acid
Amine	-anamine

Ester	-anoate
Anhydride	Alkanoic alkanonic anhydride
Acid Halide	-anoyl halide
Amide	-anamide

### Naming Alcohols, Ethers, Aldehydes, Ketones, Carboxylic Acids, and Amines

The rules for naming alcohols, ethers, aldehydes, ketones, carboxylic acids, amines, and carboxylic acid derivatives in this tutorial build on those from the previous tutorial entitled "Organic Nomenclature I: How to Name Alkanes, Alkenes, Alkynes, and Alkyl Halides." The following are rules for naming alcohols, ethers, aldehydes, ketones, carboxylic acids, and amines:

1. Determine the appropriate alkyl prefix and functional group suffix for the parent chain in the molecule.
2. Number the chain so that the C-O or C-N bond has the lowest possible number. Indicate the position of the functional group using a number in front of the parent chain name.
3. For ethers, the compound is named as an alkane with the -OR group named as a substituent of the parent chain.
4. For amines, give the location of the attachment of the nitrogen to the parent amine and identify any groups attached to the nitrogen as substituents.
5. Give the location of each substituent with a number. Use numerical prefixes if more than one identical group is present.
6. Alphabetize the substituents, ignoring all numerical prefixes, in front of the parent chain's name.

### Naming Carboxylic Acid Derivatives

In addition to the rules seen thus far for naming organic compounds, the following are IUPAC rules to be used in the naming of acid derivatives:

1. An ester is named by numbering the longest carbon chain beginning at the carbonyl carbon. List the alkyl group attached to the oxygen before any substituents.
2. An anhydride is named as an alkanonic alkanonic anhydride.
3. An acid halide is named as an alkanoyl halide.
4. An amide is named as an alkanamide. Any group attached to the nitrogen is numbered as "N".

### Common Nomenclature

In addition to the common nomenclature rules seen thus far, the following are common nomenclature rules for naming alcohols, ethers, ketones, and amines:

1. Use common prefixes as needed.
2. An alcohol is named as an alkyl alcohol.
3. An ether is named as an alkyl alkyl ether. Alphabetize the two alkyl groups, ignoring any common prefixes like tert- or iso-.
4. A ketone is named as an alkyl alkyl ketone. . Alphabetize the two alkyl groups, ignoring any common prefixes like tert- or iso-.
5. For amines, the longest carbon chain attached to the nitrogen is the parent chain. List any additional substituents on the nitrogen in alphabetical order.



## 05: Drawing Organic Structures

### Chapter Summary

Structures, not formulas, must be used in drawing organic structures. Double and triple bonds need to be shown in the structures. Structural formulas can be described as Lewis structures, condensed structures, skeletal structures, and sawhorse structures. Isomers can be classified as constitutional, configurational, or conformational. The common organic abbreviations are given in terms of names and structures.

### Tutorial Features

- Concept map showing inter-connections of concepts.
- Definition slides introduce terms as they are needed.
- Examples given throughout to illustrate how the concepts apply.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

#### Importance of Drawing Structures

- Structures, not Formulas
- Show Multiple Bonds

#### Types of Structures

- Lewis Structures
- Condensed Structures
- Skeletal Structures
- Sawhorse Structures

#### Isomers

- Constitutional Isomers
- Configurational Isomers
- Conformational Isomers

#### Abbreviations

- Names
- Structures

### Chapter Review

#### Importance of drawing structures

A structure must be given, otherwise the product of the reaction cannot be determined. The location of single, double, and triple bonds must be specified.

#### Types of Structures

In Lewis structures, all individual bonds are shown. Formal charge is a way of keeping track of the electrons. Formal charge is equal to  $[\text{number of valence electrons}] - \frac{1}{2} [\text{nonbonding electrons}] - \frac{1}{2} [\text{bonding electrons}]$ . In condensed structural formulas, atoms

are bonded to a central atom are listed after the atom. In a skeletal structure, carbon atoms are assumed to be where two lines meet or at the end of the line. Hydrogens are not shown. In a sawhorse structure, the drawing is looking down the carbon-carbon bond.

### Isomers

Constitutional isomers have the same formula, but different points of attachment. Configurational isomers have the same formula and the same point of attachment, but different orientation in space. Conformational isomers have the same formula and the same point of attachment, but the rotation about single bonds is different. In the eclipsed conformation of ethane, the front hydrogens block the back hydrogens. In the staggered conformation, the hydrogens are as far away from each other as possible. The staggered conformation is the most stable. For the conformations of butane, the front two carbons remain in place and the back two carbons rotate around the carbon 2 and carbon 3 bond. In the totally eclipsed conformation, one methyl blocks the other methyl. In the gauche conformation, the methyls are  $60^\circ$  apart. In the eclipsed conformation, the methyls are  $120^\circ$  apart. In the anti conformation, the methyls are  $180^\circ$  apart. The stability of butane is anti > gauche > eclipsed > totally eclipsed.

### Abbreviations

Me is an abbreviation for methyl, a  $\text{CH}_3$ -. Et is an abbreviation for ethyl, a  $\text{CH}_3\text{CH}_2$ -. Pr is an abbreviation for propyl, a  $\text{CH}_3\text{CH}_2\text{CH}_2$ -. Butyl is an abbreviation for butyl, a  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$ -. Ph is an abbreviation for phenyl, a benzene ring. Ar is an abbreviation for aromatic or aryl, a benzene ring. Ac is an abbreviation for acetyl, a methyl next to a  $\text{C}=\text{O}$ . Bz is an abbreviation for benzoyl, a benzene next to a  $\text{C}=\text{O}$ . Bn is an abbreviation for benzyl, a benzene attached to a  $\text{CH}_2$ . Pyr is an abbreviation for pyridine, a six-membered ring with alternating double and single bonds and containing nitrogen.

## 06: Functional Groups and Organic Compounds

### Chapter Summary

Organic compounds can be categorized based on the functional groups they contain. Functional groups are specific, reactive groups of atoms that are responsible for the characteristics of the molecule that contains them. Molecules containing the same functional groups will undergo similar reactions. Also included in this tutorial is a section on acids and bases. Three different concepts of acidity and basicity are covered in this section: Arrhenius acid-base theory, Bronsted-Lowry acid-base theory, and Lewis acid-base theory. The different theories developed as our understanding of acids and bases grew. Finally, the tutorial looks at the basic rules for electron pushing in mechanisms.

### Tutorial Features

- Concept map showing inter-connections of new concepts in this tutorial and those previously introduced.
- Definition slides introduce terms as they are needed.
- Visual representation of concepts.
- Color coded atoms in examples to enable the reader to better follow the action.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

#### Organic Chemistry

- The chemistry of carbon
- Language of organic chemistry

#### Functional Groups

- Alkane, alkene, alkyne, aromatic
- Alkyl halide, alcohol, ether, thiol, sulfide
- Aldehyde, ketone, acid halide
- Carboxylic acid, ester, anhydride
- Amine, amide, nitrile

#### Acids and Bases

- Arrhenius
- Bronsted-Lowry
- Lewis

#### Electron Pushing

- Electrons and mechanisms
- Resonance and delocalization

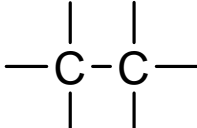
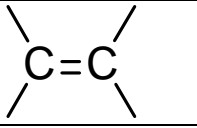
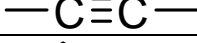
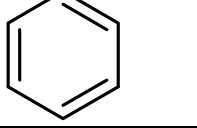
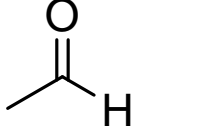
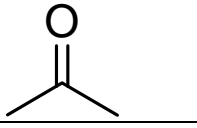
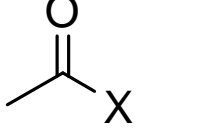
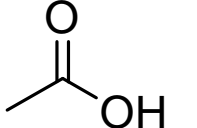
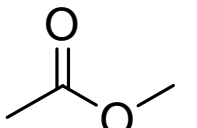
### Chapter Review

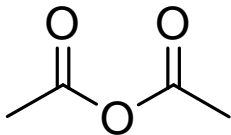
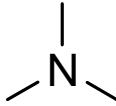
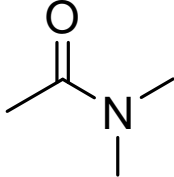
#### Organic Chemistry

The study of the chemistry of carbon compounds.

#### Functional Groups

Specific groups of atoms that impart characteristic reactivity to the molecules that contain them. The table below describes the structures of the most commonly encountered functional groups:

Functional Group	Structure
Alkane	
Alkene	
Alkyne	
Aromatic	
Alkyl Halide	$R-X$
Alcohol	$R-OH$
Ether	$R-O-R$
Thiol	$R-SH$
Sulfide	$R-S-R$
Aldehyde	
Ketone	
Acid Halide	
Carboxylic Acid	
Ester	

Anhydride	
Amine	
Amide	
Nitrile	$\text{—C}\equiv\text{N}$

**Arrhenius Acid**

A substance that dissociates to give the hydronium ion ( $\text{H}_3\text{O}^+$ ).

**Arrhenius Base**

A substance that dissociates to give the hydroxide ion ( $\text{OH}^-$ ).

**Bronsted-Lowry Acid**

A substance that can donate a proton ( $\text{H}^+$ ).

**Bronsted-Lowry Base**

A substance that can accept a proton ( $\text{H}^+$ ).

**Conjugate Acid**

A substance that results from the Bronsted-Lowry base gaining a proton ( $\text{H}^+$ ).

**Conjugate Base**

A substance that results from the Bronsted-Lowry acid losing a proton ( $\text{H}^+$ ).

**Amphoteric Compound**

A compound that can react as an acid or a base.

**Lewis Acid**

A substance that can accept electron pairs to form new bonds.

**Lewis Base**

A substance that can donate electron pairs to form new bonds.

**Mechanism**

A step by step explanation of what happens in a chemical reaction.

**Nucleophile**

The compound that donates the electrons in a mechanism (electron rich compound).

**Electrophile**

The compound that accepts the electrons in a mechanism (electron poor compound).

**Delocalization**

Electrons that are distributed among more than two atoms that are bonded together.

