# MCAT Organic Chemistry Rapid Learning Series Test-Prep Course Study Guide





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#### Introduction to MCAT Organic Chemistry

Organic chemistry is part of the two science sections of the new MCAT – Physical & Chemical Foundations and Biological & Biochemical Foundations. Its content mirrors the traditional two-semester organic chemistry course at university level. The best preparation is to comprehensively and sequentially study organic chemistry relevant to MCAT and place the focus on the weak areas of chemistry. Concept understanding and problem solving are the key to the mastery of organic chemistry.

Course Table of Contents

# **Core Unit #1 – The MCAT and the Basics of Organic Chemistry**

In this core unit, you will learn about the format of the MCAT and the basic concepts of organic chemistry. With these skills, you will form a solid foundation to understand organic chemistry and problem solving as it applies to the MCAT.

### **Chapter 01: The Guide to the MCAT Organic Chemistry**

Introduction to the MCAT Definition of the MCAT The MCAT test format Test scoring The individual sections The test day schedule Organic Chemistry on the MCAT Topics list Passage based questions Stand alone questions Test Preparation Strategies Time management Concept Mastery Practice Review **Test Taking Strategies** Overview Know the test Plan your attack Focus Choose the right answer Guessing Being SURE

#### **Chapter 02: The Covalent Bond**

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

#### Page | 3

Predicting molecular shape Structural formulas of heteroatoms Types of Carbon Molecules Stable, neutral molecules Carbanions Carbocations Radicals **Intramolecular Bond Interactions** Electronegativity Bond polarity Bonding Bond breaking Molecular Orbitals Sigma and pi bonds Hybridization Resonance Theory of resonance Delocalized electrons Intermolecular Forces London Dispersion forces Dipole-dipole forces Hydrogen bonding MCAT Strategy SURE method Practice problems

# **Chapter 03: Organic Compounds and Functional Groups**

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 Arrenhius Bronsted-Lowry Lewis Electron Pushing Electrons and mechanisms Resonance and delocalization MCAT Strategy SURE Method Practice problems

# **Chapter 04: Stereochemistry**

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 MCAT Strategy SURE method Practice problems

# Chapter 05: Organic Nomenclature I: How to Name Alkanes, Alkenes, Alkynes and Alkyl Halides

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 06: Organic Nomenclature II: How to Name Alcohols, Ethers, Aldehydes, Ketones, Amines and Carboxylic Acid Derivatives

**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

# **Core Unit #2 – Hydrocarbons and Alkyl Halides**

In this core unit, you will learn about hydrocarbons, molecules containing only carbon and hydrogen, and alkyl halides. You will study their properties, their synthesis, and the reactions these compounds undergo.

# Chapter 07: Alkanes, Cycloalkanes, and Alkyl Halides

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 MCAT Strategy SURE method Practice Problems

# Chapter 08: Unsaturated Hydrocarbons: Alkenes, Alkynes, Dienes, and Aromatics

Background Information for Alkenes, Alkynes, and Dienes Definitions Properties Uses Structure Classification of Alkenes Classification of Alkynes Nomenclature for Alkenes, Alkynes and Dienes **IUPAC** nomenclature Cis/Trans nomenclature for alkenes E/Z nomenclature for alkenes Synthesis of Alkenes Dehalogenation of alkyl halides Dehydration of alcohols Products of elimination reactions Zaitsev's rule Synthesis of Alkynes Dehydrohalogenation of vicinal dihalides Dehydrohalogenation of geminal dihalides Reactions of Alkenes Definitions Addition of hydrogen halides to alkenes Halogenation of alkenes Hydration of alkenes Hydrogenation of alkenes **Reactions of Alkynes** Addition of hydrogen halides to alkynes Halogenation of alkynes

Hydrogenation of alkynes Polymerization of Alkenes Definitions Examples Oxidation of Alkenes and Alkynes Potassium Permanganate Oxidation Ozonolysis Background Information for Aromatic Compounds Structure of benzene Drawing benzene Determining aromaticity Nomenclature for Aromatic Compounds Special names **IUPAC** nomenclature Disubstituted benzene derivatives Aromatic fused rings Reactions of Aromatic Compounds Electrophilic aromatic substitution Halogenation Nitration Sulfonation Friedel-Crafts alkylation Friedel-Crafts acylation MCAT Strategy SURE Method Practice problems

# **Core Unit #3 – Oxygen Containing Molecules**

In this core unit, you will learn about molecules that contain oxygen. You will study their properties, their synthesis, and the reactions these compounds undergo.

# **Chapter 09: Alcohols and Ethers**

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 MCAT Strategy SURE method Practice problems

# **Chapter 10: Aldehydes and Ketones**

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 MCAT Strategy SURE method Practice problems

# Chapter 11: Carboxylic Acids

Background Information for Carboxylic Acids Structure Shape Physical properties Acidity

Acidity of carboxylic acids

#### Page | 8

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 MCAT Strategy SURE method Practice problems

# **Core Unit #4 – Other Heteroatom Containing Compounds**

In this core unit, you will learn about compounds that contain heteroatoms such as oxygen, nitrogen, halogens or phosphorus. You will study their properties, their synthesis, and the reactions these compounds undergo.

