Organic Chemistry: First Semester Road Map (Part 1)

Structure and Bonding

Key Concepts

Coulomb's law
the nucleus
Electronic configuration of atoms
the octet rule
the shapes of s and p orbitals
Lewis structures
covalent versus ionic bonding
VSEPR theory
hybrid orbitals
sigma and pi bonds
sigma bonding
condensed formula
Line diagrams
Molecular orbitals

Key Terms

Structural formula, anion, cation ion, ionic bond, lone pairs, molecular orbital, node, valence electrons, sigma bond, pi bond, bonding orbital, antibonding orbital, orbital overlap, empirical formula, condensed formula, substituent,

Key Skills

Draw the shapes of s and p orbitals

Predict molecular geometry using VSEPR theory

Draw Lewis structure for a given molecule

Interconvert a molecule between a Lewis structure, structural formula, and line diagram

Identify "hidden" hydrogens and lone pairs from a line diagram

Draw sigma bonds for a simple molecule (like methane)

Draw pi bonds for a simple molecule (like ethene)

Identify hybridization state of each atom

Draw the molecular orbital diagram for ethene

Organic Compounds: Alkanes

Key Concepts

Functional groups
Alkane nomenclature
condensed formula
Line diagrams
Intermolecular forces of alkanes
Boiling points of alkanes
Constitutional isomers
Conformations
Newman projections
Torsional strain

Key Terms

Newman projection
Eclipsed, staggered, gauche, sawhorse projection, torsional strain, steric hindrance, conformation, constitutional isomer, anti, syn,

Key Skills

Identify functional groups two ways: 1) be able to name when shown structure, and 2) be able to draw structure when given name

Interpret condensed formulas

Interpret line diagrams

Identify primary, secondary, tertiary, and quaternary carbons

Given an alkane structure, determine the name
Given the name of an alkane, draw the structure

Rank alkanes according to boiling points

Given a molecular formula, draw all possible isomers

Identify molecules that are identical but drawn in different conformations.

Perform a bond rotation on a line diagram

Convert a line diagram to a Newman projection (and vice versa)

Perform a bond rotation on a Newman projection

Evaluate the relative energies of different Newman projections

Graph energies of different Newman projections versus dihedral angle

Cycloalkanes

Key Concepts

Ring strain
Cis-trans isomerism
Dash-wedge notation
Index of unsaturation
Conformations of cycloalkanes
Boat / Chair forms
Diaxial steric interactions

Key Terms

chair, boat, axial, equatorial, ring strain, cis, trans, dash, wedge, stereoisomers, torsional strain, twist-boat, bicycle, bridgehead, ring flip,

Key Skills

Identify molecules with ring strain

Draw a cyclohexane chair conformation (both directions)

Identify the lowest-energy chair conformation of a cyclohexane ring

Convert a flat cyclohexane drawing to a chair cyclohexane drawing

Demonstrate a "ring flip"

Identify cis-trans relationships on a flat ring or in a cyclohexane chair

Calculate the energies of different chair forms

Given different energies of chair forms, calculate the equilibrium constant using $K = e^{-\Delta G/RT}$

Understand why large groups "prefer" the equatorial position of cyclohexane chair

Name bicyclic alkanes

Stereochemistry

Key Concepts

Chiral and achiral molecules
Stereocenters
Stereoisomers
Enantiomers
Diastereomers
Optical rotation
R/S notation
Meso compounds
Plane of symmetry
Fischer projection

Key Terms

Racemic mixture, enantiomer, diastereomer, dextrorotatory, levorotatory optical rotation, specific rotation, absolute configuration, meso compound, plane of symmetry, stereoselective, resolution, achiral, optically active,

Key Skills

Understand how physical properties differ between types of isomers

Identify stereocenters on a molecule

Assign R/S to stereocenters

Given a chiral molecule, draw the enantiomer

Identify a meso compound

Understand the relationship between the number of stereocenters and the number of potential stereoisomers

Determine if two molecules are enantiomers, diastereomers, or the same

Determine R/S on a molecule drawn as a Newman projection

Determine R/S on a molecule drawn as a Fischer projection

Given observed rotation and concentration, calculate specific rotation

Make a flowchart for the separation of a racemic mixture of enantiomers

Radical Reactions

Key Concepts

Free radicals
Bond dissociation energies
Stability of free radicals
Homolytic cleavage
Steps of a radical reaction
Curved arrows for radical reactions
Relative reactivity of different types of C–H bonds (methyl, primary, secondary, tertiary)
Activation energy
Reaction coordinate
Prochirality
The Hammond postulate