**Electron Pushing**

The process of moving electrons in a mechanism to illustrate what is occurring during a chemical reaction. Basic rules for drawing the movement of electrons in mechanisms have been established:

1. Identify the nucleophile. The nucleophile is typically the electron rich species and as such donates the electrons in a mechanism.
2. Identify the electrophile. The electrophile is typically the electron poor species and as such accepts the electrons in a mechanism.
3. The flow of electrons in a mechanism is **always** from the most electronegative atom to the least electronegative atom (or negative to positive).

## 07: Stereochemistry

### Chapter Summary

Often times in chemistry, one runs across molecules that have the same molecular formula but possess a different structure. These molecules are called isomers. Isomers can be divided into three types: constitutional isomers, stereoisomers, and conformational isomers. The student must learn to distinguish between these three types of isomers. In this tutorial, the student will also be introduced to the concept of chirality and will learn how to find stereogenic centers in a molecule. This leads to a discussion of the different types of stereoisomers: enantiomers, diastereomers, and *cis/trans* (*E/Z*) isomers of alkenes. The student will learn how to distinguish enantiomers and diastereomers by assigning either an *R* or *S* configuration using the rules set forth in the *R/S* system. Finally, the tutorial will cover how to determine the relative and absolute configurations of alkenes including the rules for the *E/Z* system.

### Tutorial Features

- Concept map showing inter-connections of new concepts in this tutorial and those previously introduced.
- Definition slides introduce terms as they are needed.
- Visual representation of basic concepts of stereochemistry.
- Color coded atoms in examples to enable the reader to better follow the action.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

#### Isomers

- Constitutional isomers
- Stereoisomers
- Conformational isomers

#### Basic Concepts of Stereochemistry

- Stereochemistry overview
- Chirality
- Stereoisomers

- Enantiomers

- Diastereomers

#### Assigning R and S Configurations to Chiral Centers

- Distinguishing enantiomers pairs by assigning their R and S configurations
- Assigning the absolute configuration to chiral compounds
- Meso compounds

#### Stereoisomers of Alkenes

- Relative configuration
- Absolute configuration

### Chapter Review

#### Constitutional Isomers

Molecules with the same molecular formula, but different points of attachment.

### **Conformational Isomers**

Molecules with the same molecular formula and points of attachment but differ by the rotation of a single bond.

### **Chirality**

Chiral objects are not superimposable upon their mirror images while achiral objects can be superimposed upon their mirror images. Hands, ears, feet, and keys are examples of chiral objects. These objects do not contain planes of symmetry as symmetry is often an indicator of an object being achiral.

### **Chiral Carbon (Stereogenic Center, Stereocenter)**

Carbon that has four different groups attached to it.

### **Stereoisomers**

Molecules with the same molecular formula and points of attachment but different spatial orientation. There are three types of stereoisomers: enantiomers, diastereomers, and *cis/trans* (*E/Z*) isomers of alkenes. One can calculate the maximum number of stereoisomers that can exist for a chiral molecule by the solving the formula  $2^n$  where  $n$  is the number of chiral centers present in the molecule.

### **Enantiomers**

A molecule and its nonsuperimposable mirror image.

### **Assigning *R/S* Configurations to Chiral Centers**

Chiral centers are assigned either *R* or *S* configurations based on the spatial arrangement of the groups on the stereogenic carbon. The method for assigning configurations involves determining the priority of the groups bound to the carbon.

1. Assign priority to the different groups on carbon with (1) being the highest priority group and (4) being the lowest priority group. The groups with the higher atomic mass/number will be given the higher priority. If the atomic mass/number of two groups is equal, then give the higher priority to the group that contains more branching.
2. Orient the molecule so that the lowest priority group is facing away from you.
3. Trace from priority group (1) through (2) to (3). If it is clockwise, assign the *R* configuration to the center. If it is counterclockwise, assign the *S* configuration to the center.

### **Diastereomers**

Non-mirror image stereoisomers that contain more than one stereogenic center.

### **Meso Compounds**

Molecules that contain more than one chiral center but that are achiral due to the presence of a plane of symmetry.

### **Relative Configuration of Alkenes**

The relative configuration of an alkene is determined from the orientation of the parent chain through the double bond. An alkene is *trans* if the parent chain is on opposite sides of the double bond. An alkene is *cis* if the parent chain is on the same side of the double



bond. The *cis/trans* system is typically used just for disubstituted alkenes as it becomes more difficult to assign a relative configuration to tri- and tetra-substituted alkenes.

### **Absolute Configuration of Alkenes**

The absolute configuration of any alkene can be determined using the *E/Z* system. The *E/Z* system uses the priority rules used for assigning *R/S* to chiral centers. To assign the absolute configuration:

1. Divide the alkene at the double bond mentally or draw a line through the double bond to visually isolate the two ends of the double bond.
2. Assign priorities to each group attached to the double bond.
3. Compare the priorities. If the higher priority groups are coming off the same side of the double bond, then the configuration is *Z*. If the higher priority groups are coming off opposite sides of the double bond, then the configuration is *E*.

## 08: Conformational Analysis

### Chapter Summary

Constitutional isomers, stereoisomers, and conformational isomers are defined. The conformations of ethane are staggered and eclipsed. The conformations of butane are anti, eclipsed methyl-hydrogen, gauche, and eclipsed. The bond angles of the cycloalkanes are given. Cyclohexane has the conformations of chair, boat, and twist-boat. The carbons in cyclohexane can be equatorial or axial.

### Tutorial Features

- Concept map showing inter-connections of concepts.
- Definition slides introduce terms as they are needed.
- Examples given throughout to illustrate how the concepts apply.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

#### Basic Concepts

- Constitutional Isomers
- Stereoisomers
- Conformational Isomers

#### Conformations of Ethane

- Staggered
- Eclipsed

#### Conformations of Butane

- Anti
- Eclipsed Methyl-Hydrogen
- Gauche
- Eclipsed

#### Bond Angles of Cycloalkanes

#### Conformations of Cyclohexane

- Chair
- Boat
- Twisted Boat

### Chapter Review

#### Basic Concepts

Conformational analysis deals with the shapes that molecules can adopt by rotations about single bonds. These structures are called conformational isomers or conformers. The following isomers cannot interconvert between each other without breaking bonds. Constitutional isomers have the same formula, but different connectivity. Stereoisomers have the same formula, the same connectivity, but different arrangement in space. Conformational isomers are interconvertible isomers of the same molecule that result from

rotations of single bonds. They interconvert constantly and are not separable. Conformations of alkanes can best be viewed using either Newman projections or sawhorse representations. A Newman Projection is an end-on view of 2 carbons attached by a sigma bond. The front carbon is shown as the intersection of 3 bonds and the rear carbon is shown as a circle. The substituents are attached accordingly.

#### **Conformations of Ethane**

Ethane can adopt either staggered or eclipsed conformations. Staggered is the lowest energy conformer, with the hydrogens as far away from each other. Eclipsed is the highest energy conformer and the least stable. It is 3 kcal higher in energy than the staggered form due to repulsion between electrons in C-H bonds.

#### **Conformations of Butane**

As butane rotates about its sigma bond, four distinct conformational possibilities exist. Staggered, or anti, where the methyl groups are farthest apart; eclipsed methyl-H interactions; gauche, where the methyl groups are adjacent; and eclipsed, or syn, where the methyl groups are eclipsed.

#### **Cycloalkanes**

The interior angles of cycloalkanes deviate from the tetrahedral so strain develops. Cyclopropane has a bond angle of  $60^\circ$ ; Cyclobutane has a bond angle of  $90^\circ$ ; Cyclopentane has a bond angle of  $108^\circ$ ; Cyclohexane has a bond angle of  $109.5^\circ$ .

#### **Conformations of Cyclohexane**

Cyclohexane's Newman Projection illustrates the staggered, low energy conformation that the chair form results. In addition to the chair, cyclohexane can also adopt the boat form by flipping one hydrogen up. This form is higher in energy due to steric and eclipsing strain. By twisting the boat, cyclohexane adopts yet another form, the twist-boat, a result of relieving some of the boat's strain. Cyclohexane's carbons have two substitution positions, axial and equatorial. The axial is vertical and equatorial is parallel to the adjacent C-C bond in the chair.

## 09: Saturated Hydrocarbons

### Chapter Summary

Now that the student has learned the basics of organic chemistry in the first six tutorials, the student will begin learning about the more specific aspects of each functional group—their properties, uses and reactions. In this, the seventh tutorial, the physical properties, uses, structures, nomenclature, and reactions of alkanes, cycloalkanes, and alkyl halides are examined.

### Tutorial Features

- Concept map showing interconnections of new concepts in this tutorial and those previously introduced.
- Definition slides introduce terms as they are needed.
- Visual representation of basic concepts.
- Step by step mechanisms of key reactions which show the movement of the electrons in the reaction.
- Color coded atoms in examples to enable the reader to better follow the action.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

#### Definitions

- Hydrocarbons
- Alkanes
- Cycloalkanes
- Alkyl halides

#### Properties and Uses of Alkanes and Cycloalkanes

- Properties
- Structure and conformations
- Uses

#### Properties and Uses of Alkyl Halides

- Properties
- Uses

#### Alkane and Cycloalkane Nomenclature

- IUPAC nomenclature
- Common nomenclature

#### Nomenclature of Alkyl Halides

- IUPAC nomenclature
- Common nomenclature

#### Reactions of Alkanes

- Combustion
- Cracking
- Halogenation

## Chapter Review

### Hydrocarbons

Organic compounds that contain only carbons and hydrogens.

### Alkanes

Non-cyclic hydrocarbons; simplest functional group.

### Cycloalkanes

Cyclic hydrocarbons.

### Alkyl Halides

Alkanes or cycloalkanes that contain a halogen atom(s).

### Hydrophobic

Literally 'water hating'. Often used to describe molecules or parts of molecules that will not dissolve in water.

### Eclipsed Conformation

Describes a molecular conformation where the atoms attached to one carbon line up with the atoms attached to an adjacent carbon (*i.e.* the dihedral angle is 0 degrees.).

### Staggered Conformation

Describes a molecular conformation where the atoms attached to one carbon are as far away from the atoms attached to an adjacent carbon atom. Staggered conformations are more stable than eclipsed conformations.