# **Chapter 12: Acid Derivatives**

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 MCAT Strategy SURE method Practice problem

# **Chapter 13: Keto Acids and Esters**

Background Information for Keto Acids and Esters Definitions Nomenclature Acidity of the α-hydrogen Keto-enol tautomerism Reactions of Keto Acids and Esters Decarboxylation Acetoacetic acid synthesis

#### **Chapter 14: Amines**

**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

# **Chapter 15: Phosphorus Compounds**

#### **Phosphoric Acids**

Phosphoric acids Phosphoric anhydrides Phosphates Phosphate esters Reactions with Phosphorus Hydrolysis Phosphorus trihalides Wittig reaction MCAT Strategy SURE method Practice problems

# **Core Unit #5 – Molecular Structure and Spectra**

In this core unit, you will learn about the different spectroscopic techniques organic chemists use to determine molecular structure.

#### **Chapter 16: Absorption Spectroscopy**

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 MCAT Strategy SURE method Practice problems

# Chapter 17: NMR Spectroscopy and Mass Spectrometry

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 McClafferty rearrangement Analyzing Mass Spectra Guidelines for analysis Sample spectra MCAT Strategy SURE method Practice problems

# **Core Unit #6 – Separations and Purifications**

In this core unit, you will learn about the use of various separations and purifications in organic chemistry.

# **Chapter 18: Separations and Purifications**

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 MCAT Strategy SURE method Practice problems

# **Core Unit #7 – General Concepts in Organic Chemistry**

In this core unit, you will learn about general concepts used in organic chemistry including important definitions, arrow drawing rules, the different types of mechanisms, and multistep synthesis.

# **Chapter 19: Understanding Organic Reactions**

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  $H_2O$  to form alcohols Addition of  $X_2$  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  $X_2$  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  $X_2$  and catalyst to give ArX Reaction with  $HNO_3$  and  $H_2SO_4$  to give  $ArNO_2$ Reaction with  $SO_3$  and  $H_2SO_4$  to give  $ArSO_3H$ Reaction with RX and  $AlCl_3$  to give ArRReaction with R(C=O)X and  $AlCl_3$  to give ketones

#### **Reactions of Amines**

Reaction with RX, followed by lost 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<sub>3</sub>, or POCl<sub>3</sub> 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

Reactions of Aldenyues and Recones

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<sub>2</sub>CuLi 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 MCAT Strategy SURE method Practice problems **Chapter 20: Mechanisms of Organic Reactions** 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<sub>n</sub>1 reactions S<sub>n</sub>2 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 MCAT Strategy SURE method Practice problems **Chapter 21: Synthesis** Principles of Synthesis

Definition of synthesis Total synthesis Methodology Retrosynthesis Retrosynthetic analysis Disconnections Evaluation MCAT Strategy SURE method Practice problems

# **Core Unit #7 – Biological Molecules**

In this core unit, you will learn about the structure of common biological molecules and their roles in the body.

# **Chapter 22: Chemistry of Carbohydrates**

Carbohydrates Overview Classification of carbohydrates Monosaccharides Classification

Configuration Structure Reactions Derivatives Disaccharides Reducing sugars Nonreducing sugars Hydrolysis Polysaccharides Homopolysaccharides Heteropolysaccharides Glycoproteins Proteoglycans MCAT Strategy SURE method Practice problems

# **Chapter 23: Amino Acids and Proteins**

Amino Acids Structure Coding Classification Peptides Formation Classification Hydrolysis Proteins Classification Structure MCAT Strategy SURE method Practice problems

# **Chapter 24: Lipids**

Lipids Storage Membrane Terpenes Lipids and Membranes Overview Classification Storage Lipids Fatty acids Fats and oils Waxes Membrane Lipids Glycerophospholipids Sphingolipids Cholesterol Lipid Aggregates Micelles

Lipid Bilayers Liposomes Biomembranes Plasma membranes Role of lipids Membrane structure/Fluid Mosaic Model Lipoproteins Classification Structure and functions Eicosanoids Classification Prostaglandins' structure and functions Terpenes Structure Function MCAT Strategy SURE method Practice problems

# **01:** The Guide to the MCAT Organic Chemistry

#### **Tutorial Summary:**

The MCAT is a standardized exam that all students must take in order to gain admission to medical school. The MCAT consists of four sections, all of which are multiple-choice: chemical and physical, biological and biochemical, psychological and social, and critical reasoning. There is no more essay writing in the new test. There are two question formats found in the multiple choice sections. Passage questions contain a short reading section with related questions. These types of questions rely not only on information in the passage but they also rely on outside knowledge. Stand alone questions are without any supporting text and require only outside knowledge. You can improve your score on the MCAT by following the study suggestions outlined in this tutorial. The test taking and test preparation strategies can help greatly.

#### **Tutorial Features:**

- Detailed outline of test features, schedule, and contents.
- Concept map showing inter-connections of concepts introduced.
- 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.

#### Concepts Covered:

Introduction to the MCAT Definition of the MCAT MCAT test format Test scoring Schedule Physics and the MCAT Passage based questions Stand alone questions Test preparation strategies Time management Planning Studying hints Test taking strategies Answer selection hints

#### **Content Review:**

#### MCAT

The Medical College Admissions Test is a standardized exam required to gain admission to medical school.

#### **MCAT Courses**

The new four-sections MCAT requires seven college courses – general chemistry, organic chemistry, biochemistry, biology, physics, psychology and sociology.

### **Passage-Based Question**

It is a question relating to information in an accompanying passage. The answer may or may not be in the passage.

#### **Discrete Question**

It is a question that has a topic independent of a passage or other questions with four possible answer options.

#### **Test Sections**

(1) Chemical and physical foundations (2) Critical Analysis and Reasoning Skills (3) Biological and Biochemical Foundations (4) Psychological, Social and Biological foundations.

# **Organic Chemistry**

MCAT requires students to take two semesters of college-level organic chemistry for premed.