Key Terms

radical, initiation, propagation, termination, activation energy, reaction coordinate, bond dissociation energy, prochiral, Hammond postulate, bond dissociation energy, homolytic cleavage, heterolytic cleavage

Key Skills

Understand the factors that affect stability of free radicals

Understand the relative reactivity of different C–H bonds

Understand the relative reactivity of different halogens (F_2, Cl_2, Br_2, I_2)

Identify each of the three steps of a free radical reaction

Draw a mechanism for a typical free radical reaction (e.g. chlorination)

Given an alkane, identify how many products would result from a chlorination reaction

Understand why radical reactions are not stereoselective

Calculate the relative reactivities of different types of C–H bonds in alkane halogenation, adjusting for statistical considerations

Polar bonds, Formal Charge, and Resonance

Key Concepts

Electronegativity
Polarizability
Dipole moment
Formal charge
Polar covalent bonding
Dipoles
Hydrogen bonding
Ionic bonds
Dipole-dipole interactions
London forces (dispersion)
Boiling and melting points
Resonance structure
Resonance hybrid
Curved arrows
Factors that stabilize negative charge
Factors that stabilize positive charge

Key Terms

Resonance, resonance hybrid, formal charge, anion, cation, polar covalent bond, carbocation, carbanion, curved arrows, dipoles, delocalization, ionic bond, dipole-dipole interaction, London (dispersion) forces, intermolecular forces, dipole moment, hydrogen bond

Key Skills

Apply electronegativity to determine dipoles

Determine whether a molecule has a dipole moment
Calculate formal charge of an atom

Know the *difference* between formal charge and electron density

Given the formal charge of an atom, draw full Lewis structure

Understand how the four intermolecular forces affect boiling points

Draw the resonance forms of a given molecule

Draw curved arrows to interconvert resonance forms

Evaluate the stability of different resonance forms

Organic Chemistry: First Semester Road Map (Page 2)

Acid-Base Reactions

Key Concepts

Definition of Lewis / Bronsted acidity
Acid-base equilibria
Conjugate acids and bases
Factors that affect acidity:
- Charge
- Electronegativity
- Polarizability
- Resonance
- Inductive effects
- Orbitals (sp, sp^2, sp^3)

pKa
Curved arrows (for reactions)

Key Terms

Lewis acid, Lewis base, Bronsted acid, Bronsted base, acid dissociation constant, pKa, conjugate acid, conjugate base, protonation

Reactions

Acid base reactions

Key Skills

Identify acids and bases
Given an acid, draw the conjugate base
Given a base, draw the conjugate acid
Understand the relationship between acidity and the stability of the conjugate base
Draw a curved-arrow mechanism for an acid-base reaction
Rank molecules according to acid strength
Understand the relationship between pKa and acid strength
Understand how to use a pKa table to understand whether a reaction will occur

Substitution Reactions

Key Concepts

Nucleophilic substitution reactions
Nucleophilicity
Electrophilicity
Leaving groups
Carbocation stability
Steric hindrance
Rate laws
Stereochemical inversion
Difference between nucleophilicity and basicity
The SN1 reaction
The SN2 reaction
Reaction coordinate diagrams
Carbocation rearrangements (hydride and alkyl shifts)

Key Terms

solvation, solvolysis, polar protic solvent, polar aprotic solvent, transition state, reaction coordinate, intermediate, backside attack, inversion, concerted reaction, hydride shift, alkyl shift

Reactions

SN1, SN2, hydride shift, alkyl shift

Key Skills

Identify a substitution reaction
Understand the factors affecting nucleophilicity:
- Charge
- Electronegativity
- Polarizability
- Solvent
- Steric bulk

What makes a good leaving group? Rank leaving group ability
Draw the mechanism of an S_N1 reaction
Understand relationship between S_N1 and carbocation stability
Draw mechanism of an S_N2 reaction
Understand relationship between steric hindrance and the S_N2 reaction
Compare and contrast the stereochemistry of the S_N1 and S_N2 reactions
Draw reaction coordinates for S_N1 and S_N2 reactions
Understand when rearrangement can occur with S_N1
Draw examples of S_N1 reactions with hydride shifts and alkyl shifts
Understand the factors affecting substitution in cyclohexane rings
Given a substitution product provide a method for its synthesis
Given reaction conditions, predict whether a reaction will proceed through S_N1 or S_N2
Draw an example of an intramolecular substitution reaction

Alkenes and Elimination Reactions

Key Concepts

Degree of unsaturation
π bonding
Nomenclature of alkenes
E and *Z* nomenclature for alkenes
Factors affecting alkene stability
Elimination reactions
Zaitsev's rule
Relationship between elimination and heat
The E1 reaction
The E2 reaction
Bulky bases