### Gauche Conformation

Describes a molecular conformation where two observed atoms on adjacent carbons are 60 degrees apart.

### Anti Conformation

Describes a molecular conformation where two observed atoms on adjacent carbons are 180 degrees apart.

### Chair Conformation

Describes a molecular conformation of cyclohexane where the hydrogens on the ring are the furthest apart. This is the most stable conformer of cyclohexane.

### Boat Conformation

Describes a molecular conformation of cyclohexane where the hydrogens are very close to each other. This is the least stable conformer of cyclohexane.

### Alkane and Cycloalkane Nomenclature

The student is reintroduced to alkane nomenclature, both IUPAC and common, in this tutorial. In addition, new rules for cycloalkanes are covered. The following are the IUPAC rules for naming cycloalkanes:

1. Number the cycloalkane so that the lowest possible combination of numbers are used for the substituents.

- If the compound contains an aliphatic ring and a chain, the parent compound is the one with the most carbons.

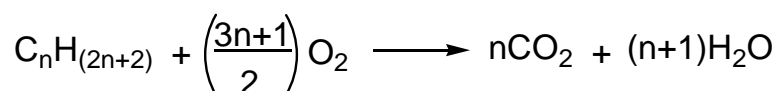
The common rules for naming cycloalkanes:

- Use the common prefixes as needed.
- List substituents alphabetically in front of the cycloalkane name.

### Key Reactions of Alkanes:

#### 1) Combustion of Alkanes

Converts alkanes to carbon dioxide and water. To determine what the balanced reaction equation would be for any alkane, one can use the following formula where n is the number of carbons in the alkane:



#### 2) Cracking of Alkanes

Cracking of hydrocarbons at high temperatures (usually a catalyst is also required) yields a mixture of smaller alkanes and alkenes.

#### 3) Halogenation of Alkanes

Alkanes can be halogenated in the presence of heat or light and  $\text{X}_2$ , where X is a halogen. Halogenation of alkanes occurs through a radical mechanism that can be divided into three different types of steps: initiation, propagation, and termination.

##### Initiation Step

The first step of a radical halogenation reaction of an alkane. In this step, the initial halogen radicals are formed by the interaction of a diatomic halogen with light or heat.

##### Propagation Step

The second part of a radical halogenation reaction of an alkane where radicals are both consumed and formed. In these steps, the initial halogen radical attacks an alkane and abstracts a hydrogen from it to form an alkyl radical and a molecule of HX. Next, the alkyl radical attacks a molecule of  $\text{X}_2$  to form a haloalkane and a halogen radical. One should always (1) have a radical on either side of the arrow in propagation steps and (2) reform the initial halogen radical at the end of the second propagation step.

##### Termination Step

The last step of a radical halogenation reaction where radicals are consumed. Two radicals will react to form a neutral, stable organic compound.

## 10: Unsaturated Hydrocarbons

### Chapter Summary

Background information for alkenes, alkynes, and dienes are described in terms of definitions, properties, uses, structures, and classification. The rules for the IUPAC nomenclature of alkenes, alkynes, and dienes are discussed. Alkenes are additionally named using cis and trans or E and Z. Alkenes are synthesized by the dehalogenation of alkyl halides and the dehydration of alcohols. Alkynes are synthesized by the dehydrohalogenation of vicinal and geminal dihalides. Alkyl halides are formed by the reaction of alkenes with hydrogen halides. Alkenes are halogenated to give dihaloalkanes. Alkenes are hydrated to give alcohols. Reduction of alkenes give alkanes. Alkynes react with hydrogen halides to give dihaloalkanes or with halogens to give tetrahaloalkanes. Hydrogenation of alkynes give alkanes. Alkenes are polymerized. Alkenes are oxidized to diols with potassium permanganate or to aldehydes and / or ketones with ozone. Alkynes are oxidized to diketones with potassium permanganate or to carboxylic acids with ozone.

### Tutorial Features

- Concept map showing inter-connections of concepts.
- Definition slides introduce terms as they are needed.
- Examples given throughout to illustrate how the concepts apply.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

#### Background Information for Alkenes, Alkynes, and Dienes

Definitions

Properties

Uses

Structure

Classification

#### Nomenclature of Alkenes, Alkynes, and Dienes

IUPAC

Cis and Trans

E and Z

#### Synthesis of Alkenes

Dehalogenation of Alkyl Halides

Dehydration of Alcohols

Products of Elimination Reactions

#### Synthesis of Alkynes

Dehydrohalogenation of Vicinal Dihalides

Dehydrohalogenation of Geminal Dihalides

#### Reactions of Alkenes

Definitions

Addition of Hydrogen Halides

- Halogenation
- Hydration
- Hydrogenation
- Reactions of Alkynes
  - Addition of Hydrogen Halides
  - Halogenation
  - Hydrogenation
- Polymerization of Alkenes
  - Definitions
  - Examples
- Oxidation of Alkenes and Alkynes
  - Potassium Permanganate Oxidation
  - Ozonolysis

## Chapter Review

### Background for Alkenes, Alkynes, and Dienes

Alkenes contain carbon-carbon double bonds. Alkynes contain carbon-carbon triple bonds. Dienes contain more than one carbon-carbon double bond. Alkenes, alkynes, and dienes are less dense than water, are nonpolar, and have boiling points and melting points similar to alkanes. The carbon in an alkene is  $sp^2$ , has a bond angle of  $120^\circ$ , and a trigonal planar shape. A carbon-carbon double bond contains one sigma bond and one pi bond. No rotation is possible around a carbon-carbon double bond. The carbon in an alkyne is  $sp$ , has a bond angle of  $180^\circ$ , and a linear shape. A carbon-carbon triple bond contains one sigma bond and two pi bonds. In dienes, allenes contains two double bonds that share a carbon. Conjugated dienes have double bonds that alternate with single bonds. Isolated dienes have double bonds that are separated by two or more single bonds. In an unsubstituted alkene, no alkyl groups are attached to a carbon-carbon double bond. In a monosubstituted alkene, one R group is attached to the carbon-carbon double bond. In a disubstituted alkene, two alkyl groups are attached to the carbon-carbon double bond. In a trisubstituted alkene, three alkyl groups are attached to the carbon-carbon double bond. In a tetrasubstituted alkene, four alkyl groups are attached to the carbon-carbon double bond. A terminal alkyne contains at least one hydrogen attached to the carbon-carbon triple bond. An alkyne that is not terminal contains two alkyl groups attached to the carbon-carbon triple bond.

### Nomenclature of Alkenes, Alkynes, and Dienes

Circle the longest continuous carbon chain as the parent compound. Use  $\text{ene}$  for alkene, and  $\text{yne}$  for alkyne. Number from whichever end that gives the lowest possible number for the multiple bonds. Name and number substituents. If both a double bond and a triple bond are present, number from whichever end that gives the lowest possible number for the multiple bonds. If the double bond and a triple bond are equal distance, then the double bond has priority over the triple bond. Name compounds with a double bond and a triple bond as enyne, giving positions of the multiple bonds. OH has priority over double and triple bonds. Cis has the same group on the same side. Trans has the same group on opposite sides. In the Cahn-Ingold-Prelog rules, Z has the highest ranking group on the same side and E has the highest ranking group on opposite sides. Rank the first atoms directly attached to the carbon-carbon double bond. The atom with the highest atomic number has the highest ranking. If the priority cannot be determined by Rule 1, then compare the next group of atoms. Double bonds are duplicated and triple bonds are triplicated, with imaginary atoms.



**Synthesis of Alkenes**

Alkyl halides are dehydrohalogenated with base to form alkenes. Alcohols are dehydrated with heat and acid to form alkenes. The product with the most number of carbons attached to the carbon-carbon double bond is formed in the higher yield.

**Synthesis of Alkynes**

Vicinal dihalides are dehydrohalogenated twice with base to form alkynes. Geminal dihalides are dehydrohalogenated twice with base to form alkynes.

**Reactions of Alkenes**

In Markovnikov addition, H of HZ adds to carbon with most hydrogens directly attached; the more stable carbocation intermediate is formed. In anti addition, the groups add on opposite sides of the double bond. In syn addition, the groups add on the same side of the double bond. A regioselective reaction is a reaction in which one of two possible isomers predominates. A regiospecific reaction is a reaction in which one of two possible isomers is formed exclusively. An hydrogen halide adds across a double bond to form an alkyl halide, via Markovnikov addition. Halogen adds across a double bond to form a dihaloalkane, with anti addition. Water adds across a double bond to produce an alcohol, via Markovnikov addition. Hydrogen adds across a double bond, via syn addition, to form an alkane.

**Reactions of Alkynes**

Hydrogen halide adds across a triple bond, via Markovnikov addition and with anti or syn addition, to form dihaloalkanes. Halogen adds across a triple bond to form a tetrahaloalkane. Hydrogen adds across a triple bond to make an alkane.

**Polymers of Alkenes**

Ethylene is polymerized to polyethylene, which is used for bags, films, and bottles. Propylene is polymerized to polypropylene, which is used for plastics. Styrene is polymerized to polystyrene, which is used for plastics, plastic cups, and foam insulation. Methyl  $\alpha$ -methacrylate is polymerized to polymethyl  $\alpha$ -methacrylate, which is used for plexiglass and Lucite paints. Acrylonitrile is polymerized to polyacrylonitrile, which is used as Orlon or Acrilan fibers. Tetrafluoroethylene is polymerized to polytetrafluoroethylene, which is used as Teflon. Vinyl chloride is polymerized to polyvinyl chloride, which is used in plastics, films, and plumbing. Vinylidene chloride is polymerized to polyvinylidene chloride, which is used in Saran.

**Oxidation Reactions of Alkenes and Alkynes**

Potassium permanganate oxidizes alkenes to diols, with syn addition. Ozone oxidizes alkenes to aldehydes and / or ketones. Potassium permanganate oxidizes alkenes to diketones. Ozone oxidizes alkynes to carboxylic acids.