#### **Computer-based Test**

MCAT is 100% to be taken on computer with on-screen timer and but no calculator provided.

#### Registration

- The MCAT is offered multiple times a year.
- Register here: <u>http://www.aamc.org/mcat/</u>
- Plan ahead six months before taking the exam.

#### Scoring

Four sectional scores and one total score with midpoint

- Chem/Phys Section: 118-132 (midpoint = 125)
- Critical/Reasoning: 118-132 (midpoint = 125)
- Bio/Biochem 118-132 (midpoint = 125)
- Psy/Social 118-132 (midpoint = 125)
- Composite Score: 472-528 (midpoint = 500)

# Test Day Schedule (4 sections 10-min break each)

- Chem/Phys: 95 minutes, 59 questions.
- Critical/Reasoning: 90 minutes, 53 questions.
- Bio/Biochem: 95 minutes, 59 questions.
- Psy/Social: 95 minutes, 59 questions.

# 02: The Covalent Bond

#### Tutorial 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:**

- Step by step explanation of example problems: electronic configuration, Lewis structures, hybridization.
- 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.
- Section on applying the SURE method to the MCAT and relevant practice problems.

#### Concepts Covered:

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 Structural formulas of heteroatoms Types of Carbon Molecules Stable, neutral molecules Carbanions Carbocations Radicals Intramolecular Bond Interactions Electronegativity Bond polarity Bonding Bond breaking Molecular Orbitals Sigma and pi bonds Hybridization Resonance Theory of resonance Delocalized electrons Intermolecular Forces London Dispersion forces

Dipole-dipole forces Hydrogen bonding

#### Content 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:

Formal charge = [number of valence electrons] - [nonbonding electrons] - 1/2[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: Organic Compounds and Functional Groups**

#### Tutorial 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:**

- Examples and practice problems in each tutorial: the structure of functional groups, identifying functional groups in a molecule, acid-base theory, and electron pushing.
- 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.
- Section on applying the SURE method to the MCAT and relevant practice problems.

# Concepts Covered:

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

#### Content Review:

#### **Organic Chemistry**

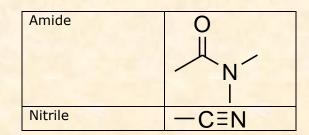
The study of the chemistry of carbon compounds.

#### **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	
	-C-C-
10000	ĪĪ
Alkene	
AIKEIIE	
	C=C
Alkyne	
Aromatic	
And the second state	
Alkyl Halide	R-X
Alcohol	R-OH
Ether	R-O-R
and the second second second	
Thiol	R-SH
Sulfide	R-S-R
Aldehyde	0
	Ŭ
	<u> </u>
Ketone	0
120 F. M. S.	
Acid Halide	0
171	
	X
Carboxylic Acid	0
	Ĭ
	OH
Ester	0
Anhydride	
Annyunde	
	/ `0/ \
Amine	
	N

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#### **Arrhenius Acid**

A substance that dissociates to give the hydronium ion  $(H_3O^+)$ .

#### **Arrhenius Base**

A substance that dissociates to give the hydroxide ion (<sup>-</sup>OH).

## **Bronsted-Lowry Acid**

A substance that can donate a proton  $(H^+)$ .

#### **Bronsted-Lowry Base**

A substance that can accept a proton  $(H^+)$ .

#### **Conjugate Acid**

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

#### **Conjugate Base**

A substance that results from the Bronsted-Lowry acid losing a proton (H<sup>+</sup>).

#### **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).

# **04: Stereochemistry**

#### Tutorial 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:**

- Examples and practice problems in each tutorial: drawing constitutional and configurational isomers, identifying chiral molecules, and assigning *R* and *S* configurations to chiral centers.
- 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.
- Section on applying the SURE method to the MCAT and relevant practice problems.

# Concepts Covered:

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

#### Content 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<sup>n</sup> 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.

- 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*.

# **05: Organic Nomenclature I**

#### Tutorial 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 and on the MCAT, the student is expected to be familiar with two systems of nomenclature: IUPAC nomenclature IUPAC nomenclature is a system of naming chemical and common nomenclature. 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:**

#### **Specific Tutorial Features:**

• Examples and practice problems in the tutorial: Naming alkanes, alkenes, alkynes, and alkyl halides using IUPAC and common nomenclature rules.

#### **Series 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.

#### Concepts Covered:

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

#### Content 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:

Alkyl Prefix
Meth-
Eth-
Prop-
But-
Pent-
Hex-
Hept-
Oct-
Non-
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-)	CH3-HTsz
Iso-	- son
Secondary (sec-)	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
Tertiary (tert-)	J.s.
Neo-	- Solar

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.

# **06: Organic Nomenclature II**

#### Tutorial 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:**

#### **Specific Tutorial Features:**

• Examples and practice problems in the tutorial: Naming alcohols, ethers, aldehydes, ketones, amines and carboxylic acid derivatives.

#### **Series Features:**

- 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.

#### Concepts Covered:

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

#### Content 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 alkanoic 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 alkanoic alkanoic 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.

# 07: Alkanes, Cycloalkanes, & Alkyl Halides

#### **Tutorial 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:**

### **Specific Tutorial Features:**

• Examples and practice problems in the tutorial: conformations of alkanes and cycloalkanes, nomenclature of alkanes, cycloalkanes and alkyl halides, and reactions of alkanes.

#### **Series 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.
- Section on applying the SURE method to the MCAT and relevant practice problems.