Key Terms

elimination, regioselectivity, stereoselectivity, base, *anti*, syn, cis, trans, *Z*, *E*, degree of unsaturation, bulky base, dehydration, catalyst

Reactions

E1, E2, hydride shift, alkyl shift

Key Skills

Given an alkene structure, provide the name
Given an alkene name, draw the structure
Apply the E / Z convention to name substituted alkenes
Rank alkenes in order of stability
Given a molecular formula, calculate degree of unsaturation
Given starting material and base, draw elimination product (apply Zaitsev's rule)
Draw mechanisms for E1 and E2 reactions
Understand how carbocation stability affects the rate of the E1 reaction
Understand how acid can promote the dehydration of alcohols
Understand the stereochemistry of the E2 reaction
Apply the E2 reaction on a cyclohexane ring (stereochemistry!)
Show an E2 reaction occurring on a molecule drawn as a Newman projection
Understand when rearrangement reactions can occur with E1
Draw examples of E1 reactions with hydride shifts and alkyl shifts
Identify a bulky base, and understand how it affects the products of elimination reactions
Given an elimination product, draw the starting material

Addition Reactions

Key Concepts

Addition reactions
Carbocations
Markovnikoff's rule
Addition reactions (>10)
Stereochemistry of addiition reactions
Regiochemistry of addition reactions
Carbocation rearrangements
Oxidative cleavage

Key Terms

Regioselectivity, stereoselectivity, addition, syn, anti, concerted mechanism, oxidative cleavage, Markovnikoff's rule, halonium ion,

Reactions

Addition of hydrogen halides; hydration; halogenation; halohydrin formation; oxymercuration; hydroboration; hydrogenation; epoxidation; dihydroxylation; cyclopropanation; ozonolysis (reductive and oxidative workup); oxidative cleavage w/ $KMnO_4$ radical addition of HBr

Key Skills

Given starting alkene, be able to draw products of various addition reactions (below) with proper regiochemistry and stereochemistry
Draw mechanisms for each addition reaction, where appropriate
Draw reaction coordinate for an addition reaction involving a carbocation
Determine the product of an oxidative cleavage reaction on an alkene
Determine whether a given addition reaction will produce enantiomers, diastereomers, or a single product
Given addition product and reactants, be able to identify starting alkene
Understand why Markovnikov's rule operates
Understand why hydroboration proceeds with anti-Markovnikoff selectivity
Given products of addition reactions, draw the starting material

Spectroscopy

Key Concepts

Infrared spectroscopy
Functional groups
Index of unsaturation
Vibration
Wavenumber
NMR spectroscopy
Chemical shift
Coupling constant
Integration
Chemical environment

Key Terms

Bond stretch; infrared spectroscopy; J coupling; chemical shift; coupling constant; integration; multiplicity

Key Skills

Given molecular formula, calculate index of unsaturation
Identify an OH group on an IR spectrum
Identify a C=O group on an IR spectrum
Use IR to determine presence or absence of alcohols, ketones, aldehydes, esters, carboxylic acids and ethers
Identify positions of various functional groups in NMR spectrum
Given NMR spectrum, determine if it is consistent with structure
Understand relationship between chemical shift and electronegativity
Understand integration
Understand splitting (n+1 rule)
Given spectrum and molecular formula, determine structure of molecule
Given molecule, identify number of NMR signals that will be seen
Understand relationship between symmetry and peaks seen in NMR spectrum

Alkynes

Key Concepts

Bonding in alkynes
Nomenclature of alkynes
Acidity of alkynes
Addition reactions
Substitution reactions
Alkyne synthesis through elimination
Stereochemistry of addition reactions

Key Terms

Terminal alkyne, internal alkyne, tautomerization, enol, syn, anti, sp hybridization

Reactions

Deprotonation; S_N2 with alkyl halides; partial hydrogenation (Lindlar, Na/NH_3); hydroboration; oxymercuration; hydration; halogenation; addition of halogen halides; hydrogenation; formation of alkynes via elimination of dihalides

Key Skills

Given an alkene structure, provide the name
Given an alkene name, draw the structure
Make a drawing showing how p orbitals form the π bonds in an alkyne
Understand the increased acidity of alkynes
Given starting alkyne, be able to draw products of various addition reactions, with proper regiochemistry and stereochemistry.
Draw example of alkyne acid-base reaction
Draw examples of alkynyl anions (acetylides) in various SN2 reactions
Employ partial reduction techniques such as Lindlar/H_2 and Na/NH_3
Methods for alkyne synthesis
Draw mechanisms for each addition reaction, where appropriate
Given products of addition reactions, draw the starting material

Given reaction conditions, predict whether an SN1/SN2/E1/E2 reaction will occur