## 11: Aromatic Compounds and Aromaticity

### Chapter Summary

Kekule proposed the structure of benzene in 1865. The carbons in benzene are  $sp^2$  hybridized, have a bond angle of  $120^\circ$ , and have a trigonal planar shape. The equation for Huckel's rule is given. The criteria for aromatic, antiaromatic, and not aromatic are described. The special names for the monosubstituted benzenes are listed. The rules for the nomenclature of aromatic compounds are described. Ortho, meta, and para definitions are given. The structures of anthracene, naphthalene, and phenanthrene are drawn out. The mechanism for electrophilic aromatic substitution is discussed, along with specific examples of other examples. Halogenation of benzene produces halobenzene. Nitration of benzene gives nitrobenzene. Sulfonation of benzene yields benzenesulfonic acid. The Friedel-Craft alkylation of benzene gives alkylbenzene. The Friedel-Craft acylation of benzene produces a ketone.

### Tutorial Features

- Concept map showing inter-connections of concepts.
- Definition slides introduce terms as they are needed.
- Examples given throughout to illustrate how the concepts apply.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

#### Background Information for Aromatic Compounds

- History Lesson
- Structure of Benzene
- Drawing Benzene
- Determining Aromaticity

#### Nomenclature of Aromatic Compounds

- Special Names
- IUPAC Nomenclature
- Disubstituted Benzene Derivatives
- Aromatic Fused Rings

#### Reactions of Aromatic Compounds

- Electrophilic Aromatic Substitution
- Halogenation
- Nitration
- Sulfonation
- Friedel-Craft Alkylation
- Friedel-Craft Acylation

## Chapter Review

### Background for Aromatic Compounds

Kekule proposed the structure of benzene in 1865. The carbons in benzene are  $sp^2$  hybridized, have a bond angle of  $120^\circ$ , and have a trigonal planar shape. Benzene can be drawn with all carbons and hydrogens, with just lines, or using a circle in the ring.

### Aromaticity, Huckel=s rule

Pi electrons are counted as follows: each double bond counts as two pi electrons, each + charge counts as zero pi electrons, each  $\pi$  charge counts as two pi electrons, each radical counts as one pi electron. Set the total number of pi electrons as equal to  $4n + 2$ ; solve for n. If the compound is aromatic, then it is cyclic with a continuous ring of overlapping p orbitals and n equals a whole number. If the compound is antiaromatic, then it is cyclic with a continuous ring of overlapping p orbitals, but n does not equal a whole number. If the compound is not aromatic, then it is noncyclic or is cyclic without a continuous ring of overlapping p orbitals.

### Nomenclature of Aromatic Compounds

$C_6H_5CH_3$  is named toluene.  $C_6H_5OH$  is named phenol.  $C_6H_5NH_2$  is named aniline.  $C_6H_5OCH_3$  is named anisole.  $C_6H_5CH=CH_2$  is named styrene. A benzene with an aldehyde group is named benzaldehyde. A benzene with a methyl ketone group is called acetophenone. A benzene with a carboxylic acid group is named benzoic acid. The benzene is the parent compound. Number the ring so that the groups have the lowest possible numbers. If a special name is used for a benzene derivative, then that group is in position one; then number the other groups. Ortho means that the two groups are on adjacent carbons or on the 1,2 positions. Meta means that the two groups are separated by one carbon or on the 1,3-positions. Para means that the two groups are on opposite ends or on the 1,4-positions. The fused ring structures of anthracene, naphthalene, and phenanthrene are drawn out.

### Reactions of Aromatic Compounds

Benzene is halogenated with bromine and iron (III) bromide; chlorine and aluminum chloride; or iodine and nitric acid to give a halobenzene. Nitration of benzene with nitric acid, in the presence of sulfuric acid, produces nitrobenzene. Benzene is sulfonated with sulfur trioxide, in the presence of sulfuric acid, to yield benzenesulfonic acid. In Friedel-Craft alkylation, benzene reacts with aluminum chloride and alkyl halide to form an alkylbenzene. In Friedel-Craft acylation, benzene reacts with aluminum chloride and an acid halide to form a ketone.

## 12: Alcohols and Ethers

### Chapter Summary

Alcohols and ethers are both oxygen containing functional groups. In this tutorial, the student will learn about the structures and properties of each functional group. The IUPAC nomenclature of alcohols and ethers will also be re-introduced. The different reactions used to synthesis alcohols and ethers will be covered as will the reactions each functional group undergoes.

### Tutorial Features

- Concept map showing interconnections of new concepts in this tutorial and those previously introduced.
- Definition slides introduce terms as they are needed.
- Step by step mechanisms of key reactions which show the movement of the electrons in the reaction.
- Color coded atoms in examples to enable the reader to better follow the action.
- Visual representation of basic concepts.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

#### Background Information for Alcohols and Ethers

Definitions

Properties

Uses

Classification of alcohols

#### Nomenclature for Alcohols and Ethers

IUPAC nomenclature

Common nomenclature

#### Physical Properties of Alcohols

Hydrogen bonding

Boiling points of alcohols

Water solubility of alcohols

Acidity of alcohols

#### Synthesis of Alcohols

From alkenes

From alkyl halides

From organometallic reagents reacting with aldehydes and ketones

From reduction of aldehydes and ketones

#### Reactions of Alcohols

Formation of alkoxide ions

Formation of alkyl halides

Dehydration

Oxidation

Esterification

Pinacol rearrangement

Preparation of leaving groups

Synthesis and Reactions of Ethers  
Williamson ether synthesis  
Cleavage of ethers

## Chapter Review

### **0° Alcohol**

Alcohol with no alkyl groups attached to the carbon bearing the hydroxyl group.

### **Primary Alcohol**

Alcohol with one alkyl group attached to the carbon bearing the hydroxyl group.

### **Secondary Alcohol**

Alcohol with two alkyl groups attached to the carbon bearing the hydroxyl group.

### **Tertiary Alcohol**

Alcohol with three alkyl groups attached to the carbon bearing the hydroxyl group.

### **Phenol**

Alcohol where the hydroxyl group is attached to a benzene ring.

### **Nomenclature for Alcohols and Ethers**

The student is re-introduced to the IUPAC and common nomenclature rules used to name alcohols and ethers. Remember that ethers are named as an alkane with the -OR group given as a substituent.

### **Reactions Used to Synthesis Alcohols:**

#### **1) Hydration of Alkenes**

Alkenes react with water in the presence of acid to form alcohols.

#### **2) Formation from Alkyl Halides**

Alkyl halides react with a source of hydroxide to produce alcohols.

#### **3) Reaction of Organometallic Reagents with Aldehydes and Ketones**

Aldehydes and ketones react with organolithium reagents or Grignard reagents followed by treatment with an aqueous acid to produce alcohols.

#### **4) Reduction of Aldehydes and Ketones**

Aldehydes and ketones may be reduced to alcohols using several different reducing agents: hydrogen gas and Raney nickel, lithium aluminum hydride, or sodium borohydride.

### **Reactions of Alcohols:**

#### **1) Formation of Alkoxide Ions**

Alcohols are deprotonated with sodium or potassium metal to form an alkoxide ion. Hydrogen gas is a by product.

#### **2) Formation of Alkyl Halides**

(1) Alcohols react with hydrogen halides to displace the hydroxyl group and form alkyl halides. (2) Alcohols can react with phosphorus trihalides to produce alkyl halides. (3) Alcohols can react with thionyl chloride to produce alkyl chlorides.

### 3) Dehydration

Alcohols, when treated with acid and heat, will undergo elimination of the hydroxyl group to form alkenes.

### 4) Oxidation of Alcohols

(1) Primary alcohols are oxidized with PCC (pyridinium chlorochromate) to form aldehydes. (2) Primary alcohols are oxidized to carboxylic acids using several different oxidants: potassium permanganate, sodium hypochlorite, nitric acid, chromium trioxide, etc. (3) Secondary alcohols are oxidized to ketones using several different oxidants: potassium permanganate, sodium hypochlorite, nitric acid, chromium trioxide, PCC, etc.

Remember, tertiary alcohols can not be oxidized.

### 5) Esterification

Alcohols react with carboxylic acids in the presence of acid to form esters.

### 6) Pinacol Rearrangement

A reaction in which a diol is dehydrated to form a rearranged ketone product.

### 7) Preparation of Leaving Groups

Alcohols can be converted into better leaving groups by reacting them with sulfonyl chlorides to form alkyl sulfonates.

## Synthesis and Reactions of Ethers:

### 1) Williamson Ether Synthesis

Alkoxide ions will react with alkyl halides to form ethers.

### 2) Cleavage of Ethers

Ethers can be cleaved using hydrogen halides to form alkyl halides and alcohols. The alkyl group that comprises the alkyl halide is usually the least hindered alkyl group from the ether.

## 13: Aldehydes and Ketones

### Chapter Summary

Aldehydes and ketones are carbonyl containing functional groups with very interesting and useful chemistries. In this tutorial, the student will learn about the structure of these compounds, their keto-enol tautomerism, and the reactions they undergo. Additionally, the nomenclature rules for these groups will be reviewed. New functional groups will also be introduced and are summarized in a table at the end of this summary.

### Tutorial Features

- Concept map showing interconnections of new concepts in this tutorial and those previously introduced.
- Definition slides introduce terms as they are needed.
- Step by step mechanisms of key reactions which show the movement of the electrons in the reaction.
- Color coded atoms in examples to enable the reader to better follow the action.
- Visual representation of basic concepts.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

#### Background Information for Aldehydes and Ketones

Structure

Shape

Properties

$\alpha$ -Hydrogens

Keto-enol tautomerism

#### Nomenclature for Aldehydes and Ketones

IUPAC nomenclature

Common nomenclature

#### Synthesis of Aldehydes and Ketones

Oxidation of alcohols

Friedel-Crafts acylation of benzene

Ozonolysis of alkenes

From acid halides

#### Reactions of Aldehydes and Ketones

Reactions with organometallic reagents

Reduction to alcohols

Reduction to alkanes

Formation of imine derivatives

Oxidation

Acetal formation

Reactions at the  $\alpha$ -carbon

Acetoacetic ester synthesis

Aldol condensation

Haloform reaction

## Chapter Review

### $\alpha$ -Carbon

A carbon atom next to a carbonyl.