#### Concepts Covered:

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

# Content 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 described 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.
- 2. 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:

- 1. Use the common prefixes as needed.
- 2. 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:

$$C_nH_{(2n+2)} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O$$

# 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 presences of heat or light and  $X_2$ , 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  $X_2$  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.

# **08: Unsaturated Hydrocarbons**

#### Tutorial Summary:

Unsaturated hydrocarbons are compounds comprised of only carbon and hydrogen and contain pi bonds. Alkenes, alkynes, dienes, and aromatic compounds are included in this category. Their structures, properties, and uses are examined in this tutorial. The nomenclature of alkenes and alkynes are re-examined while new rules for naming aromatic compounds are introduced. The reactions to make alkenes and alkynes are covered as well as the reactions alkenes, alkynes, and aromatic compounds undergo. Pay close attention to which reactions proceed with Markovnikov addition, syn addition or anti addition.

### **Tutorial Features:**

# **Specific Tutorial Features:**

• Examples and practice problems in the tutorial: nomenclature, reactions and their mechanisms.

### **Series 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.
- Section on applying the SURE method to the MCAT and relevant practice problems.

# Concepts Covered:

Background Information for Alkenes, Alkynes, and Dienes

Definitions Properties Uses Structure Classification of Alkenes Classification of Alkynes Nomenclature for Alkenes, Alkynes and Dienes **IUPAC** nomenclature Cis/Trans nomenclature for alkenes E/Z nomenclature for alkenes Synthesis of Alkenes Dehalogenation of alkyl halides Dehydration of alcohols Products of elimination reactions Zaitsev's rule Synthesis of Alkynes Dehydrohalogenation of vicinal dihalides Dehydrohalogenation of geminal dihalides Reactions of Alkenes Definitions Addition of hydrogen halides to alkenes

Halogenation of alkenes Hydration of alkenes Hydrogenation of alkenes Reactions of Alkynes Addition of hydrogen halides to alkynes Halogenation of alkynes Hydrogenation of alkynes Polymerization of Alkenes Definitions Examples Oxidation of Alkenes and Alkynes Potassium Permanganate Oxidation Ozonolvsis Background Information for Aromatic Compounds Structure of benzene Drawing benzene Determining aromaticity Nomenclature for Aromatic Compounds Special names **IUPAC** nomenclature Disubstituted benzene derivatives Aromatic fused rings **Reactions of Aromatic Compounds** Electrophilic aromatic substitution Halogenation Nitration Sulfonation Friedel-Crafts alkylation Friedel-Crafts acylation

#### Content Review:

# Alkenes

Hydrocarbons that contain a carbon-carbon double bond.

# Alkynes

Hydrocarbons that contain a carbon-carbon triple bond.

### Dienes

Hydrocarbons that contain two carbon-carbon double bonds.

### **Classification of Alkenes**

Alkenes are classified based on the number of alkyl groups (or R groups) that are attached to the carbon-carbon double bond. There are five different classes of alkenes: unsubstituted (no R groups attached), monosubstituted, disubstituted, trisubstituted, and tetrasubstituted.

# **Classification of Alkynes**

Alkynes are classified based on their position in a chain. Terminal alkynes occur at the end of a chain and will have one hydrogen attached to the carbon-carbon triple bond. Internal alkynes occur within the chain and have two R groups attached to the carbon-carbon triple bond.

# Nomenclature of Alkenes, Alkynes, and Dienes

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The student is reintroduced to the IUPAC nomenclature for alkenes and alkynes and the *cis/trans* and E/Z systems for alkenes in this section. In addition, new rules for naming dienes or compounds containing both double and triple bonds are covered:

- 1. If both a double bond and a triple bond are present in the molecule, number from the end that gives the lowest possible numbers to the multiple bonds.
- 2. If a double bond and a triple bond are equal distance (meaning you get the same location numbers any way you number the chain), then the double bond has priority over the triple bond and should receive the lowest number.
- 3. Name compounds with a double bond and a triple bond using the suffix –enyne.
- 4. Remember, that alcohols have priority over double and triple bonds.

# Synthesis of Alkenes:

# 1) Dehydrohalogenation of Alkyl Halides

Alkyl halides can be dehydrohalogenated with a base (like potassium hydroxide) to form alkenes.

# 2) Dehydration of Alcohols

Alcohols may be dehydrated with heat and acid to form alkenes.

## Zaitsev's Rule

Rule that predicts the order of formation of alkenes. The product with the most number of carbons attached to the carbon-carbon double bond is formed in the higher yield.

### **Vicinal Dihalides**

A compound that contains two halogen atoms on adjacent carbon atoms.

#### **Geminal Dihalides**

A compound that contains two halogen atoms on the same carbon atom.

# Synthesis of Alkynes:

# 1) Dehydrohalogenation of Vicinal Dihalides

Vicinal dihalides are dehydrohalogenated twice with base to form alkynes.

### 2) Dehydrohalogenation of Geminal Dihalides

Geminal dihalides are dehydrohalogenated twice with base to form alkynes.

### **Markovnikov Addition**

The hydrogen of hydrogen halides will add to the carbon with the most hydrogens. This means the more stable carbocation intermediate is formed.

### Regioselective

Reaction in which one of two possible isomers predominates.

### Regiospecific

Reaction in which one of two possible isomers is formed exclusively.

# **Reactions of Alkenes:**

# 1) Addition of Hydrogen Halide

Hydrogen halides add across a double bond to form an alkyl halide. Proceeds with Markovnikov addition.

### 2) Halogenation of Alkenes

Diatomic halogens will add across a double bond to form a dihaloalkane. Proceeds with anti addition.

### 3) Hydration of Alkenes

Water adds across a double bond in the presence of an acid catalyst to produce an alcohol. Proceeds with Markovnikov addition.

## 4) Hydrogenation of Alkenes

Hydrogen in the presence of a metal (Pt, Pd, Ni) will add across a double bond to form an alkane. Proceeds with syn addition.

### **Reaction of Alkynes:**

### 1) Addition of Hydrogen Halide

Hydrogen halides add across a triple bond twice to form dihaloalkanes. Proceeds with Markovnikov addition and both syn and anti addition.

## 2) Halogenation

Diatomic halogens add across triple bonds twice to form tetrahaloalkanes. Proceeds with both syn and anti addition.

### 3) Hydrogenation

Hydrogen adds across triple bonds to form alkanes. Proceeds with syn addition.

#### Monomer

An alkene used to make polymers.

### Polymer

Large molecule made up of many monomers.

# **Oxidation Reactions of Alkenes and Alkynes:**

#### 1) Potassium Permanganate Oxidation

(1)  $KMnO_4$  will oxidize alkenes to diols. Proceeds with syn addition. (2)  $KMnO_4$  will oxidize alkynes to diketones. Proceeds with syn addition.

### 2) Ozonolysis

(1) Ozone oxidizes alkenes to aldehydes and/or ketones. The substitution pattern of the alkene determines whether aldehydes or ketones or a mix of both are obtained. (2) Ozone oxidizes alkynes to carboxylic acids.

### **Huckel's Rule**

Rule that can help one determine if a compound is aromatic. To determine aromaticity, set the equation 4n + 2 equal to the total number of pi electrons in a given compound. For aromatic compounds, n will equal a whole number.

### **Table of Benzene Derivatives**

The table below lists common benzene derivatives whose names are often used in nomenclature of aromatic compounds. The R indicates the group attached to the benzene ring in each specific compound:

Name of Benzene Derivative	R Group
Toluene	-CH <sub>3</sub>
Phenol	-OH
Aniline	-NH <sub>2</sub>
Anisole	-OCH <sub>3</sub>
Styrene	
Benzaldehyde	H H
Acetophenone	O CH <sub>3</sub>
Benzoic Acid	ОН

# **IUPAC Nomenclature of Aromatic Compounds:**

The student will be introduced to the IUPAC nomenclature rules for naming aromatic compounds.

- 1. The benzene is the parent compound.
- 2. Number the ring so that the substituents have the lowest possible numbers.
- 3. If a special name is used for a benzene derivative, then that group is in position one; then number the other groups.

### Ortho

Description of a benzene derivative when two substituents are on adjacent carbons.

### Meta

Description of a benzene derivative when two substituents are separated by one carbon.

# Para

Description of a benzene derivative when two substituents are on opposite ends of the ring.

# **Reactions of Aromatic Compounds:**

# **Electrophilic Aromatic Substitution**

Reaction in which a hydrogen on a benzene ring is substituted with an electrophile. The following reactions of aromatic compounds are all examples of electrophilic aromatic substitution.

# **Benzenonium Ion**

A carbocation formed from the attack of benzene onto an electrophile.

### 1) Halogenation

Benzene is halogenated in the presence of the following reagents: bromine and iron tribromide to give bromobenzene; chlorine and aluminum trichloride to give chlorobenzene; or iodine and nitric acid to give iodobenzene.

### 2) Nitration

Benzene can be nitrated with nitric acid in the presence of sulfuric acid to give nitrobenzene.

# 3) Sulfonation

Benzene is sulfonated with sulfur trioxide in the presence of sulfuric acid to give benzenesulfonic acid.

# 4) Friedel-Crafts Alkylation

Benzene reacts with aluminum trichloride and an alkyl halide to form an alkylbenzene. Due to the mechanism of this reaction, carbocation rearrangements are possible and must be considered when predicting the product.

# 5) Friedel-Crafts Acylation

Benzene reacts with aluminum trichloride and an acid halide to form a ketone.

# **09: Alcohols and Ethers**

### Tutorial 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:**

# **Specific Tutorial Features:**

• Examples and practice problems in each tutorial: Alcohol and ether nomenclature, mechanisms of alcohol and ether reactions.

# **Series 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.
- Section on applying the SURE method to the MCAT and relevant practice problems.

## Concepts Covered:

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

# Content Review:

# **0<sup>0</sup> 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

 Primary alcohols are oxidized with PCC (pyridinium chlorochromate) to form aldehydes.
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.

# **10: Aldehydes and Ketones**

### Tutorial 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:**

# **Specific Tutorial Features:**

• Examples and practice problems in each tutorial: Keto-enol tautomerism, aldehyde and ketone nomenclature, mechanisms of key reactions that aldehydes and ketones undergo.

# **Series 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.
- Section on applying the SURE method to the MCAT and relevant practice problems.

## Concepts Covered:

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

### Content Review:

### **α-Carbon**

A carbon atom next to a carbonyl.

# **α-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

Primary alcohols are oxidized with PCC (pyridinium chlorochromate) to form aldehydes.
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 α-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.

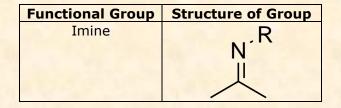
# (4) Aldol Condensation

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.

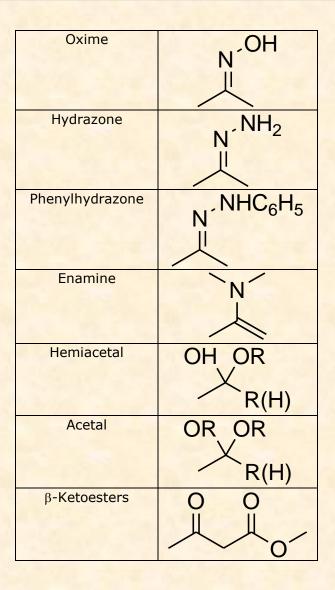
### (5) Haloform Reaction

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  $(CHX_3)$  and a carboxylic acid.

# New Functional Groups Introduced in this Tutorial:



# Page | 51



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# **11: Carboxylic Acids**

### Tutorial 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:**

- Examples and practice problems in each tutorial: Acidity trends of carboxylic acids, carboxylic acid nomenclature, mechanisms of key reactions that carboxylic acids undergo.
- 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.
- Section on applying the SURE method to the MCAT and relevant practice problems.

# Concepts Covered:

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

### **Content Review:**

### **Carboxylate Anion**

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

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# **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.

# **12: Carboxylic Acid Derivatives**

#### Tutorial 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:**

- Examples and practice problems in each tutorial: Carboxylic acid derivatives' nomenclature rules, mechanisms of key reactions the derivatives undergo.
- 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.
- Section on applying the SURE method to the MCAT and relevant practice problems.

### Concepts Covered:

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

# Content 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

Amides are hydrolyzed with aqueous acid to form carboxylic acids and ammonium ions.
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  $POCI_3$  or  $P_2O_5$  to form nitriles.

# **13: Keto Acids and Esters**

### Tutorial 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:**

- Examples and practice problems in each tutorial: nomenclature, reactions of keto acids and esters.
- 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.

# Concepts Covered:

Background Information for Keto Acids and Esters Definitions

Nomenclature Acidity of the α-hydrogen Keto-enol tautomerism Reactions of Keto Acids and Esters Decarboxylation Acetoacetic acid synthesis

# Content Review:

### **β-Keto Acid**

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

### **β-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-".

# α-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** β-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**

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.

# 14: Amines

### Tutorial 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:**

- Examples and practice problems in each tutorial: basicity of amines, nomenclature, reactions of amines.
- 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.

### Concepts Covered:

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  $-NO_2$ ) can be reduced using  $H_2$ /catalyst or  $H^+$ /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  $H_3O^+$ , 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  $H_3O^+$ .

# (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  $(Na_2NO_2)$  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.

# **15: Phosphorus Compounds & Reactions**

### **Tutorial Summary:**

Phosphorus containing compounds play an important role in the body and in synthesis. The structure, types, and uses of phosphorus compounds are examined in this tutorial. The important reactions phosphorus compounds participate in, such as the Wittig reaction, are also covered.

# **Tutorial Features:**

- Examples and practice problems in each tutorial: reactions with phosphorus trihalide compounds, Wittig reaction.
- 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.
- Section on applying the SURE method to the MCAT and relevant practice problems.

### Concepts Covered:

Phosphoric Acids Phosphoric acids Phosphoric anhydrides Phosphates Phosphate esters Reactions with Phosphorus Hydrolysis Phosphorus trihalides Wittig reaction

### Content Review:

# **Orthophosphoric Acid**

Another name for orthophosphoric acid is phosphoric acid. Phosphoric acid is a triprotic acid (has three acidic protons).

# ATP (Adenosine Triphosphate)

The principal energy carrying molecule of the body.

### **Key Reactions of Phosphorus Compounds:**

#### (1) Phosphorylation

The addition of a phosphoryl group to a molecule.

# (2) Hydrolysis of Phosphoric Acids

Reaction in which polyphosphoric acids are split into their individual phosphoric acid units.

# (3) Reaction of Alcohols with Phosphorus Trihalides

Reaction in which an alcohol is converted into an alkyl chloride or bromide using phosphorus trichloride or tribromide respectively.

# (4) Wittig Reaction

A method which uses phosphonium ylides for converting aldehydes and ketones to alkenes.

# **Phosphonium Ylide**

A phosphorus containing compound that has both negative and positive charges in it. It acts as a nucleophile in the Wittig reaction.

# Betaine

The first intermediate of the Wittig reaction that is the result of the ylide attacking the carbonyl compound.

# Oxaphosphetane

The second intermediate of the Wittig reaction that is the result of the betaine collapsing. Its formation is driven by the formation of the P-O bond.

# **16: Absorption Spectroscopy**

### Tutorial 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:**

- Examples in the tutorial: Index of Hydrogen Deficiency, predicting IR frequencies, solving IR spectra, Beer-Lambert Law, estimating  $\lambda_{max}$ .
- 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.
- Section on applying the SURE method to the MCAT and relevant practice problems.

Concepts Covered: 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 **Content 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 (1450-400 cm<sup>-1</sup>) 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.

### номо

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:

 $A = \varepsilon c I$ 

A = absorbance  $\varepsilon$  = molar absorptivity c = concentration of sample I = path length

# **Molar Absorptivity**

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

### Conjugation

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

# **17: NMR Spectroscopy & Mass Spectrometry**

### **Tutorial 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:** 

- Examples and practice problems in each tutorial: predicting the splitting for hydrogens in NMR spectroscopy, NMR problem solving, analyzing mass spectra.
- 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.
- Section on applying the SURE method to the MCAT and relevant practice problems.

# Concepts Covered:

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 McClafferty rearrangement Analyzing Mass Spectra Guidelines for analysis Sample spectra

# **Content 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 <sup>1</sup>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 <sup>13</sup>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.

# **18: Separations and Purifications**

#### Tutorial 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:**

• Examples in the tutorial: acid-base extractions

- 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.

### Concepts Covered:

### 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

# Content 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.

# **19: Understanding Organic Reactions**

### Tutorial 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:**

- Examples and practice problems in each tutorial:
- 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.
- Section on applying the SURE method to the MCAT and relevant practice problems.

# Concepts Covered:

# 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  $H_2O$  to form alcohols Addition of  $X_2$  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  $X_2$  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  $X_2$  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  $AICI_3$  to give ketones

# **Reactions of Amines**

Reaction with RX, followed by lost 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<sub>3</sub>, or POCl<sub>3</sub> 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<sub>2</sub>CuLi 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

# Content 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.

# **20: Mechanisms of Organic Chemistry**

#### **Tutorial 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:** 

• Examples and practice problems in each tutorial: reaction mechanisms.

- 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.
- Section on applying the SURE method to the MCAT and relevant practice problems.

## Concepts Covered:

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<sub>n</sub>1 reactions

S<sub>n</sub>2 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

#### Content 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 carbonhydrogen 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 carboncarbon bond it is involved in and moves to an adjacent carbon.

# **21: Multistep Synthesis & Retrosynthesis**

## Tutorial 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:**

## **Specific Tutorial Features:**

• Examples and practice problems in each tutorial: types of total synthesis, retrosynthetic analysis.

## **Series 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.
- Section on applying the SURE method to the MCAT and relevant practice problems.

## Concepts Covered:

Principles of Synthesis Definition of synthesis Total synthesis Methodology Retrosynthesis Retrosynthetic analysis Disconnections Evaluation

## Content 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.

# 22: Chemistry of Carbohydrates

#### Tutorial Summary:

Carbohydrates, made of carbon, hydrogen, and oxygen, are the most abundant biological molecules on earth. In this tutorial, the student will learn about the different types of carbohydrates and the established convention for classifying them, their functions and uses in our bodies, and their chirality. The reactions that carbohydrates can undergo will also be examined.

**Tutorial Features:** 

- Examples and practice problems in each tutorial: structures and reactions of carbohydrates.
- 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.
- Section on applying the SURE method to the MCAT and relevant practice problems.

## Concepts Covered:

Carbohydrates Overview Classification of carbohydrates Monosaccharides Classification Configuration Structure Reactions Derivatives Disaccharides Reducing sugars Nonreducing sugars Hydrolysis Polysaccharides Homopolysaccharides Heteropolysaccharides Glycoproteins

Proteoglycans

## Content Review:

#### Carbohydrates

Polyhydroxy aldehyde or polyhydroxy ketone or substance that yields such compounds on hydrolysis. They serve as energy storage molecules, structural elements in cells, and as starting materials for other organic molecules in the body.

## Monosaccharides (Simple Sugar)

Consists of a single polyhydroxy aldehyde or ketone unit.

## Disaccharides

Consists of two monosaccharide units.

## Oligosaccharides

Consist of three to twelve monosaccharide units.

#### Polysaccharides

Consist of more than twelve monosaccharide units. Also known as glycans.

## Aldose

Saccharide containing an aldehyde group.

## Ketose

Saccharide containing a ketone group.

## Epimers

Sugars that differ in configuration at a single asymmetric carbon.

## **Anomeric Carbon**

New stereocenter created in forming the cyclic form of a monosaccharide.

#### **Glycosidic Bond**

The linkage between two monosaccharide units.

#### **Reducing Sugars**

Aldoses or ketoses that are capable of being oxidized while they reduce cupric ions. The reducing action of monosaccharides depends on the free anomeric carbon in their molecules.

## **Key Reactions of Carbohydrates:**

#### (1) Benedict's Reaction

Reaction where a sugar reduces cupric ions to cuprous ions while being oxidized itself.

## (2) Oxidation/Reduction of Sugars

Reaction in which the terminal hydroxyl group of a sugar is oxidized to a carboxylic acid. The reverse of this oxidation reaction is a reduction reaction from the carboxylic acid to the alcohol.

#### (3) Glycoside Formation

Reaction in which the hydroxyl group of one saccharide reacts with the anomeric carbon of another saccharide to form a glycosidic linkage.

## (4) Hydrolysis of Glycosides

Reaction in which a glycoside is hydrolyzed into its component monosaccharides.

## Homopolysaccharides

Polysaccharides which contain only a single type of monosaccharide.

## Heteropolysaccharides

Polysaccharides which contain different types of monosaccharides or their derivatives.

## Glycoproteins

Proteins that are covalently associated with carbohydrates.

## Proteoglycans

Glycoproteins in which the carbohydrate content is mucopolysaccharides.

Mucopolysaccharides (Glycosaminoglycans) Large complexes of negatively charged heteropolysaccharides and made up of repeating disaccharide units.

# 23: Amino Acids & Proteins

#### Tutorial Summary:

Amino acids are the building blocks of proteins, a group of complex macromolecules that are essential for the proper functioning of organisms. The structure, types, and characteristics of amino acids are examined first in this tutorial. Two different conventions for coding amino acids will also be reviewed. Finally, the reactions used for constructing complex proteins from amino acid residues and the different levels of protein structure will be covered.

## **Tutorial Features:**

- Examples and practice problems in each tutorial: chirality of amino acids, coding of amino acids, classification of amino acids.
- 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.
- Section on applying the SURE method to the MCAT and relevant practice problems.

#### Concepts Covered:

Amino Acids

Structure Coding Classification Peptides

> Formation Classification Hydrolysis

#### Proteins

Classification Structure

## Content Review:

## **Amino Acids**

Building blocks of proteins. Consists of an amine group, carboxylic acid group and an  $\alpha$ -carbon that is attached to a unique side chain. There are 20  $\alpha$ -amino acids that are relevant to mammalian proteins.

## Zwitterion

A compound that is electronically neutral but carries negative and positive charges on different atoms.

## Peptide Bond (Peptide Linkage)

Amide bond formed between two amino acids during a dehydration reaction.

## Oligopeptide

Peptide fragment that consists of 10-20 amino acids.

#### Polypeptide

Peptide fragment that consists of 20+ amino acids.

## **Key Reactions of Amino Acids and Proteins:**

## (1) Amidation

Reaction where an amine is substituted onto a carboxylic acid to form an amide.

## (2) Peptide Hydrolysis

Reaction where water is added to an amide to form a carboxylic acid and an amine. When preformed on a peptide chain, the reaction yields the individual amino acids.

## **Primary Structure of Proteins**

The linear number and order of the amino acids present in a peptide.

#### Secondary Structure of Proteins

Conformations conferred upon proteins by the ordered array of amino acids. Structural motifs included in this level of protein structure are  $\alpha$ -helices and  $\beta$ -pleated sheets.

## **Tertiary Structure of Proteins**

Refers to the complete 3D structure of the polypeptide units of a given protein. Describes the relationship of different domains to one another within a protein.

## **Quaternary Structure of Proteins**

Describes proteins containing several distinct polypeptide chains along with the non-protein groups.

#### **α-Helix**

A common structure of proteins, characterized by a single, spiral chain of amino acids stabilized by hydrogen bonds.

## **β-Pleated Sheets**

A sheet like structure formed by the interaction between two or more extended polypeptide chains. Can be either parallel or antiparallel. Considered to be a secondary structure element.

## **Random Coil**

A protein that completely lacks secondary structure.

# 24: The Chemistry of Lipids

## Tutorial Summary:

Lipids, also known as fats, are a heterogeneous group of substances of biological origin that is insoluble in water but soluble in organic solvents. These substances serve many purposes in the body from acting as a storage form of energy to comprising the biological membranes of cells. The types of lipids, their differing structures and functions are covered in this tutorial.

## **Tutorial Features:**

- Examples and practice problems in each tutorial: structures of lipids types, finding terpene subunits in molecules.
- 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.
- Section on applying the SURE method to the MCAT and relevant practice problems.

## Concepts Covered:

Lipids Storage Membrane Terpenes Lipids and Membranes Overview Classification Storage Lipids Fatty acids Fats and oils Waxes Membrane Lipids Glycerophospholipids **Sphingolipids** Cholesterol Lipid Aggregates Micelles Lipid Bilayers Liposomes Biomembranes Plasma membranes Role of lipids Membrane structure/Fluid Mosaic Model Lipoproteins Classification Structure and functions Eicosanoids Classification Prostaglandins' structure and functions

Terpenes Structure Function

## Content Review:

## Lipids

A heterogeneous group of substances of biological origin that is insoluble in water but soluble in organic solvents. These substances serve many purposes in the body from acting as a storage form of energy to comprising the biological membranes of cells.

## **Fatty Acids**

Monocarboxylic acids that contain a long hydrocarbon side chain and act as a building block of fats and other lipids.

#### Amphipathic

Refers to a molecule that contains both hydrophobic and hydrophilic groups.

## Saturated versus Unsaturated Fatty Acids

Saturated fatty acids contain no double bonds in their hydrocarbon side chains. Unsaturated fatty acids contain one or more double bonds in their side chains.

## **Triacylglycerols (Triglycerides or Fats)**

A form of lipid that is composed of three fatty acids attached via ester linkages to a single molecule of glycerol.

## Glycerophospholipids (Phosphoglycerides)

Lipid that is a derivative of phosphatidic acid. They are comprised of a molecule of glycerol, two fatty acids, a phosphoric acid group, and a nitrogenous group. Due to their amphipathic nature, they can serve as membrane lipids.

## Sphingolipids

A type of lipid that is a derivative of sphingosine (an 18 carbon amino alcohol). They consist of a molecule of sphingosine and a fatty acid. Some sphingolipids also have a phosphocholine group or a sugar residue in their structure.

#### Sterols

Contain a rigid system of four fused hydrocarbon rings with a hydroxyl group on it.

#### Micelles

The sphere aggregates of amphipathic lipids where the polar head groups are on the exterior of the micelle and the nonpolar tails are in the interior.

#### **Lipid Bilayer**

Basic structure of a cell membrane that consists of two rows of lipids where the polar head groups are on the exterior while the hydrophobic tails are in the interior.

#### Liposomes

A spherical vesicle that is created when a lipid bilayer closes on itself.

## Fluid Mosaic Model

A model used to describe a cell's plasma membrane. In this model, the cell membrane is described as a semipermeable lipid bilayer that has proteins and glycoproteins embedded in it.

## **Peripheral Proteins**

Proteins that exist on the surface of the lipid bilayer membrane.

## **Integral Membrane Proteins**

Proteins that are deeply embedded in the cell's lipid bilayer membrane.

## Lipoproteins

Lipid-protein complexes found in the plasma. The lipids and proteins are not covalently bound together. They are classified based on the differences in their densities.

## **Eicosanoids**

Physiologically and pharmacologically active compounds like prostanoids and leukotrienes.

## Terpenes

Biological molecules that have been synthesized by adding isoprene units together.