

ORGANIC CHEMISTRY

Organic chemistry plays an important role in the understanding of many biological reactions. You will be expected to call upon your knowledge of organic compounds and reactions and to explain results, arguments, and experimental procedures in terms of reactions or principles of organic compounds. Because nomenclature, classifications of functional groups, and reaction mechanisms are important to the understanding of organic reactions, these areas will also be tested within the scope of the categories outlined below.

BIOLOGICAL MOLECULES

You should be familiar with the general types of molecules that are biologically active and the respective reactions of these molecules. Emphasis will be placed on the descriptions and reactions of the molecules described below.

A. Amino acids and proteins

1. Description

- a. Absolute configuration at the alpha position
- b. Amino acids as dipolar ions
- c. Classification
 - i. Acidic or basic
 - ii. Hydrophobic or hydrophilic

2. Reactions

- a. Sulfur linkage for cysteine and cystine
- b. Peptide linkage
- c. Hydrolysis

3. General principles

- a. 1° structure of proteins
- b. 2° structure of proteins
- c. 3° structure of proteins
 - i. Role of proline, cystine
 - ii. Hydrophobic bonding
- d. Isoelectric point

B. Carbohydrates

1. Description

- a. Nomenclature and classification, common names
- b. Absolute configuration
- c. Cyclic structure and conformations of hexoses
- d. Epimers and anomers

2. Oxidation of monosaccharides

3. Hydrolysis of the glycoside linkage

C. Lipids

1. Description, structure

- a. Free fatty acids
- b. Triacyl glycerols
- c. Steroids
- D. Phosphorus compounds

1. Phosphoric acid - chemistry and structure of anhydrides and esters

OXYGEN-CONTAINING COMPOUNDS

The principal reactions of oxygen-containing compounds are critical to the interpretation of many reactions in organic compounds. The fundamental principles and mechanisms of these reactions offer a good guide to the understanding of organic reactions. The concepts of nucleophiles, electrophiles, organic acids and bases, acidic protons, oxidations, reductions, and physical properties of various oxygen containing compounds are outlined below. In addition, the major reactions involving condensations, rearrangements, steric and electronic effects of substituents, and dimerizations will be covered.

A. Alcohols

- 1. Important reactions
 - a. Dehydrations (formation of carbocations)
 - b. Substitution reactions (S_N1 or S_N2 depending on alcohol and derived product)
- 2. General principles
 - a. Hydrogen bonding
 - b. Effect of chain branching on physical properties

B. Aldehydes and ketones

- 1. Important reactions
 - a. Nucleophilic addition reactions at C=O bond
 - i. Acetal, ketal, hemiacetal, hemiketal
 - ii. Imine, enamine
 - b. Reactions at adjacent positions
 - i. Aldol condensation
 - ii. Keto-enol tautomerism
- 2. General principles
 - a. Effect of substituents on reactivity of C=O
 - b. Steric hindrance
 - c. Acidity of α -H
 - d. Carbanions
 - e. α, β , unsaturated carbonyls

C. Carboxylic acids

- 1. Important carboxyl group reactions
 - a. Decarboxylation
 - b. Esterification
- 2. General principles

- a. H bonding
- b. Inductive effect of substituents
- c. Resonance stability of carboxylate anion

D. Common acid derivatives (acid chlorides, anhydrides, amides, esters, keto acids)

- 1. Important reactions
 - a. Hydrolysis of fats and glycerides (saponification)
 - b. Hydrolysis of amides
- 2. General principles
 - a. Relative reactivity of acid derivatives
 - b. Steric effects

E. Ethers

- 1. Cleavage by acid
- 2. Weak basicity of ethers

F. Phenols

- 1. General principles
 - a. Effects of substituents on acidity
 - b. Hydrogen bonding

AMINES

Nitrogen-containing compounds often have unique properties due to their basicity and electronic effects. The stabilization of adjacent carbocations and the solubility properties of the ammonium salts are vital to a wide area of biological and organic reactions. Major reactions of amide formation and alkylations are also important. You should understand these concepts in order to answer questions in this section.

A. Description

- 1. Stereochemistry and physical properties

B. Major reactions

- 1. Amide formation
- 2. Alkylation

C. General principles

- 1. Basicity
- 2. Stabilization of adjacent carbonium ions (carbocations)
- 3. Effect of substituents on basicity of aromatic amines

D. Quaternary salts

1. Solubility properties

HYDROCARBONS

The chemistry of alkanes, alkenes, and benzene derivatives is a major part of organic chemistry. Combustion, stability of free radicals and carbocations, ring strain or stabilization, and resonance stability will be included in this section, with emphasis on the properties of saturated, unsaturated, and aromatic compounds. Resonance stability and delocalization of aromatic compounds will also be included. You will need to understand these concepts in order to answer questions in this section.

A. Saturated (alkanes)

1. Description, physical properties
2. Important reactions
 - a. Combustion
 - b. Substitution reactions with halogens, etc.
3. General principles
 - a. Stability of free radicals
 - b. Chain-reaction mechanism
 - c. Inhibition
 - d. Ring strain in cyclic compounds

B. Unsaturated (alkenes)

1. Description
 - a. Structure and isomerization
 - b. Physical properties
2. Electrophilic addition (e.g., HBr, H₂O)

C. Aromatic (benzene)

1. Description
2. Resonance stability, delocalization of electrons

MOLECULAR STRUCTURE OF ORGANIC COMPOUNDS

The structures, bond descriptions, and bond strengths of organic compounds are important when determining the reactions and chemistry of organic molecules. You should be familiar with common nomenclature, methods for measuring stereochemistry, hybrid orbitals, bond strengths, and resonance.

A. σ and π bonds

1. Hybrid orbitals (Sp³, Sp², Sp and respective geometries)
2. Structural formulas for molecules involving H, C, N, O, F, S, P, Si, Cl.
3. Delocalized electrons and resonance in ions and molecules

B. Multiple bonding

1. Effect on bond length and bond energies
2. Rigidity in molecular structure

C. Stereochemistry of covalently bonded molecules

1. Isomers
 - a. Structural isomers
 - b. Stereoisomers (e.g., diastereomers, enantiomers, cis/trans isomers)
 - c. Conformational isomers
2. Polarization of light, specific rotation
3. Absolute and relative configuration
 - a. Conventions for writing R and S forms
4. Racemic mixtures

SEPARATIONS AND PURIFICATIONS

While reactions and properties of organic compounds make up a major portion of organic chemistry, another important feature is the separation and purification of these compounds. You should be familiar with the methods used in these processes, as well as with the features of the different organic compounds that make the separation or purification possible.

A. Extraction (distribution of solute between two immiscible solvents)

B. Chromatography

1. Gas-liquid chromatography
2. Thin-layer chromatography

C. Distillation

D. Recrystallization, solvent choice from solubility data

USE OF SPECTROSCOPY IN STRUCTURAL IDENTIFICATION

The identification of organic compounds is of prime interest when determining the products of a particular reaction. You should understand the major spectroscopic techniques employed to determine the structures of the major groups of organic compounds, as well as the features of the compounds that affect their spectroscopy. You should especially be familiar with NMR (nuclear magnetic resonance) and IR (infrared) spectroscopy and the characteristic absorptions for common functional groups.

A. Infrared region

1. Intramolecular vibrations and rotations
2. Recognizing common characteristic group absorptions

B. NMR spectroscopy

1. Protons in a magnetic field, equivalent protons
2. Spin-spin splitting