### $\alpha$ -Hydrogen

A hydrogen on an  $\alpha$ -carbon. These hydrogens are somewhat acidic due to the negative charge on the resulting enolate being delocalized by resonance.

### Keto-Enol Tautomerism

Process by which an aldehyde or ketone and its enol equilibrate.

### Nomenclature of Aldehydes and Ketones

The student is re-introduced to the IUPAC and common nomenclature rules applied to aldehydes and ketones that were originally covered in tutorial 6.

### Synthesis of Aldehydes and Ketones:

#### 1) Oxidation of Alcohols

- (1) Primary alcohols are oxidized with PCC (pyridinium chlorochromate) to form aldehydes.
- (2) Secondary alcohols can be oxidized with several different oxidants: potassium permanganate, sodium hypochlorite, nitric acid, PCC, chromium trioxide, etc.

#### 2) Friedel-Crafts Acylation of Benzene

Benzene will react with acid halides in the presence of aluminum trichloride to produce ketones.

#### 3) Ozonolysis of Alkenes

Alkenes are oxidized to aldehydes/ketones with ozone ( $O_3$ ). Whether one obtains aldehydes, ketones, or a mix of both depends on the substitution pattern of the alkene.

#### 4) Conversion from Acid Chlorides

- (1) Acid halides can be reduced with tri-tert-butyl lithium aluminum hydride to form aldehydes.
- (2) Acid chlorides react with dialkyl copper lithium reagents to form ketones.

### Reactions of Aldehydes and Ketones:

#### 1) Reaction with Organometallics

Aldehydes and ketones react with organolithium or Grignard reagents, followed by acidification, to produce alcohols.

#### 2) Reduction to Alcohols

Several different reducing agents can reduce aldehydes and ketones to alcohols: hydrogen and Raney nickel, lithium aluminum hydride, or sodium borohydride.

#### 3) Reduction to Alkanes

- (1) Aldehydes and ketones are reduced to alkanes with zinc-mercury amalgam ( $Zn(Hg)$ ) and hydrochloric acid. This is called the **Clemmenson reduction**.
- (2) Aldehydes and ketones are reduced to alkanes with hydrazine ( $NH_2NH_2$ ) and potassium hydroxide. This is called the **Wolff-Kishner reduction**.



**4) Formation of Imine Derivatives**

(1) Aldehydes and ketones react with ammonia, primary amines, and their derivatives in the presence of an acid catalyst to form imine derivatives.

**5) Formation of Enamines**

Secondary amines will react with aldehydes or ketones to form enamines. The  $\beta$ -carbon of an enamine is nucleophile and can react readily with primary and secondary alkyl halides and acid halides.

**6) Oxidation to Carboxylic Acids**

Aldehydes can be oxidized to carboxylic acids using several different oxidants: potassium permanganate, nitric acid, chromium trioxide, sodium hypochlorite, etc.

**7) Acetal Formation**

Aldehydes and ketones react with alcohols to form hemiacetals and acetals.

**Reactions at the  $\alpha$ -Carbon of Ketones and Aldehydes:****1) Reactions of Enamines**

Enamines, formed by the reaction of aldehydes or ketones with secondary amines, can act as nucleophiles and attack different electrophiles like alkyl halides and acid halides.

**2) Oxidative Cleavage of Cyclic Ketones**

Cyclic ketones can undergo oxidative cleavage at the  $\alpha$ -carbon via reaction with their enol forms.

**3) Acetoacetic Ester Synthesis**

$\beta$ -Keto esters contain acidic  $\alpha$ -hydrogens that can be deprotonated to form an enolate anion. The enolate, which is nucleophilic, can then be used to attack electrophiles. This type of reaction would form a new bond between the  $\alpha$ -carbon and the electrophile. In addition, the ester may be hydrolyzed to the  $\beta$ -keto acid and then decarboxylated to form a ketone product.

**4) Aldol Condensation**

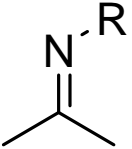
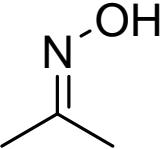
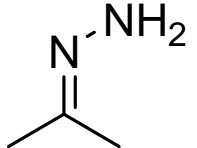
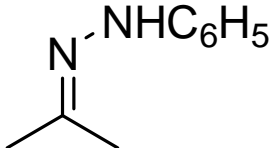
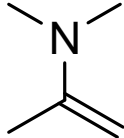
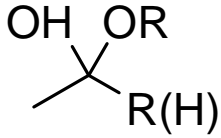
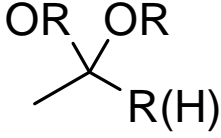
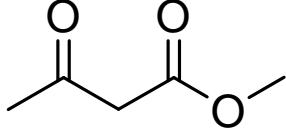
Condensation of two aldehydes or ketones that can be either base- or acid-catalyzed. The initial product of the aldol condensation is a  $\beta$ -hydroxyketone. The  $\beta$ -hydroxyketone will dehydrate in the presence of heat and an acid catalyst to form a  $\alpha, \beta$ -unsaturated ketone.

**5) Haloform Reaction**

A base catalyzed (usually a hydroxide base) halogenation of methyl ketones that proceeds via an enolate anion. If an excess of base is present, the trihalomethyl ketone, the initial product, will then undergo nucleophilic attack from the hydroxide ion to yield a haloform ( $\text{CHX}_3$ ) and a carboxylic acid.

**New Functional Groups Introduced in this Tutorial:**

Functional Group	Structure of Group
------------------	--------------------

Imine	
Oxime	
Hydrazone	
Phenylhydrazone	
Enamine	
Hemiacetal	
Acetal	
$\beta$ -Ketoesters	

## 14: Carboxylic Acids

### Chapter Summary

Carboxylic acids act not only as a functional group but also as the source for several other functional groups known collectively as acid derivatives. In this tutorial, the student will learn about the structure, acidity and other properties of carboxylic acids. The IUPAC nomenclature rules for naming acids are re-introduced. Finally, the different reactions used to synthesize acids and the reactions acids undergo will be examined.

### Tutorial Features

- Concept map showing interconnections of new concepts in this tutorial and those previously introduced.
- Definition slides introduce terms as they are needed.
- Step by step mechanisms of key reactions which show the movement of the electrons in the reaction.
- Color coded atoms in examples to enable the reader to better follow the action.
- Visual representation of basic concepts.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

#### Background Information for Carboxylic Acids

- Structure
  - Shape
  - Physical properties
- Acidity
  - Acidity of carboxylic acids
  - Resonance stability of the carboxylate anion
  - Inductive effects on acidity
- Nomenclature of Carboxylic Acids
  - IUPAC nomenclature
  - Common nomenclature
- Synthesis of Carboxylic Acids
  - Oxidation of primary alcohols
  - Oxidation of aldehydes
  - Carboxylation of Grignard reagents
  - Hydrolysis of nitriles
- Reactions of Carboxylic Acids
  - Reduction to primary alcohols
  - Conversion to acid halides
  - Esterification
  - Conversion to anhydrides
  - Decarboxylation

### Chapter Review

**Carboxylate Anion**

The anion formed with the acidic proton of a carboxylic acid is deprotonated. This anion is resonance stabilized.

**IUPAC Nomenclature Rules for Carboxylic Acids**

The rules for naming carboxylic acids, previously introduced in tutorial 6, are examined again.

**Reactions Used to Synthesize Carboxylic Acids:****1) Oxidation of Primary Alcohols**

Primary alcohols may be oxidized to the carboxylic acid using a number of different oxidants: nitric acid, sodium hypochlorite, potassium permanganate, chromium trioxide, etc.

**2) Oxidation of Aldehydes**

Aldehydes may be oxidized to the carboxylic acids using a number of different oxidants: nitric acid, sodium hypochlorite, chromium trichloride, etc.

**3) Carboxylation of Grignard Reagents**

Reaction of Grignard reagents with carbon dioxide followed by treatment with aqueous acid forms carboxylic acids.

**4) Hydrolysis of Nitriles**

Nitriles may be hydrolyzed with aqueous acid to form carboxylic acids.

**Reactions of Carboxylic Acids:****1) Reduction to Alcohols**

Acids may be reduced to primary alcohols using lithium aluminum hydride followed by treatment with aqueous acid.

**2) Conversion to Acid Halides**

Carboxylic acids react with thionyl chloride to form acid chlorides.

**3) Esterification**

Reaction of carboxylic acids with alcohols in the presence of acid forms esters.

**4) Conversion to Anhydrides**

Reaction of carboxylic acids with acid chlorides to form anhydrides.

**5) Decarboxylation**

When heated, carboxylic acids can undergo loss of carbon dioxide.

## 15: Acid Derivatives

### Chapter Summary

Acid derivatives are different functional groups that can all be synthesized directly from carboxylic acids. The different acid derivatives (acid halides, anhydrides, esters, amides) are introduced in this tutorial. The student will learn about their structure, relative reactivity, nomenclature, and reactions.

### Tutorial Features

- Concept map showing interconnections of new concepts in this tutorial and those previously introduced.
- Definition slides introduce terms as they are needed.
- Step by step mechanisms of key reactions which show the movement of the electrons in the reaction.
- Color coded atoms in examples to enable the reader to better follow the action.
- Visual representation of basic concepts.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

#### Background Information for Acid Derivatives

Structure

Shape

Properties

Relative reactivity of acid derivatives

#### Nomenclature of Acid Derivatives

Rules for acid halides

Rules for esters

Rules for anhydrides

Rules for amides

#### Reactions of Acid Halides

Hydrolysis

Conversion to esters

Conversion to amides

Reduction to alcohols

Reduction to aldehydes

Conversion to ketones

#### Reactions of Esters

Hydrolysis

Saponification

Transesterification

Reduction to alcohols

Conversion to amides

#### Reactions of Anhydrides

Hydrolysis

Conversion to esters

Conversion to amides  
Reactions of Amides  
Hydrolysis  
Hofmann Rearrangement  
Reduction to amines  
Dehydration

## Chapter Review

### Acid Derivatives

Functional groups that can be made directly from carboxylic acids.

### IUPAC Nomenclature Rules for Naming Acid Derivatives

The student is re-introduced to the IUPAC nomenclature rules for naming acid derivatives that were originally covered in tutorial 6.

### Reactions of Acid Halides

#### 1) Hydrolysis

Acid halides are hydrolyzed to carboxylic acids using water.

#### 2) Conversion to Esters

Acid halides will react with alcohols to form esters.

#### 3) Conversion to Amides

Amines will react with acid halides to form amides.

#### 4) Reduction to Alcohols

Acid halides can be reduced to form alcohols using lithium aluminum hydride.

#### 5) Reduction to Aldehydes

Using tri-tert-butyl lithium aluminum hydride, acid halides can be reduced to form aldehydes.

#### 6) Conversion to Ketones

Acid halides can be converted to ketones by using dialkyl copper lithium reagents.

### Reactions of Esters:

#### 1) Hydrolysis

Esters are hydrolyzed to carboxylic acids and alcohols using aqueous acid.

#### 2) Saponification

Base catalyzed hydrolysis of esters using a strong base to form the salt of a carboxylic acid and an alcohol.

#### 3) Transesterification

Reaction of an ester with an alcohol in the presence of an acid catalyst to form a new ester.

#### 4) Reduction to Alcohols

Esters react with lithium aluminum hydride to produce alcohols.

**5) Conversion to Amides**

Esters react with amines to yield amides and alcohols.

**Reactions of Anhydrides:****1) Hydrolysis**

Anhydrides can be hydrolyzed with water to form carboxylic acids.

**2) Conversion to Esters**

Anhydrides react with alcohols to produce esters and carboxylic acids.

**3) Conversion to Amides**

Anhydrides can be converted to amides and carboxylic acids using amines.

**Reactions of Amides:****1) Hydrolysis**

(1) Amides are hydrolyzed with aqueous acid to form carboxylic acids and ammonium ions.

(2) Amides can be hydrolyzed with base to form anions of carboxylic acids and amines.

**2) Hofmann Rearrangement**

Reaction in which amides are converted to a primary amine with one less carbon than the starting amide. The reaction is catalyzed by a strong base and diatomic bromine.

**3) Reduction**

Amides are reduced in the presence of lithium aluminum hydride to form amines.

**4) Dehydration**

Primary amides can be dehydrated with  $\text{POCl}_3$  or  $\text{P}_2\text{O}_5$  to form nitriles.

## 16: Keto Acids and Esters

### Chapter Summary

Keto acids and esters offer a large range of synthetic possibilities to a chemist. In this tutorial, the student will learn about their structure, their nomenclature, and the reactions they undergo. The student will also examine their keto-enol tautomerism and will learn how their tautomerism differs from that of a compound containing a single carbonyl functionality.

### Tutorial Features

- Concept map showing interconnections of new concepts in this tutorial and those previously introduced.
- Definition slides introduce terms as they are needed.
- Step by step mechanisms of key reactions which show the movement of the electrons in the reaction.
- Color coded atoms in examples to enable the reader to better follow the action.
- Visual representation of basic concepts.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

Background Information for Keto Acids and Esters

Definitions

Nomenclature

Acidity of the  $\alpha$ -hydrogen

Keto-enol tautomerism

Reactions of Keto Acids and Esters

Decarboxylation

Acetoacetic acid synthesis

### Chapter Review

#### $\beta$ -Keto Acid

Carboxylic acids with a carbonyl group two carbons away at the  $\beta$  position (carbon-3).

#### $\beta$ -Keto Ester

Esters with a carbonyl group two carbons away at the  $\beta$  position (carbon-3).

#### Nomenclature of Keto Acids and Esters

The IUPAC nomenclature rules for naming keto acids and esters are covered in this tutorial:

1. Keto acids are named as carboxylic acids. The ketone group is listed as a substituent using the prefix "oxo-".
2. Keto esters are named as esters. The ketone group is listed as a substituent using the prefix "oxo-".



**$\alpha$ -Hydrogen**

A hydrogen on the carbon between the carbonyls of a keto acid or ester. This type of hydrogen is acidic due to the resonance stabilization of the enolate resulting from deprotonation.

**Keto-Enol Tautomerism**

If at least one  $\alpha$ -hydrogen is present on the  $\alpha$ -carbon of a keto acid or ester, then the compounds will exist in equilibrium with their enol forms.

**Decarboxylation of  $\beta$ -Keto Acids**

A type of reaction that  $\beta$ -keto acids undergo, but not  $\beta$ -keto esters, where the carboxylic acid group of the molecule, when heated, is lost as a molecule of carbon dioxide. A ketone is the final product of this reaction.

**Acetoacetic Synthesis**

Previously covered in tutorial 10, "Aldehydes and Ketones," this reaction involved deprotonating the  $\alpha$ -carbon of a  $\beta$ -keto ester to form an enolate. The enolate anion acts as a nucleophile and attacks an electrophile forming a new carbon-carbon bond to the  $\alpha$ -carbon. One may isolate the alkylated  $\beta$ -keto ester or the ester product can then be hydrolyzed to form a carboxylic acid and then decarboxylated to form a ketone.

## 17: Amines

### Chapter Summary

Amines are one of the few functional groups that can act both as a nucleophile and base. In this tutorial, the student will learn about the structure of amines, their physical properties, and their basicity. In addition, the IUPAC and common nomenclature rules for naming amines are revisited. Finally, the reactions that form amines or use amines as a reagent are covered.

### Tutorial Features

- Concept map showing interconnections of new concepts in this tutorial and those previously introduced.
- Definition slides introduce terms as they are needed.
- Step by step mechanisms of key reactions which show the movement of the electrons in the reaction.
- Color coded atoms in examples to enable the reader to better follow the action.
- Visual representation of basic concepts.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

#### Background Information for Amines

- Classification of amines
- Shape
- Properties
- Uses

#### Nomenclature of Amines

- IUPAC nomenclature
- Common nomenclature
- Amine salts

#### Synthesis of Amines

- Reduction of nitro compounds
- Reduction of nitriles
- Reduction of amides
- Alkylation of amines
- Reductive amination of aldehydes and ketones

#### Reactions of Amines

- Reaction with alkyl halides
- Reaction with aldehydes and ketones
- Acylation
- Reaction with sulfonyl chlorides
- Hofmann elimination
- Reaction with nitrous acid

### Content Review

**Primary Amine**

An amine with one alkyl group attached to the nitrogen.

**Secondary Amine**

An amine with two alkyl groups attached to the nitrogen.

**Tertiary Amine**

An amine with three alkyl groups attached to the nitrogen.

**Quaternary Amine**

An amine with four alkyl groups attached to the nitrogen.

**IUPAC and Common Nomenclature for Amines**

The IUPAC and common nomenclature rules for amines are re-introduced in this tutorial. In addition, a new common nomenclature rule for amine salts are given: Amine salts are named as ammonium salts.

**Ways to Synthesize Amines:****1) Reduction of Nitro Compounds**

Nitro compounds (those containing  $-\text{NO}_2$ ) can be reduced using  $\text{H}_2/\text{catalyst}$  or  $\text{H}^+/\text{metals}$  to primary amines.

**2) Reduction of Nitriles**

Nitriles are reduced to primary amines with hydrogen and nickel.

**3) Reduction of Amides**

Amides are reduced to amines using lithium aluminum hydride followed by hydrolysis. The classification of the amine product (primary, secondary, or tertiary) depends on how many carbons were attached to the nitrogen in the amide.

**4) Reaction of Alkyl Halides with Amines**

Alkyl halides react with ammonia or amines to yield amines.

**5) Reductive Amination of Oximes**

Aldehydes and ketones react with hydroxylamine and acid to form oximes. Oximes can then be reduced to the amine using several different conditions: hydrogen and nickel; lithium aluminum hydride then  $\text{H}_3\text{O}^+$ , or zinc and hydrochloric acid.

**6) Reductive Amination of Imines**

Aldehydes and ketones react with primary amines and acid to form imines. Imines can then be reduced to the secondary amine using various conditions: hydrogen and nickel; or lithium aluminum hydride then  $\text{H}_3\text{O}^+$ .

**7) Reductive Amination of Enamines**

Aldehydes and ketones react with secondary amines and acid to form imines. Imines can then be reduced to the tertiary amine using sodium triacetoxyborohydride.

**Key Reactions of Amines:****1) Formation of Ammonium Salts**

Amines react with hydrogen halides to form ammonium salts.

### **2) Formation of Imines**

Aldehydes and ketones react with ammonia derivatives and in the presence of acid to form imine derivatives.

### **3) Formation of Amides**

Acid chlorides react with amines to form amides.

### **4) Sulfonamide Formation**

Sulfonyl chlorides react with amines to yield sulfonamides.

### **5) Hofmann Elimination**

Quaternary ammonium halides undergo  $\beta$ -elimination when treated with strong bases to form a tertiary amine and the less substituted alkene.

### **6) Formation of Arenediazonium Salts**

Primary aromatic amines react with nitrous acid ( $\text{Na}_2\text{NO}_2$ ) to form arenediazonium salts. These salts are extremely electrophilic so they react readily with various nucleophiles to form a wide range of products.

### **Sandmeyer Reaction**

Reaction of an arenediazonium salt with a copper salt.

## 18: Infrared and UV Spectroscopy

### Chapter Summary

Often in the laboratory, a chemist synthesizes a compound and needs to confirm its structure or is confronted with an unknown compound and needs to determine its structure. Techniques are available to chemists that allow them to determine the structure of a compound. This tutorial covers two such techniques called infrared spectroscopy and UV/Vis spectroscopy.

### Tutorial Features

- Concept map showing interconnections of new concepts in this tutorial and those previously introduced.
- Definition slides introduce terms as they are needed.
- Visual representation of basic concepts.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

#### Basic Information for Infrared

- Background
- Intensity of infrared absorptions
- Bonds with similar infrared absorptions
- Molecular vibrations
- Index of hydrogen deficiency
- Functional groups

#### Infrared Interpretation Trends

- Zones
- By functional groups

#### Infrared Absorption Frequency Tables

- Abbreviations
- Frequencies

#### Infrared Spectra Problem Solving

- Steps
- Examples

#### Basics of UV/Vis Spectroscopy

- Theory of UV/Vis spectroscopy
- Absorption of UV/Vis light
- Conjugation

### Chapter Review

#### Infrared Spectroscopy

Method of structure determination based upon the amount of infrared light absorbed by a compound.

#### Index of Hydrogen Deficiency

A calculation that gives the total number of pi bonds and rings present in a molecule from the molecular formula.

### **Infrared Interpretation Trends**

Similar functional groups have similar atoms and will absorb photons of similar energies. In an infrared spectrum, similar functional groups will predictably show absorbances in the same region of the spectrum. Because of this fact, it is possible to scan an IR spectrum and determine the functional groups present in a sample and from that determine the structure of the molecule.

### **Fingerprint Region**

Region of an IR spectrum ( $1450\text{-}400\text{ cm}^{-1}$ ) that contains many absorptions specific to a given molecule.

### **Electronic Spectrum**

The spectrum produced when an organic molecule absorbs light in the visible or ultraviolet region that results in an electronic excitation.

### **Electronic Transition**

The movement of a single electron from an occupied orbital to an unoccupied orbital.

### **HOMO**

Highest Occupied Molecular Orbital

### **LUMO**

Lowest Unoccupied Molecular Orbital

### **Beer-Lambert Law**

Law that states the absorption of UV radiation is dependent on the sample, the concentration of the sample, and the size of the sample. The mathematical representation of the law is below:

$$A = \epsilon cl$$

A = absorbance

$\epsilon$  = molar absorptivity

c = concentration of sample

l = path length

### **Molar Absorptivity**

Measure of how strongly the sample absorbs light at that wavelength.

### **Conjugation**

Alternating single and multiple bonds (either double or triple bonds). Conjugation decreases the energy gap between the HOMO and LUMO energy levels in a molecule.

## 19: NMR and Mass Spectrometry

### Chapter Summary

In the previous tutorial, the student learned about two techniques used by chemists to determine a molecule's structure. Two more techniques are introduced in this tutorial. The first technique, NMR spectroscopy, is a method of structure determination based on the relative position of hydrogens and carbons in spectra. The second technique, mass spectrometry, can help elucidate the molecular formula and structure of a compound by analyzing how the compound fragments after it is hit by electron beam.

### Tutorial Features

- Concept map showing interconnections of new concepts in this tutorial and those previously introduced.
- Definition slides introduce terms as they are needed.
- Visual representation of basic concepts.
- Color coded atoms in examples to enable the reader to better follow the action.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

#### Basic Information for NMR

- Background
- Theory
- Definitions
- Index of hydrogen deficiency

#### Proton NMR Spectroscopy

- Background information
- Splitting of signals
- Proton resonance frequencies tables
- Problem solving
- Examples

#### Carbon-13 NMR Spectroscopy

- Background information
- Carbon magnetic frequencies tables
- Problem solving
- Examples

#### Background Information for Mass Spectrometry

- History
- The mass spectrometer
- The molecular ion
- The base peak
- Isotopes and mass spectrometry

#### The Mass Spectrum

- Fragmentations of alkanes
- Fragmentations of alcohols
- Fragmentations of amines

- Fragmentations of ethers
- Fragmentations of aldehydes and ketones
- The McLafferty rearrangement
- Analyzing Mass Spectra
  - Guidelines for analysis
  - Sample spectra

## Chapter Review

### **Nuclear Magnetic Resonance (NMR) Spectroscopy**

Method of structure determination based on the relative positions of hydrogens and carbons in the spectra.

#### **Chemical Shift**

The difference in parts per million (ppm) between the frequency of TMS and the frequency of the observed atom.

#### **Tetramethylsilane (TMS)**

An internal standard for NMR spectroscopy that has a chemical shift of  $\delta 0.00$ .

#### **Integration**

The area under a peak that is proportional to the number of hydrogens that gave rise to the signal.

#### **Spin-Spin Splitting**

A splitting of signals into multiplets when the magnetic field of the proton is affected by protons on adjacent carbons.

#### **Coupling Constant**

Distance between the peaks of a multiplet.

#### **Proton NMR Spectroscopy**

Type of NMR spectroscopy based on the hydrogen nucleus. In  $^1\text{H}$  NMR, the number of signals equals the number of different types of protons present in the molecule. The chemical shift is indicative of the electronic environment of the observed proton and the splitting of the signal indicates the number of protons on adjacent carbons.

#### **Carbon-13 NMR Spectroscopy**

Type of NMR spectroscopy based on the carbon-13 nucleus. In  $^{13}\text{C}$  NMR, the number of signals equals the number of different types of carbons present. The chemical shift indicates the type of functional group the observed carbon is a part of and the splitting of the signal is determined by the number of hydrogens attached to the observed carbon.

#### **Mass Spectrometry**

An analytical tool used to determine the molecular formula and molecular structure for unknown organic compounds.

#### **Molecular Ion**

The species formed when the sample molecule loses one electron to become a radical cation. Also known as the parent peak.



**Base Peak**

The peak in a mass spectrum that is set to 100% relative abundance.

**McClafferty Rearrangement**

A rearrangement undergone by carbonyl compounds in mass spectrometry. In this rearrangement, the  $\gamma$  hydrogen is abstracted by the carbonyl resulting in the formation of an alkene and an enol.

## 20: Separations and Purifications

### Chapter Summary

As important as synthesizing compounds is in organic chemistry, the separation and purification of these compounds is just as important. There are several techniques that a chemist may use to purify compounds made in the laboratory. This tutorial covers techniques like distillation, extraction, chromatography, and recrystallization.

### Tutorial Features

- Concept map showing interconnections of new concepts in this tutorial and those previously introduced.
- Definition slides introduce terms as they are needed.
- Visual representation of basic concepts.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

#### Extractions

- Theory of extraction
- Liquid-liquid extraction
- Acid-base extraction

#### Distillation

- Boiling points
- Theory of distillation
- Simple distillation

#### Chromatography

- Theory of chromatography
- Column chromatography
- Gas-liquid chromatography
- Paper chromatography
- Thin-layer chromatography

#### Recrystallization

- Theory of recrystallization
- Solvent selection

### Chapter Review

#### Extraction

The process of selectively removing one or more components of a solid, liquid, or gaseous mixture into a separate phase.

#### Liquid-Liquid Extraction

An extraction where the components of a mixture are partitioned between two immiscible liquids.

#### Acid-Base Extractions

A type of extraction that is useful for separation of acidic or basic compounds from a mixture.

**Distillation**

A chemical technique used to separate a component of a mixture from less volatile components on the basis of boiling points.

**Boiling Point**

The temperature at which the vapor pressure of a liquid is equal to the atmospheric pressure.

**Chromatography**

The separation of components of a mixture based on their unequal distribution between two immiscible phases.

**Column Chromatography**

A form of solid-liquid adsorption chromatography.

**Eluant**

The solvent system used for chromatography.

**Gas-Liquid (GC) Chromatography**

A common analytical technique used for separating mixtures whose components may differ in boiling point by as little as 0.5 °C.

**Retention Time**

The elapsed time from injection of a mixture to detection of the desired component.

**Paper Chromatography**

A form of solid-liquid chromatography where the stationary phase is a piece of paper.

**Retention Factor (R<sub>f</sub> Factor)**

A physical constant for a compound that can be used for qualitative analysis by comparing the experimental value to standard values. It is calculated by dividing the distance the sample traveled up the chromatography paper by the distance the solvent traveled.

**Thin-Layer Chromatography (TLC)**

A form of solid-liquid chromatography where the stationary phase is either alumina or silica gel that has been deposited on a glass plate.

**Recrystallization**

Dissolution of a solid in an appropriate solvent at elevated temperatures and the subsequent reformation of the crystals upon cooling such that any impurities present are left in the solution.

**Dielectric Constant**

A measure of a solvent's polarity.

## 21: Organic Reactions

### Chapter Summary

Students will be introduced to more organic terminology in this tutorial with the aim that understanding the terms will translate to a better understanding of organic reactions. Reactions from previous tutorials are also reviewed here.

### Tutorial Features

- Concept map showing interconnections of new concepts in this tutorial and those previously introduced.
- Definition slides introduce terms as they are needed.
- Visual representation of basic concepts.
- Color coded atoms in examples to enable the reader to better follow the action.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

#### Terminology of Organic Reactions

Mechanism, stoichiometry, thermodynamics, kinetics

Transition state, activation energy, Hammond postulate

Kinetic versus thermodynamic control, reactive intermediate, catalyst, solvent effect

#### Reactions of Alkyl Halides

Substitution with nucleophiles to form other compounds

Elimination with KOH to form alkenes

Reaction with lithium to form alkyl lithiums

Reaction with magnesium to form Grignard reagents

#### Reactions of Alkenes

Addition of HX to form alkyl halides

Addition of H<sub>2</sub>O to form alcohols

Addition of X<sub>2</sub> to form dihaloalkanes

Addition of hydrogen to form alkanes

Oxidation with KMnO<sub>4</sub> to form diols

Oxidation with O<sub>3</sub> to form aldehydes and ketones

#### Reactions of Alkynes

Addition of 2 HX to give dihaloalkanes

Addition of 2 X<sub>2</sub> to give tetrahaloalkanes

Addition with 2 H<sub>2</sub> to give alkanes

Oxidation with KMnO<sub>4</sub> to give diketones

Oxidation with O<sub>3</sub> to give carboxylic acids

#### Reactions of Aromatic Compounds

Reaction with X<sub>2</sub> and catalyst to give ArX

Reaction with HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> to give ArNO<sub>2</sub>

Reaction with SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> to give ArSO<sub>3</sub>H

Reaction with RX and AlCl<sub>3</sub> to give ArR

Reaction with R(C=O)X and AlCl<sub>3</sub> to give ketones

#### Reactions of Amines

Reaction with RX, followed by loss of HX, to yield larger amines

- Reaction with HX, to yield ammonium salts
- Reaction with acid halides to yield amides
- Reaction with sulfonyl chlorides to yield sulfonamides
- Reactions of Alcohols
  - Reaction with metals to yield alkoxide ions
  - Reaction with HX,  $PX_3$ , or  $POCl_3$  to yield RX
  - Reaction with heat and acid to yield alkenes
  - Dihalides are treated with 2 KOH to yield alkynes
  - Oxidation
    - Reaction with  $RCOOH$  and acid to yield esters
- Reactions of Aldehydes and Ketones
  - Reduction to alcohols
  - Reduction to alkanes
  - Reaction with organometallic reagents to form alcohols
  - Reaction with primary amines to yield imines
  - Reductive amination to yield amines
  - Oxidation of aldehydes to carboxylic acids
- Reactions of Carboxylic Acids
  - Reduction to alcohols
  - Reaction with thionyl chloride to yield acid chlorides
  - Reaction with alcohols and acid to give esters
  - Reaction with acid halides to give anhydrides
- Reactions of Acid Halides
  - Hydrolysis to form carboxylic acids
  - Reaction with alcohols to form esters
  - Reaction with amines to form amides
  - Reduction to alcohols
  - Reduction to aldehydes
  - Reaction with  $R_2CuLi$  to form ketones
- Reactions of Esters
  - Reaction with water and acid to yield carboxylic acids and alcohols
  - Reduction to alcohols
  - Reaction with amines to yield amides and alcohols
- Reactions of Anhydrides
  - Hydrolysis of anhydrides to yield carboxylic acids
  - Reaction with alcohols to yield esters and carboxylic acids
  - Reaction with amines to yield amides and carboxylic acids
- Reactions of Amides
  - Reaction with aqueous acid to yield carboxylic acids and ammonium ions
  - Reaction with water and hydroxide ion to yield carboxylate anions and amines
  - Reduction to amines
  - Dehydration to nitriles

## Chapter Review

### Mechanism

Complete step-by-step description of the bond breaking and the bond forming steps of a reaction.

### Stoichiometry

The relationship between reactants and products in a chemical reaction.

**Thermodynamics**

The study of the energy changes that accompany the physical and chemical changes.

**Kinetics**

The study of the rates of chemical reactions.

**Transition State**

The energy state between reactants and products.

**Activation Energy**

The energy needed to initiate a chemical reaction.

**Hammond Postulate**

States the structure of a transition state is most similar to the structure of the stable species closest to it in energy.

**Kinetic versus Thermodynamic Control**

In a reaction, the kinetic product predominates at low temperatures while the thermodynamic product predominates at high temperatures.

**Reactive Intermediate**

A short lived species that is an intermediate in a chemical reaction.

**Catalyst**

A compound that increases the rate of reaction without being consumed.

**Solvent Effect**

The effect that a solvent has on the rate of reaction.

**Reactions Listed in Tutorial**

The reactions in this tutorial are from previous tutorials and are listed for review purposes.

## 22: Synthesis, Multistep and Retrosynthesis

### Chapter Summary:

Multistep synthesis is an important goal of organic chemistry as most molecules can not be made in just one reaction. Different types of multistep syntheses are covered in this tutorial as well as a problem solving process called retrosynthesis analysis that can be used to determine the best synthetic route to a target molecule.

### Tutorial Features

- Definition slides introduce terms as they are needed.
- Visual representation of basic concepts.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

#### Principles of Synthesis

- Definition of synthesis
- Total synthesis
- Methodology

#### Retrosynthesis

- Retrosynthetic analysis
- Disconnections
- Evaluation

### Chapter Review:

#### Synthesis

Purposeful execution of chemical reactions to get to a desired product.

#### Synthetic Intermediate

A compound that is a product of one reaction and a starting material for the next reaction.

#### Total Synthesis

Complete chemical synthesis of complex organic molecules from simple, commercially available precursors.

#### Linear Synthesis

A type of total synthesis where each reaction produces a synthetic intermediate that is used as a starting material for the next reaction.

#### Convergent Synthesis

A type of total synthesis where a set of synthetic intermediates are formed. These intermediates are then joined together to form the final product.

#### Methodology

The development of reactions and methods that give high yields and are reliable for a broad range of substrates.

**Retrosynthetic Analysis**

A problem-solving technique for transforming the structures of a synthetic target molecule to a sequence of progressively simpler molecules along a pathway that eventually leads to simple, commercially available compounds.

**Retrosynthesis**

A series of reactions that work backwards from a target molecule to the starting material.

**Synthon**

A structural unit within a molecule which is related to possible synthetic operations.

**Disconnections**

Strategic bonds in the target molecule that are potential synthetic linkages.



## 23: Organic Reaction Mechanisms

### Chapter Summary

Understanding reaction mechanisms in organic chemistry enables students to better predict the products obtained in a reaction. In this tutorial, more reaction terminology, mechanism and arrow drawing basics, and criteria for good reaction intermediates are covered. Several reactions from prior tutorials are reviewed in detail with particular attention paid to their mechanisms. The mechanistic details of these reactions illustrate the basic types of reactions common to organic chemistry.

### Tutorial Features

- Concept map showing interconnections of new concepts in this tutorial and those previously introduced.
- Definition slides introduce terms as they are needed.
- Step by step mechanisms of key reactions which show the movement of the electrons in the reaction.
- Color coded atoms in examples to enable the reader to better follow the action.
- Visual representation of basic concepts.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

#### Terminology in Mechanisms

Double headed arrows, heterolytic bond cleavage, heterogenic bond formation

Single headed arrows, homolytic bond cleavage, homogenic bond formation

Polar reactions

#### Substitution Reactions

$S_n1$  reactions

$S_n2$  reactions

#### Elimination Reactions

E1 reactions

E2 reactions

#### Mechanism of Addition Reactions

Mechanism for the addition of HX to alkenes

Mechanism for addition of halogens to alkenes

#### Nucleophilic Addition to Carbonyl Compounds

Reaction of a Grignard reagent with aldehydes

Reaction of aldehydes with primary amines

#### Electrophilic Aromatic Substitution

Mechanism of electrophilic aromatic substitution

Example

#### Acid-Base Reactions

Deprotonation

Protonation

#### Carbocation Mechanisms

1,2-Hydride shift

1,2-Alkyl shift

### Anion Mechanisms

Mechanism for the alkylation of carbonyl compounds with LDA

Mechanism for the addition of the hydride ion

### Radical Reactions

Halogenation of alkenes

### Mechanism Basics

Understanding mechanisms

### Arrow Drawing Skills

Basic arrow drawing skills for heterolytic bonds

Examples of nucleophiles

Basic arrow drawing skills for homolytic bonds

### Movement of Electrons with Arrows

An unshared electron pair becomes a shared electron pair

A shared electron pair becomes an unshared electron pair

A shared electron pair becomes another shared electron pair

### Intermediates

Formation of intermediates

Characteristics of good intermediates

Characteristics of unlikely intermediates

## Chapter Review

### Double Headed Arrow

Arrow used to show the movement of a pair of electrons.

### Heterolytic Cleavage

A type of bond breaking where one atom involved in the bond receives both electrons while the other atom receives no electrons.

### Heterogenic Bond Formation

Bond formation in which one reactant donates both electrons to form the bond.

### Single Headed Arrow

Arrow used to show the movement of one electron.

### Homolytic Bond Cleavage

A type of bond breaking in which each atom involved in the bond receives one electron.

### Homogenic Bond Formation

Bond formation in which each reactant donates an electron to form the bond.

### Polar Reaction

A reaction in which a nucleophilic species attacks an electrophilic species.

### S<sub>N</sub>1 Reaction

Substitution reaction in which a nucleophile attacks an electrophile displacing a leaving group. The reaction proceeds with first order of kinetics and through a carbocation intermediate.

### S<sub>N</sub>2 Reaction

Substitution reaction in which a nucleophile attacks an electrophile displacing a leaving group. The reaction proceeds with second order kinetics and is a concerted reaction.

**Protic Solvents**

Solvents that can participate in hydrogen bonding.

**Aprotic Solvents**

Solvents that can not participate in hydrogen bonding.

**Concerted Reactions**

Reactions in which all the bond breaking and formation occur in a single step. In contrast to a stepwise reaction involving intermediates.

**E1 Reaction**

Elimination reaction in which a base deprotonates an alkyl halide displacing a leaving group to form an alkene. The reaction proceeds with first order kinetics and through a carbocation intermediate.

**E2 Reaction**

Elimination reaction in which a base deprotonates an alkyl halide displacing a leaving group to form an alkene. The reaction proceeds with second order kinetics and is a concerted reaction.

**Deprotonation**

Reaction in which a base abstracts an acidic hydrogen in a molecule.

**Protonation**

Reaction in which a molecule gains a proton from an acid.

**1,2 Hydride Shift**

A carbocation rearrangement in which a hydrogen takes the electrons from the carbon-hydrogen bond it is involved in and moves to an adjacent carbon.

**1,2 Alkyl Shift**

A carbocation rearrangement in which an alkyl group takes the electrons from the carbon-carbon bond it is involved in and moves to an adjacent carbon.

## 24: Acid-Base Chemistry

### Chapter Summary

In this tutorial you will learn about the definitions of acids and bases including Arrhenius acids and bases, Brønsted-Lowry Theory, Lewis acids and bases. You will also learn about Conjugate acids and bases As well as Equilibria in acid-base reactions. Finally, we will look at molecular structure considerations including Resonance and Inductive effects.

### Tutorial Features

- Concept map showing inter-connections of concepts.
- Definition slides introduce terms as they are needed.
- Examples given throughout to illustrate how the concepts apply.
- A concise summary is given at the conclusion of the tutorial.

### Key Concepts

Definitions of acids and bases

Arrhenius acids and bases

Brønsted-Lowry Theory

Lewis acids and bases

Conjugate acids and bases

Equilibria in acid-base reactions

Molecular structure considerations

Resonance in acid-base chemistry

Inductive effects

### Chapter Review

#### Arrhenius

Acids increase  $H^+$ ; Bases increase  $OH^-$ .

#### Brønsted-Lowry

Acids donate protons; Bases accept protons.

#### Lewis

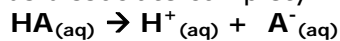
Acids accept a pair of electrons from Bases forming a new covalent bond.

#### Conjugate Acid-Base Pair

1. **Acid** that donates a proton becomes a **Conjugate Base**
2. **Base** that accepts a proton becomes a **Conjugate Acid**

#### Acid Strength

Strong acids dissociate completely in aqueous solution:



Weak acid dissociation is an equilibrium process. Stability of  $A^-$  is key to acid strength:

