Preparing for Organic Chemistry

A Conceptual Guide to the Foundations You'll Need

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Contents

Welcome

This handbook exists to close the gap: a conceptual guide to reinforcing the foundations you'll need for organic chemistry, useful whether you're brushing up after time away, studying alongside someone else, or simply building a foundation before the course begins.

It does not replace a textbook or lecture course. Instead, it offers a philosophy for approaching the subject, a review of essential general chemistry, and a curated set of resources — with an emphasis on understanding over memorization.

Use the navigation on the left to move through the handbook in order, or jump to any section directly. If a term feels unfamiliar along the way, the glossary at the end collects definitions for quick reference.

Note

Prefer reading offline? Download the PDF or EPUB version.

I

Part I: Introduction to this Guide

Preparing for Organic Chemistry

Organic chemistry has a reputation for being one of the most difficult courses in the undergraduate sciences. It is common to approach it with anxiety, and even those who have done well in previous science courses can find themselves frustrated by the amount of information, unfamiliar terminology, and apparent need for memorization.

Yet experienced students and instructors frequently point out that organic chemistry is not primarily a memorization course.

Organic chemistry is better understood as a visual language and a system of recurring patterns. The subject becomes much more manageable when approached through understanding rather than memorization, and when new concepts are connected to a small number of fundamental ideas.

This guide was created for students who are preparing for Organic Chemistry I after spending some time away from chemistry, as well as for study partners, tutors, and anyone interested in building a strong foundation before beginning the course.

The purpose of this document is not to replace a textbook or lecture course. Instead, it is intended to offer:

- A philosophy for approaching organic chemistry.
- Guidance for reviewing essential general chemistry.
- A curated collection of high-quality resources.
- Practical study methods and organizational systems.
- Suggestions for developing intuition and confidence over time.

The goal is not to learn the entire course before it begins. **The goal is familiarity**.

A Philosophy of Preparation

It is common to believe that success in organic chemistry depends on intelligence or exceptional memory. In reality, success depends far more on consistency, pattern recognition, and a willingness to revisit concepts repeatedly.

Preparation should therefore focus on becoming comfortable with the language and ideas of chemistry rather than attempting to memorize hundreds of reactions.

The following principles reflect how organic chemistry works as a subject, not just how to study it.

1. Understanding Is More Valuable Than Memorization

Many reactions that appear unrelated are governed by the same underlying principles.

With an understanding of:

- electron movement,
- molecular stability,
- acidity and basicity,
- and structural relationships,

it becomes possible to reason through unfamiliar problems instead of relying on memory alone.

2. Organic Chemistry Is a Visual Subject

Structures, mechanisms, stereochemistry, and reaction pathways are most easily learned by drawing.

Reading alone is insufficient.

Progress comes from repeatedly sketching:

- molecules,
- resonance structures,
- chair conformations,

- reaction mechanisms,
- and synthesis pathways.

For this reason, notebooks, graph paper, whiteboards, and visual summaries are emphasized throughout this guide.

3. Repetition Builds Intuition

Organic chemistry rarely becomes clear after a single reading. Understanding develops through repeated exposure. Concepts that seem confusing at first often become intuitive after encountering them several times in different contexts. Confusion should therefore be expected and accepted as a normal part of the learning process.

4. A Few Ideas Explain Much of the Course

Although organic chemistry contains many topics, much of the subject revolves around several recurring themes:

- Structure determines properties.
- Electrons drive chemical reactions.
- Stability explains reactivity.
- Acids and bases influence many mechanisms.
- Patterns are more important than isolated facts.

These ideas will appear repeatedly throughout the course.

5. The Goal Is Fluency, Not Perfection

Learning chemistry is similar to learning a language. Fluency does not come from memorizing dictionaries. Instead, it develops through repeated practice, increasing familiarity, and gradual exposure to more complex ideas. Organic chemistry should be approached in the same way. **Progress matters more than perfection.**

Reviewing General Chemistry

Returning to chemistry after a gap can feel daunting, but most of the material needed for organic chemistry can be reviewed efficiently. Only a focused subset of general chemistry is essential — Part II covers these topics in detail, along with recommended resources and a suggested review schedule.

The purpose of review is not to relearn an entire year of chemistry. The objective is to rebuild enough familiarity that organic chemistry concepts have a foundation on which to rest.

How to Use This Guide

This document is intended to be used alongside:

- textbooks,
- online resources,
- university lecture notes,
- spreadsheets and reference materials,
- notebooks and sketches,
- practice problems,
- and class lectures.

As the semester progresses, the guide can evolve into a personal handbook containing notes, diagrams, summaries, and references.

Over time, it becomes less a document and more a record of understanding.

The objective is not to know everything before Organic Chemistry begins. **The objective is to become comfortable enough that the subject begins to make sense.**

II

Part II: Refreshing General Chemistry

Why Review General Chemistry?

Organic chemistry builds upon concepts introduced in general chemistry, but it does not require mastery of every topic from a year-long sequence.

Students returning to chemistry after a gap often fear they have forgotten too much. Fortunately, only a subset of general chemistry concepts are essential for success in Organic Chemistry I.

The purpose of review is not to repeat an entire chemistry course.

The purpose is to rebuild familiarity and confidence.

A few weeks of focused review can provide an excellent foundation and make the transition into organic chemistry much smoother.

Estimated Review Time

For most students who completed general chemistry several years ago, an effective review can be accomplished in approximately:

4–6 weeks with **20–30 minutes per day** or roughly **10–20 total hours of study.**

This estimate assumes a gradual approach emphasizing understanding rather than memorization.

Consistency matters much more than intensity. The goal is not to relearn an entire chemistry sequence.

The goal is to become familiar enough that the ideas encountered in Organic Chemistry I feel recognizable rather than entirely new.

Topics Worth Reviewing

The following topics provide the strongest foundation for Organic Chemistry I.

High Priority

Organic chemistry instructors generally expect familiarity with these topics from day one. Reviewing them thoroughly prevents the most common gaps that slow students down in the early weeks of the course. Students are not expected to remember every equation — organic chemistry emphasizes conceptual reasoning far more than calculation.

- Atomic structure
- Periodic trends
- Chemical bonding
- Electronegativity
- Lewis structures
- Formal charge
- Molecular geometry
- Hybridization
- Polarity
- Acids and bases
- Equilibrium
- pKa and molecular stability

Medium Priority

If time allows, a light pass through these topics can build useful context, but none are required before day one. The same resources used for High Priority topics — OpenStax Chemistry 2e and Khan Academy — cover all of them well.

- Intermolecular forces
- Molecular orbitals

- Thermodynamic concepts
- Reaction energetics

Resonance is worth special mention: it is covered in depth in Part III, but a brief introduction now can make that coverage easier to follow when it arrives.

Lower Priority

These topics are useful but should not dominate preparation time.

- Stoichiometry
- Gas laws
- Calorimetry
- Solution concentrations
- Electrochemistry
- Extensive calculations

Organic chemistry relies much more heavily on conceptual understanding than mathematical problem solving.

Topic Deep Dives

Atomic Structure and Periodic Trends

Topics

- Protons, neutrons, and electrons
- Electron configurations
- Periodic table organization
- Electronegativity
- Atomic size
- Ionization energy

What to Focus On

For organic chemistry, electron configurations matter mainly for understanding valence electrons — the electrons in the outermost shell that form bonds. Full configurations beyond the first two rows are rarely needed.

Electronegativity and periodic trends are the highest-value concepts here. Understanding why electronegativity increases across a period and up a group explains bond polarity and acidity trends that appear throughout the course. Knowing that F, O, N, and Cl are the most electronegative atoms in organic chemistry is more useful than memorizing any table.

Why It Matters

These ideas help explain bond polarity, acidity, and molecular reactivity.

Recommended Resources

Reading

OpenStax Chemistry 2e

- Chapter 6

Videos

- Khan Academy — Electronic structure
- Khan Academy — Periodic trends
- OCT — Periodic trends and electronegativity

Gentle Exercises

Explain:

- Why is oxygen more electronegative than carbon?

- Why are O–H bonds polar?
- Why is fluorine highly electronegative?

Chemical Bonding

Topics

- Ionic and covalent bonds
- Sigma and pi bonds
- Bond polarity
- Electronegativity differences

What to Focus On

Organic chemistry is almost entirely covalent, so ionic bonding is background knowledge rather than a focal point. The concepts that matter most are sigma and pi bonds — sigma bonds form the backbone of every organic molecule, while pi bonds create double and triple bonds and are considerably more reactive.

Bond polarity is the other key idea: when two atoms with different electronegativities share electrons, the distribution is uneven, and that uneven distribution drives most of what happens in an organic reaction.

Why It Matters

Bonding concepts form the language of organic chemistry.

Recommended Resources

Reading

OpenStax Chemistry 2e

- Chapter 7

Videos

- Khan Academy — Chemical bonds
- OCT — Ionic and covalent bonds

Gentle Exercises

Identify:

- Which bonds are polar.
- Which atoms carry partial charges.

Explain:

- Why C–H bonds are relatively nonpolar.
- Why O–H bonds are polar.

Lewis Structures

Topics

- Valence electrons
- Octet rule
- Formal charge
- Drawing molecules

What to Focus On

Lewis structures are one of the most important skills to have before day one. Every mechanism, every reaction, and every discussion of reactivity starts with drawing a molecule. The goal here is fluency, not just accuracy — being able to draw structures quickly keeps the bigger picture in focus.

Formal charge is the detail most often skipped and most often needed. Being able to calculate it quickly matters, since it appears in nearly every chapter.

Why It Matters

Nearly every chapter in organic chemistry begins with structure.

Students who are comfortable drawing Lewis structures often find later topics much easier.

Recommended Resources

Reading

OpenStax Chemistry 2e

- Chapter 7

Videos

- Khan Academy — Lewis diagrams and formal charge
- OCT — Lewis structures and formal charge

Gentle Exercises

Draw:

- CH_4
- NH_4^+
- NO_3^-

Determine:

- Formal charges
- Double bonds
- Resonance possibilities

Molecular Geometry

Topics

- VSEPR theory
- Molecular shape
- Bond angles

What to Focus On

Focus on the geometries that appear most often in organic chemistry: tetrahedral (four groups around carbon), trigonal planar (three groups, as in a double bond), linear (two groups, as in a triple bond), bent (as in water, where two lone pairs compress the bond angle), and trigonal pyramidal (as in amines, where one lone pair does the same).

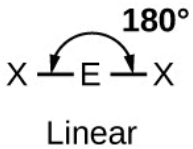
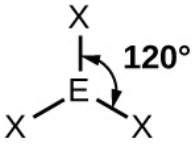
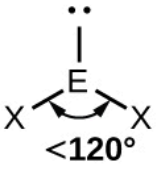
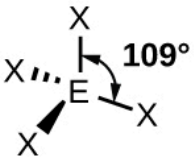
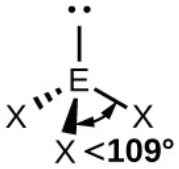
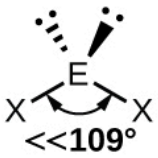
Number of electron pairs	Electron pair geometries: 0 lone pair	1 lone pair	2 lone pairs
2	 Linear		
3	 Trigonal planar	 Bent or angular	
4			

Figure II.1. VSEPR geometries by number of electron domains and lone pairs: linear, trigonal planar, bent/angular, tetrahedral, and trigonal pyramidal — the shapes that recur throughout organic chemistry. ("VSEPR molecular geometries" by OpenStax, CC BY 4.0, via Chemistry LibreTexts.)

Lone pairs are worth special attention. They affect shape, but they also make atoms like oxygen and nitrogen reactive as nucleophiles — a concept that reappears throughout the course.

Why It Matters

Organic chemistry is inherently three-dimensional.
Shape determines properties and reactivity.

Recommended Resources

Reading

OpenStax Chemistry 2e

- Chapter 7

Videos

- Khan Academy — Molecular geometry
- OCT — Molecular geometry and VSEPR

Gentle Exercises

Predict the geometry of:

- CH_4
- NH_3
- H_2O
- CO_2

Hybridization

Topics

- sp^3
- sp^2
- sp

What to Focus On

Hybridization and geometry are two sides of the same idea: sp^3 carbon is tetrahedral, sp^2 is trigonal planar, and sp is linear. Being able to assign hybridization by looking at a structure — rather than working through orbital math — is the practical goal.

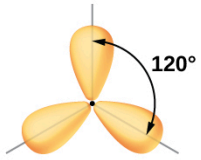
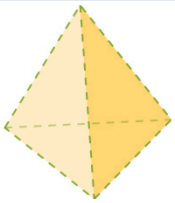
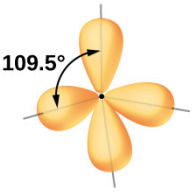
Regions of Electron Density	Arrangement		Hybridization	
2		linear	*sp*	
3		trigonal planar	sp^2	
4		tetrahedral	sp^3	

Figure II.2. sp, sp^2, and sp^3 hybridization alongside the geometry and angle each produces: sp = linear (180°), sp^2 = trigonal planar (120°), sp^3 = tetrahedral (109.5°). ("Hybridization and molecular geometry" by OpenStax, CC BY 4.0, via Chemistry LibreTexts.)

This concept appears in the first week of Organic Chemistry I and does not leave. It is worth becoming comfortable with before the course begins.

Why It Matters

Hybridization appears throughout the course and influences molecular geometry and bonding.

Recommended Resources

Reading

OpenStax Chemistry 2e

- Chapter 8

Videos

- Khan Academy — Hybridization
- OCT — Hybridization and sigma/pi bonds

Gentle Exercises

Determine the hybridization of carbon in:

- Methane

- Ethene
- Acetylene

Acids and Bases

Topics

- Brønsted-Lowry definitions
- Conjugate acids and bases
- Equilibrium
- pKa
- Factors affecting acidity

What to Focus On

Focus on the Brønsted-Lowry framework — proton donors are acids, proton acceptors are bases — since organic chemistry uses this definition almost exclusively.

pKa is the key tool: lower pKa means stronger acid. More important than calculating pKa values is being able to compare them and predict which direction a reaction favors. The factors that affect acidity — electronegativity, atomic size, and resonance stabilization of the conjugate base — reappear in nearly every chapter of Organic Chemistry I.

Why It Matters

Acid-base chemistry appears repeatedly throughout Organic Chemistry I.

Many instructors consider this the single most important topic to understand well.

Recommended Resources

Reading

OpenStax Chemistry 2e

- Chapter 14

Videos

- Khan Academy — Acids and bases
- OCT — Acids, bases, and pKa

Gentle Exercises

Identify:

- Acids
- Bases
- Conjugate acids
- Conjugate bases

Explain:

Why is HCl more acidic than CH_4?

Equilibrium

Topics

- Reversible reactions
- Le Châtelier's principle
- Equilibrium constants

What to Focus On

The most important idea here is conceptual: most reactions reach a balance rather than going completely to products, and the position of that balance is predictable. Le Châtelier's principle at a qualitative level

— adding reactants, removing products, or changing temperature shifts the equilibrium in a predictable direction — is more useful than working through calculations.

The connection to pKa is worth noting: pKa is simply –log(Ka), and reactions favor formation of the weaker acid. This rule is one of the most practical tools in organic chemistry.

Why It Matters

Chemical reactions are governed by energetics and equilibrium.

Understanding equilibrium makes many organic reactions easier to interpret.

Recommended Resources

Reading

OpenStax Chemistry 2e

- Chapter 13

Videos

- Khan Academy — Chemical equilibrium
- OCT — Le Chatelier's principle

Gentle Exercises

Explain:

- Why reactions do not always proceed completely to products.
- How equilibrium differs from reaction speed.

Suggested Review Schedule

Weeks 1–2

Topics

- Atomic structure
- Periodic trends
- Bonding
- Lewis structures

Goal

Become comfortable drawing structures and understanding electron distribution.

Week 3

Topics

- Molecular geometry
- Hybridization
- Polarity

Goal

Begin thinking in three dimensions.

Week 4

Topics

- Acids and bases
- Equilibrium
- pKa

Goal

Develop intuition about molecular stability.

Week 5

Topics

- Revisit any High Priority topics that felt unclear
- Work through the Gentle Exercises in each section
- Complete the Progress Checklist

Goal

Consolidate understanding through practice. Identify gaps before moving on.

Week 6 (Optional)

Topics

- Resonance (preview — covered in depth in Part III)
- Intermolecular forces
- Thermodynamic concepts
- Reaction energetics

Goal

Build additional depth with more preparation time. None of these are required before day one, but a light review can make Part III easier to follow.

Study Methods

The objective is not speed.
The objective is familiarity.
Effective review often includes:

- Watching short videos.
- Reading selectively.
- Drawing structures repeatedly.
- Maintaining a graph-paper notebook.
- Summarizing ideas in one's own words.
- Revisiting concepts several times.

Twenty to thirty minutes per day over several weeks is usually more effective than intensive cramming.

Progress Checklist

The goal is confidence rather than perfection.

Structure

☐ I can determine valence electrons.
☐ I can draw Lewis structures.
☐ I understand formal charge.
☐ I understand bond polarity.

Geometry

☐ I understand molecular shape.
☐ I recognize sp^3, sp^2, and sp hybridization.
☐ I understand sigma and pi bonds.

Acids and Bases

☐ I understand conjugate acids and bases.
  ☐ I understand the meaning of pKa.
  ☐ I recognize the importance of molecular stability.

Concepts

☐ I understand electronegativity.
  ☐ I understand equilibrium conceptually.
  ☐ I am comfortable drawing molecules.

Confidence

☐ I no longer feel that I need to review all of general chemistry.
  ☐ I feel prepared to begin Organic Chemistry I.

Looking Ahead

By this point, the goal is not mastery.

The objective is to rebuild enough familiarity with chemistry that the central ideas of organic chemistry become approachable.

Fortunately, much of Organic Chemistry I revolves around a surprisingly small set of concepts.

The next section introduces five ideas that explain much of the subject:

1. Functional Groups
2. Resonance
3. Acids and Bases
4. Stereochemistry
5. Electron Flow and Mechanisms

These ideas appear repeatedly throughout the course and form the foundation upon which later topics are built.

Understanding them well will make the remainder of Organic Chemistry I considerably easier.

III

Part III: Foundations of Organic Chemistry

The Language of Organic Chemistry

The previous sections reviewed the chemical principles necessary to begin studying organic chemistry. This part introduces the foundational ideas that govern nearly every topic encountered throughout both semesters. Although organic chemistry can initially appear to involve a large number of reactions and structures, much of the subject rests upon a relatively small number of recurring concepts.

These concepts influence:

- stability,
- reactivity,
- mechanisms,
- and molecular structure.

8 Things I Wish I'd Known Before Organic Chemistry

Before the content begins, it is worth keeping a few things in mind.

1. Draw Everything

Organic chemistry is visual. Reading alone is rarely sufficient. Draw molecules, mechanisms, and structures repeatedly.

2. Confusion Is Normal

Few people understand organic chemistry immediately. Repeated exposure matters far more than instant understanding.

3. Repetition Beats Cramming

Organic chemistry resembles language acquisition more than memorization. Short, consistent sessions are usually more effective than marathon study sessions.

4. Learn Functional Groups Early

Functional groups become the vocabulary of the subject. Recognizing them quickly makes everything else easier.

5. Acids and Bases Matter Everywhere

Acid-base chemistry appears throughout both semesters and deserves special attention.

6. Don't Memorize Reactions Too Soon

Memorization without understanding quickly becomes overwhelming. Learn why electrons move before trying to memorize products.

7. Follow the Electrons

This may be the most important habit to develop. Most of organic chemistry can be understood by asking:

Where are the electrons, and where do they want to go?

8. Progress Matters More Than Perfection

Organic chemistry becomes manageable through repeated exposure and gradual development of intuition. The objective is not mastery before the course begins. The objective is familiarity.

The Big Five

The chapters in this part explore five fundamental themes.

1. Functional Groups

The vocabulary of organic chemistry. Functional groups provide a framework for recognizing recurring patterns in molecular structure and reactivity.

2. Resonance

The grammar of organic chemistry. Resonance explains electron distribution, stability, and many important reaction patterns.

3. Acids and Bases

The logic of organic chemistry. Understanding acidity and basicity provides insight into equilibrium, reactivity, and mechanisms.

4. Stereochemistry

The importance of shape. Three-dimensional structure influences physical properties, biological activity, and chemical behavior.

5. Electron Flow

Following the electrons. Electron movement governs bonding, reactivity, and chemical change.

Interconnected Concepts

The five ideas introduced here should not be viewed as isolated chapters. They are deeply interconnected.

- Functional groups influence acidity.
- Resonance affects stability.
- Stereochemistry influences reactions.
- Electron flow governs mechanisms.

Throughout the course, these themes appear repeatedly in different contexts.

Together, these ideas form the intellectual foundation upon which the remainder of organic chemistry is built. The goal of this part is not memorization. Instead, the emphasis is on developing intuition and recognizing the patterns that repeatedly appear throughout the subject. By understanding these concepts, it becomes clear that organic chemistry is not a collection of isolated facts, but a coherent system governed by a surprisingly small number of principles.

Chapter 1: Functional Groups

The Vocabulary of Organic Chemistry

Introduction

One of the most important transitions students make in organic chemistry is learning to stop viewing molecules as collections of individual atoms and instead beginning to recognize recurring patterns.

These patterns are known as functional groups.

Functional groups are the vocabulary of organic chemistry.

Just as words provide meaning to sentences, functional groups determine much of a molecule's:

- polarity,
- acidity,
- intermolecular forces,
- physical properties,
- and chemical reactivity.

Experienced chemists rarely analyze molecules atom by atom.

Instead, they recognize familiar arrangements and use those patterns to predict how molecules are likely to behave.

Learning to recognize functional groups quickly is therefore one of the most important skills developed during Organic Chemistry I.

Why Functional Groups Matter

Functional groups influence nearly every aspect of a molecule.

They determine:

Physical Properties

- boiling point,
- melting point,
- solubility,
- intermolecular forces.

Chemical Properties

- acidity and basicity,
- nucleophilicity,
- electrophilicity,
- reaction mechanisms.

Spectroscopy

Functional groups produce characteristic signals in:

- infrared spectroscopy,
- nuclear magnetic resonance spectroscopy,
- mass spectrometry.

Biological Activity

Many biological molecules derive their properties from their functional groups.

For example:

- alcohols appear in carbohydrates,
- amines appear in amino acids,
- carboxylic acids appear in fatty acids,
- amides form peptide bonds in proteins.

Thinking in Functional Groups

Beginning students often attempt to memorize entire molecules.
Experienced chemists rarely do this.
Instead, they identify:

- the important functional groups,
- how those groups interact,
- and how one functional group can be transformed into another.

Much of organic chemistry can therefore be viewed as the study of functional group transformations.

Major Functional Group Families

Hydrocarbons

Alkanes

Contain only single bonds. Generally nonpolar and relatively unreactive.

Alkenes

Contain carbon-carbon double bonds. More reactive than alkanes. Important in addition reactions.

Alkynes

Contain carbon-carbon triple bonds. Highly useful synthetic intermediates.

Oxygen-Containing Functional Groups

Alcohols

Contain O–H groups. Capable of hydrogen bonding. Common in biological molecules.

Ethers

Contain oxygen atoms between two carbon groups. Less reactive than alcohols. Frequently used as solvents.

Aldehydes

Contain terminal carbonyl groups. Reactive toward nucleophiles.

Ketones

Contain internal carbonyl groups. Among the most important functional groups in Organic Chemistry II.

Carboxylic Acids

Contain both carbonyl and hydroxyl groups. Relatively acidic. Common in biological systems.

Esters

Contain a carbonyl bonded to an alkoxy group (–C(=O)–O–). Important in fats and lipids. Often possess pleasant odors.

Nitrogen-Containing Functional Groups

Amines

Organic bases containing nitrogen. Common in pharmaceuticals and amino acids.

Amides

Contain a carbonyl bonded to a nitrogen (–C(=O)–N–). Found in proteins and peptides. Exceptionally important in biochemistry.

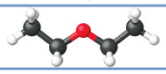
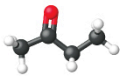
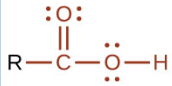
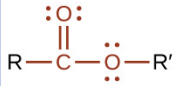
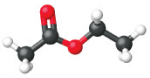
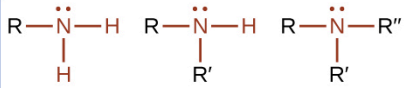
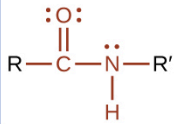
Compound Name	Structure of Compound and Functional Group (red)	Example	
		Formula	Name
alkene		C_2H_4 	ethene
alkyne		C_2H_2 	ethyne
alcohol		CH_3CH_2OH 	ethanol
ether		$(C_2H_5)_2O$ 	diethyl ether
aldehyde		CH_3CHO 	ethanal
ketone		$CH_3COCH_2CH_3$ 	methyl ethyl ketone
carboxylic acid		CH_3COOH 	acetic acid
ester		$CH_3CO_2CH_2CH_3$ 	ethyl acetate
amine		$C_2H_5NH_2$ 	ethylamine
amide		CH_3CONH_2 	acetamide

Figure 1.1. Structure and a worked example for each major functional group family: alkenes and alkynes (hydrocarbons); alcohols, ethers, aldehydes, ketones, carboxylic acids, and esters (oxygen-containing); amines and amides (nitrogen-containing). Alkanes are omitted because they have no functional group to highlight — they are the unreactive baseline every other family is defined against. ("Functional group table" by OpenStax, CC BY 4.0, via Wikimedia Commons.)

Naming Organic Compounds

IUPAC nomenclature provides a systematic method for naming organic molecules. Knowing the naming system is practical from the start: course materials, textbook problems, and exam questions all use IUPAC names, often alongside common names.

The goal at this stage is not to master every rule. The goal is to understand the logic well enough to name simple molecules and recognize names when they appear.

The Basic Framework

Every IUPAC name has three components:

Parent chain — the longest continuous carbon chain in the molecule.
Suffix — signals the highest-priority functional group.
Prefixes and locants — identify substituents and their positions on the chain.

Parent Chain Prefixes

The prefix identifies the number of carbons in the parent chain.

Carbons	Prefix	Example
1	meth-	methane
2	eth-	ethane
3	prop-	propane
4	but-	butane
5	pent-	pentane
6	hex-	hexane
7	hept-	heptane
8	oct-	octane
9	non-	nonane
10	dec-	decane

These prefixes are combined with a suffix to produce the full name.

Functional Group Suffixes

The suffix indicates the principal functional group. When multiple functional groups are present, the one with the highest priority in the IUPAC system determines the suffix; the others become prefixes.

Functional Group	Suffix	Example
Alkane	-ane	propane
Alkene	-ene	propene
Alkyne	-yne	propyne
Alcohol	-ol	propan-1-ol
Aldehyde	-al	propanal
Ketone	-one	propan-2-one
Carboxylic acid	-oic acid	propanoic acid
Ester	-oate	methyl propanoate
Amide	-amide	propanamide
Amine	-amine	propan-1-amine

Numbering the Chain

The chain is numbered from the end that gives the principal functional group the lowest possible locant.

For example: a three-carbon chain with a hydroxyl group on the terminal carbon is propan-**1**-ol, not propan-3-ol.

Substituents

Groups attached to the parent chain other than the principal functional group are named as prefixes:

- methyl– ($-CH_3$)
- ethyl– ($-CH_2CH_3$)
- fluoro–, chloro–, bromo–, iodo– (halogens)
- hydroxy– (–OH, when not the principal group)

When multiple substituents are present, they are listed alphabetically.

Ring Systems

Cyclic compounds use the prefix **cyclo–** before the parent chain name. A six-carbon ring of single bonds is cyclohexane. Benzene is named as its own parent structure.

Common Names

Many compounds have common names that predate the IUPAC system and remain in wide use.

Common Name	IUPAC Name
Acetone	propan-2-one
Acetic acid	ethanoic acid
Formaldehyde	methanal
Ethanol	ethanol (same)
Chloroform	trichloromethane

Courses typically use both systems. Learning to recognize common names alongside IUPAC names is practical from the start.

A complete naming reference with step-by-step rules, worked examples, and an expanded common-name table is provided in Appendix E.

Relationships Between Functional Groups

Functional groups are not isolated entities.

Students are not expected to memorize every relationship immediately.

Instead, it is helpful to first recognize broad families of compounds and gradually develop pattern recognition through repeated exposure.

As familiarity grows, deeper relationships begin to emerge.

For example:

Oxygen-Containing Family

- Alcohols
- Ethers

Both contain oxygen, but alcohols possess O–H bonds while ethers do not.

Carbonyl Family

- Aldehydes
- Ketones
- Carboxylic acids
- Esters
- Amides

These compounds all contain carbon-oxygen double bonds and become central to Organic Chemistry II.

Nitrogen-Containing Family

- Amines
- Amides

These groups are especially important in biological chemistry and pharmaceuticals.
Developing this pattern recognition gradually is one of the goals of Organic Chemistry I.

Functional Group Transformations

Much of organic chemistry can be viewed as the conversion of one functional group into another.
Examples include:
Alcohol → Alkene
Alkene → Alcohol
Alcohol → Aldehyde
Aldehyde → Carboxylic Acid
Carboxylic Acid → Ester
Later chapters will explore the mechanisms that make these transformations possible.

Gentle Exercises

For each molecule encountered:

1. Identify the functional group.
2. Determine whether the molecule is likely to be polar or nonpolar.
3. Determine whether hydrogen bonding is possible.
4. Predict whether the molecule is likely to be acidic or basic.
5. Identify other functional groups that are structurally related.
6. Write the IUPAC name for the compound, identifying the parent chain and principal functional group.
7. Given an IUPAC name, draw or describe the structure it represents.

Common Mistakes

Trying to Memorize Complete Molecules

Better approach:
Recognize recurring patterns.

Viewing Functional Groups as Unrelated

Better approach:
Notice families of related structures.

Ignoring Structure

Better approach:
Draw molecules repeatedly. Recognition improves through repeated exposure.

Self-Assessment

I can:
☐ Recognize alkanes.
☐ Recognize alkenes and alkynes.
☐ Identify alcohols and ethers.
☐ Distinguish aldehydes and ketones.

☐ Recognize carboxylic acids, esters, and amides.
☐ Identify amines and amides.
☐ Group related functional groups into families.
☐ Appreciate that organic chemistry largely studies transformations between functional groups.
☐ Identify the parent chain prefix for chains of 1–6 carbons.
☐ Assign the correct IUPAC suffix for alkanes, alkenes, alcohols, aldehydes, ketones, and carboxylic acids.
☐ Name simple molecules using the IUPAC parent chain + suffix framework.
☐ Recognize common names alongside their IUPAC equivalents (acetone, acetic acid, formaldehyde).

Further Study

The goal at this stage is recognition rather than memorization.

Reading

LibreTexts Organic Chemistry — Ch. 3, Functional Groups — Functional groups, hydrocarbons, alcohols and ethers, carbonyl compounds.

MIT OpenCourseWare — Lecture Handouts — Lecture notes introducing functional groups and molecular structure.

Videos

Khan Academy — Organic Chemistry — Introduction to organic chemistry; functional groups.

Organic Chemistry Tutor — Functional groups; introduction to organic chemistry.

Professor Dave Explains — Functional groups; organic nomenclature.

Reference

Appendix E (this handbook) — Complete IUPAC naming reference with step-by-step rules, worked examples, and a common-name table.

Supplementary

Master Organic Chemistry — Functional Groups; Alcohols and Ethers; Carbonyl Compounds.

Looking Ahead

Functional groups tell us what atoms are present and provide important clues about how molecules behave.

Yet molecules with identical atoms may behave very differently depending upon how electrons are distributed.

The next chapter introduces resonance, a concept that many instructors consider the single most important idea in Organic Chemistry I.

Understanding resonance provides insight into stability, acidity, charge distribution, and the mechanisms that govern chemical reactions.

Chapter 2: Resonance

The Grammar of Organic Chemistry

Introduction

Many students enter organic chemistry expecting to memorize large numbers of reactions and structures.
Yet experienced chemists often rely upon a much smaller set of ideas to explain molecular behavior.
Among these ideas, resonance is arguably one of the most important.
Resonance helps explain:

- stability,
- charge distribution,
- acidity and basicity,
- carbocation stability,
- and the behavior of many reaction intermediates.

In many cases, molecules that initially appear mysterious become understandable once electron delocalization is taken into account.

Understanding resonance transforms organic chemistry from a collection of facts into a coherent system.

Why Resonance Matters

Electrons are not always confined to a single bond or a single atom.
In many molecules, electrons are distributed over multiple atoms.
This distribution of electron density often increases stability.
Resonance therefore influences:

Stability

Charge spread over several atoms is generally more stable than charge concentrated on a single atom.

Acidity

The stability of a conjugate base frequently determines acid strength.

Basicity

Electron delocalization can reduce the availability of electron pairs.

Reactivity

Many reaction intermediates are stabilized through resonance.

Mechanisms

Resonance plays a central role in understanding electron flow.

What Resonance Really Means

Resonance structures do not represent molecules switching back and forth between different arrangements.

Instead, they represent different ways of describing a single electron distribution.

The actual molecule is a resonance hybrid.

Individual resonance structures are useful models rather than distinct species.

Thinking of resonance structures as separate molecules is one of the most common misconceptions encountered in Organic Chemistry I.

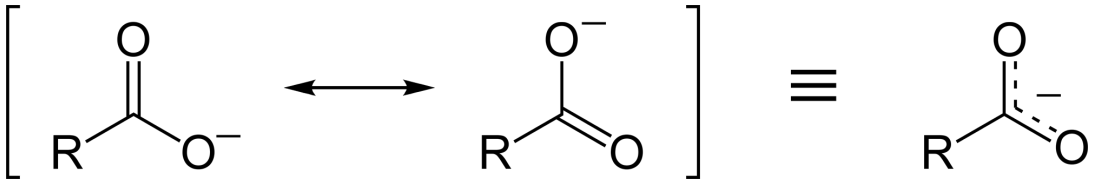


Figure 2.1. The two canonical resonance structures of a carboxylate (left, connected by the resonance double-headed arrow) are not alternating states — they are two incomplete descriptions of the single resonance hybrid (right), where the negative charge is shared evenly and both C–O bonds are equivalent. ("Carboxylate resonance, 2D skeletal" by Ben Mills, public domain, via Wikimedia Commons.)

Common Situations Where Resonance Occurs

Resonance frequently appears when:

- lone pairs are adjacent to π bonds,
- charges are adjacent to π bonds,
- multiple bonds are separated by a single bond,
- or conjugated systems are present.

Developing the ability to recognize these situations becomes easier with practice.

Formal Charge and Resonance

Formal charge is a bookkeeping device used to evaluate resonance structures.

Formal charge helps determine:

- whether a structure is reasonable,
- which resonance contributors are more important,
- and how charge is distributed throughout a molecule.

Although formal charge is not identical to actual charge, it provides a useful framework for understanding electron placement.

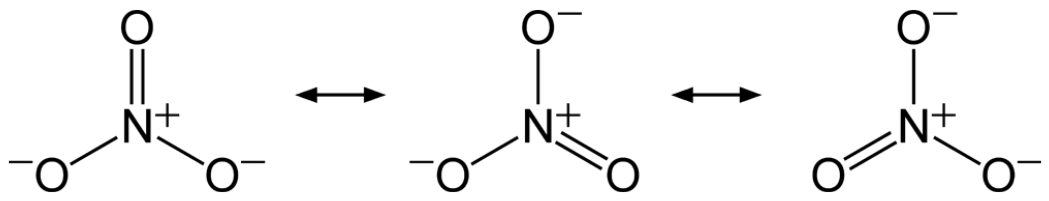


Figure 2.2. The nitrate ion, NO_3^-: three equivalent resonance structures, each placing the N=O double bond on a different oxygen. Formal charges (N: +1; double-bonded O: 0; each single-bonded O: −1) confirm all three are equally valid contributors — the actual ion is a hybrid with the negative charge spread evenly across all three oxygens. ("Nitrate ion resonance" by Ben Mills, public domain, via Wikimedia Commons.)

Stability and Delocalization

A recurring theme throughout organic chemistry is:

Delocalization increases stability.

When electrons are distributed over several atoms rather than concentrated in one location, energy is often lowered.

This idea explains:

- the stability of carboxylate ions,
- allylic carbocations,
- benzene,
- and many reaction intermediates.

Understanding stability will become increasingly important throughout both semesters.

Thinking About Resonance

Beginning students often ask:

"How do I know when to draw resonance structures?"

A useful question is:

Can electrons move without moving atoms?

If the answer is yes, resonance may be possible.

Another helpful question is:

Can a charge or lone pair be spread over multiple atoms?

If so, resonance frequently provides a better description of the molecule.

Gentle Exercises

For each molecule:

1. Identify whether resonance is possible.
2. Determine which electrons are capable of moving.
3. Draw possible resonance structures.
4. Locate formal charges.
5. Determine where charge is distributed.

Examples:

- nitrate ion,
- acetate ion,
- allylic carbocation,
- benzene.

Common Mistakes

Moving Atoms Instead of Electrons

Better approach:

Only electrons move in resonance structures. Atoms remain fixed.

Thinking Structures Alternate Back and Forth

Better approach:

View resonance structures as different representations of a single electron distribution.

Violating the Octet Rule

Better approach:
Pay attention to valence and electron counts.

Forgetting Formal Charge

Better approach:
Use formal charge as a guide to evaluate resonance contributors.

Self-Assessment

I can:
☐ Recognize situations where resonance may occur.
☐ Understand that resonance structures are models rather than separate molecules.
☐ Distinguish electron movement from atomic movement.
☐ Draw simple resonance structures.
☐ Use formal charge to evaluate structures.
☐ Appreciate that delocalization generally increases stability.
☐ Recognize the importance of resonance in acidity and reactivity.

Further Study

The goal at this stage is conceptual understanding rather than mastery.

Reading

LibreTexts Organic Chemistry — Ch. 2, Resonance (§2.3–2.5) — Resonance; formal charge; conjugation.
MIT OpenCourseWare — Lecture Handouts — Lecture notes introducing resonance and electron delocalization.

Videos

Khan Academy — Resonance and Acid-Base Chemistry — Resonance structures; formal charge.
Organic Chemistry Tutor — Resonance structures; formal charge.
Professor Dave Explains — Resonance and electron delocalization.

Supplementary

Master Organic Chemistry — Introduction to Resonance and **Evaluating Resonance Structures** — Resonance; resonance contributors; stability and charge distribution.

Looking Ahead

Resonance provides a powerful explanation for stability and electron distribution.
Yet another important question remains:
Why are some molecules more acidic than others?
Why are some atoms more willing to donate or accept electrons?
The next chapter explores acids and bases, a subject that many experienced instructors consider one of the most important themes in all of organic chemistry.

Chapter 3: Acids and Bases

The Logic of Organic Chemistry

Introduction

Acid-base chemistry appears throughout both semesters of organic chemistry.

Although students often associate acids and bases with introductory chemistry, these concepts become even more important in organic chemistry because they help explain:

- stability,
- equilibrium,
- reaction mechanisms,
- and molecular reactivity.

Many reactions encountered in organic chemistry are, in one form or another, acid-base reactions.

Understanding why molecules donate or accept protons provides a framework for understanding much of the subject.

Why Acids and Bases Matter

Acidity and basicity influence:

Equilibrium

Which side of a reaction is favored.

Stability

Stable conjugate bases generally correspond to stronger acids.

Reactivity

Acids and bases frequently initiate reaction mechanisms.

Mechanisms

Proton transfers are among the most common steps encountered in organic chemistry.

Stability Determines Acidity

One of the most important ideas in organic chemistry is:

The stability of the conjugate base determines the strength of the acid.

This principle appears repeatedly throughout both semesters.

Factors Influencing Stability

Several factors contribute to stability:

Resonance

Delocalized charge increases stability.

Atom (Electronegativity and Size)

More electronegative atoms stabilize negative charge more effectively. Atomic size matters too, and dominates within a group: acidity increases down a column (HI > HBr > HCl > HF) even though electronegativity decreases, because a larger atom spreads the negative charge over more volume.

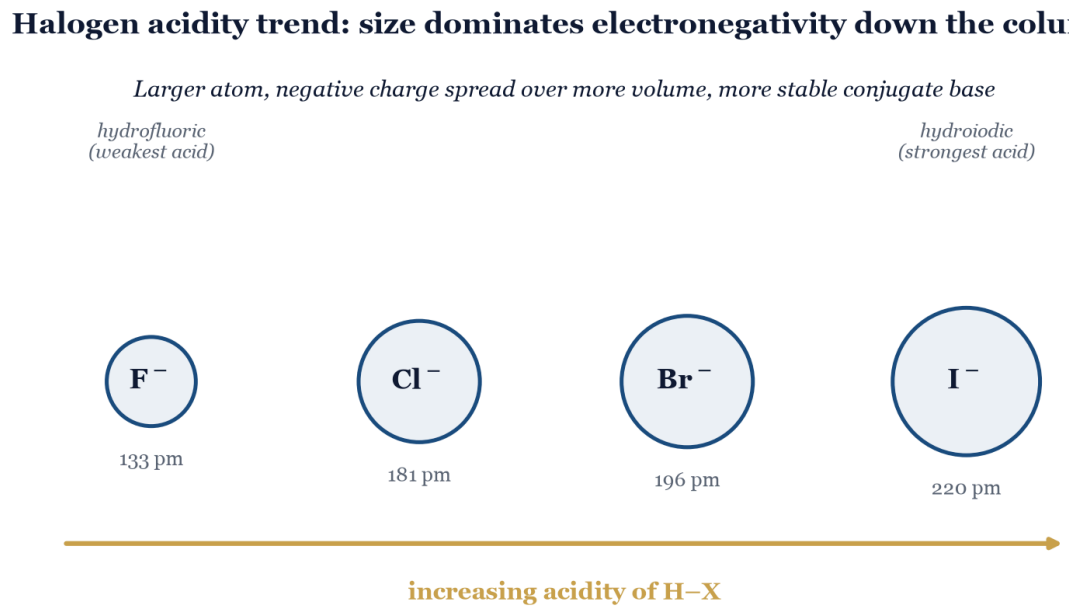


Figure 3.1. Halide ionic radii to scale (F^- 133 pm, Cl^- 181 pm, Br^- 196 pm, I^- 220 pm): as the halide grows, it spreads the negative charge over more volume, so acidity increases down the column even as electronegativity decreases.

Inductive Effects

Electron-withdrawing groups influence charge distribution.

Hybridization

Atoms with greater s-character generally stabilize charge more effectively.

These ideas eventually combine into systematic frameworks for ranking acidity.

Thinking About Acids and Bases

Helpful questions include:

- Which atom bears the charge?
- Can resonance stabilize the charge?
- Is the charge localized or delocalized?
- Which conjugate base is more stable?

Gentle Exercises

Determine:

- strongest acid,
- strongest base,
- conjugate acid,
- conjugate base.

Explain:
Why are carboxylic acids stronger acids than alcohols?

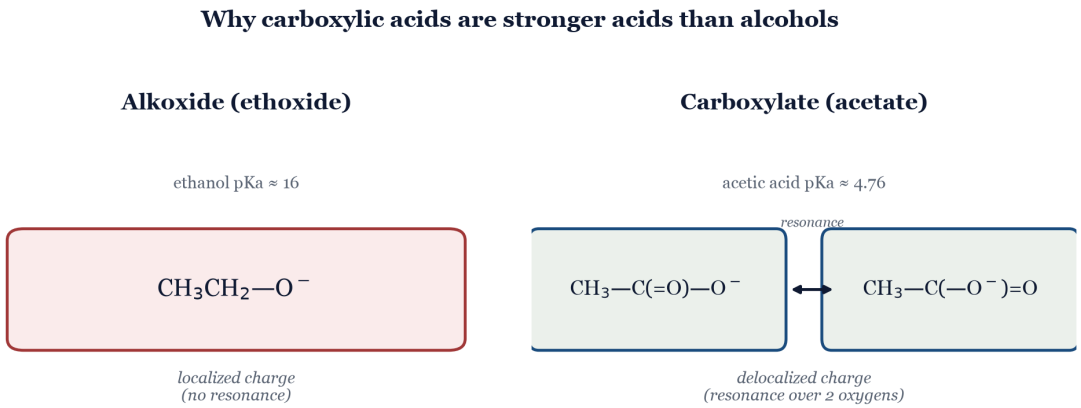


Figure 3.2. Ethoxide's negative charge is stuck on one oxygen, but acetate's is delocalized over two oxygens by resonance — the more stable conjugate base makes acetic acid the far stronger acid.

Common Mistakes

Memorizing pKa Values

Better approach:
Understand stability.

Ignoring Resonance

Better approach:
Ask whether charge can be delocalized.

Self-Assessment

I can:
- ☐ Identify acids and bases.
- ☐ Determine conjugate acids and bases.
- ☐ Understand the meaning of pKa.
- ☐ Explain acidity in terms of stability.
- ☐ Appreciate the importance of resonance.

Further Study

Reading

LibreTexts Organic Chemistry — Ch. 2, Acids and Bases — Acids and bases; pKa; stability.

Videos

Khan Academy — Resonance and Acid-Base Chemistry — Acids and bases; pKa.
Organic Chemistry Tutor — Acids and bases; pKa.

Supplementary

Master Organic Chemistry — Acidity and basicity; ARIO; pKa table.

Looking Ahead

Molecules are not merely collections of atoms.
They possess shape.
The next chapter explores stereochemistry and the importance of three-dimensional structure.

Chapter 4: Stereochemistry

The Importance of Shape

Introduction

Organic molecules exist in three dimensions.

Two molecules may possess identical atoms and bonds yet behave very differently because of their arrangement in space.

Stereochemistry provides a framework for understanding these differences.

Why Shape Matters

Shape influences:

- physical properties,
- biological activity,
- intermolecular interactions,
- and chemical reactivity.

Biological systems are especially sensitive to molecular shape.

Important Concepts

Chirality

Objects that are not superimposable upon their mirror images.

Enantiomers

Mirror-image molecules.

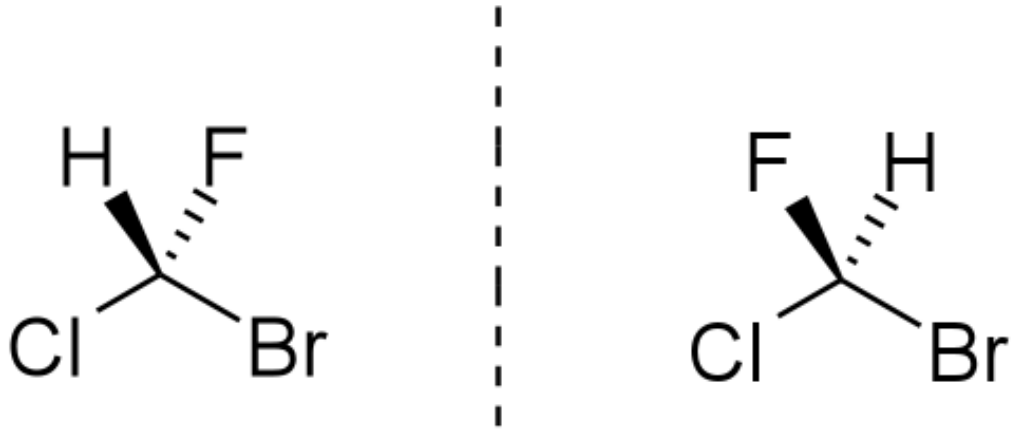


Figure 4.1. Bromochlorofluoromethane's two enantiomers: non-superimposable mirror images produced by swapping every wedge and dash at the single stereocenter. ("Bromochlorofluoromethane enantiomers" by Meodipt, public domain, via Wikimedia Commons.)

Diastereomers

Stereoisomers that are not mirror images.

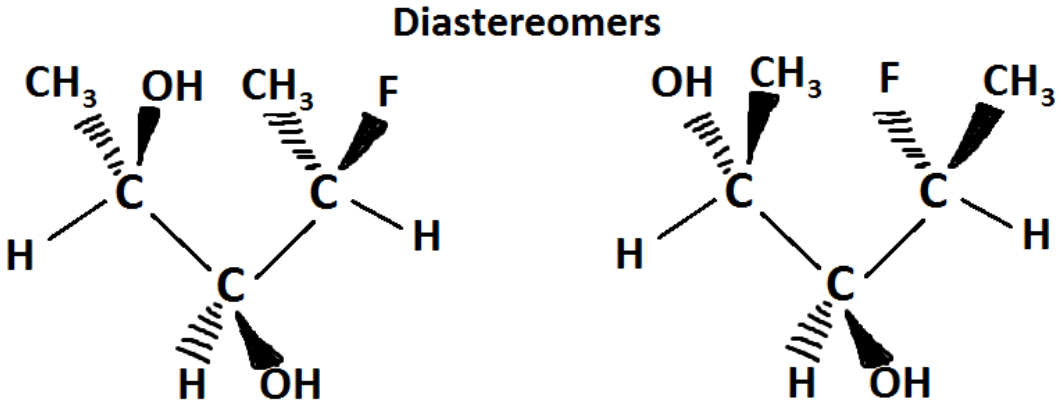


Figure 4.2. Two diastereomers of a three-stereocenter chain: the two structures share the same connectivity but differ in configuration at some (not all) stereocenters, so they are not mirror images of each other. ("Diastereomers" by Rhannosh, CC BY-SA 3.0, via Wikimedia Commons.)

R/S Configuration

A system for describing stereocenters.

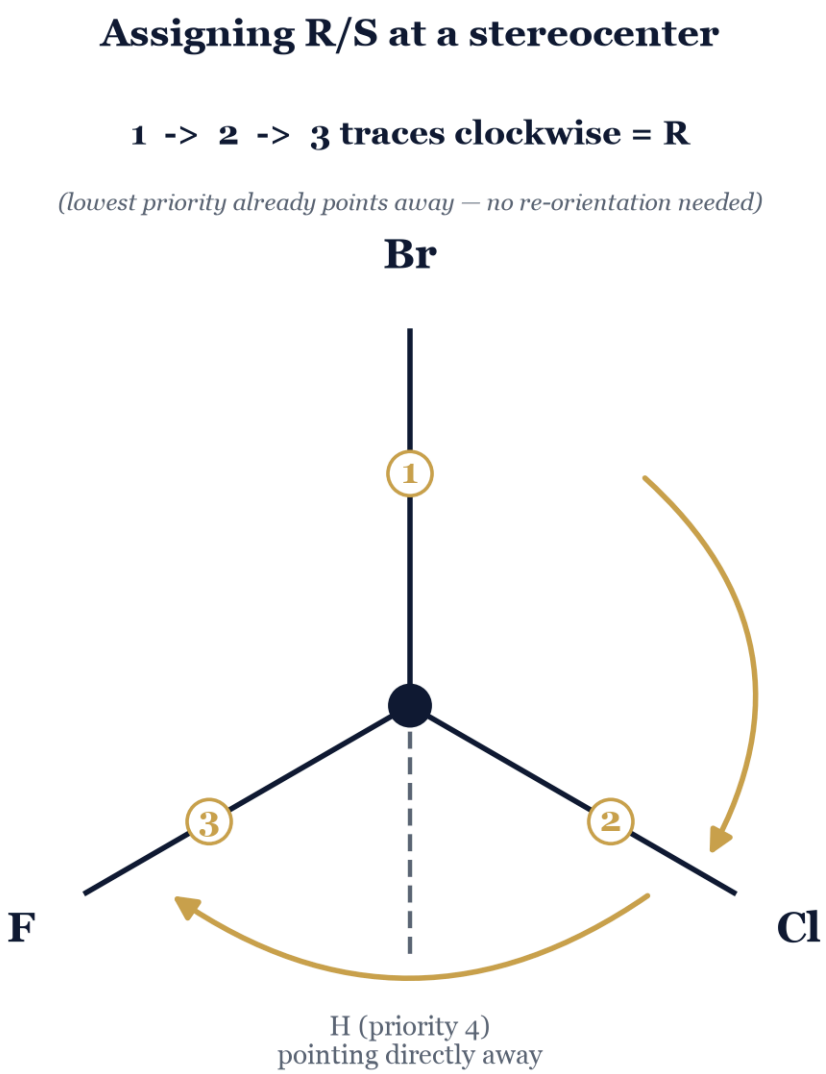


Figure 4.3. Assigning R/S at a stereocenter, step by step: (1) rank the four substituents by priority (highest atomic number wins first point of difference), (2) orient the lowest-priority group pointing away from the viewer, (3) trace 1⟶2⟶3 — clockwise is R, counterclockwise is S.

Conformations

Different spatial arrangements produced by bond rotation.

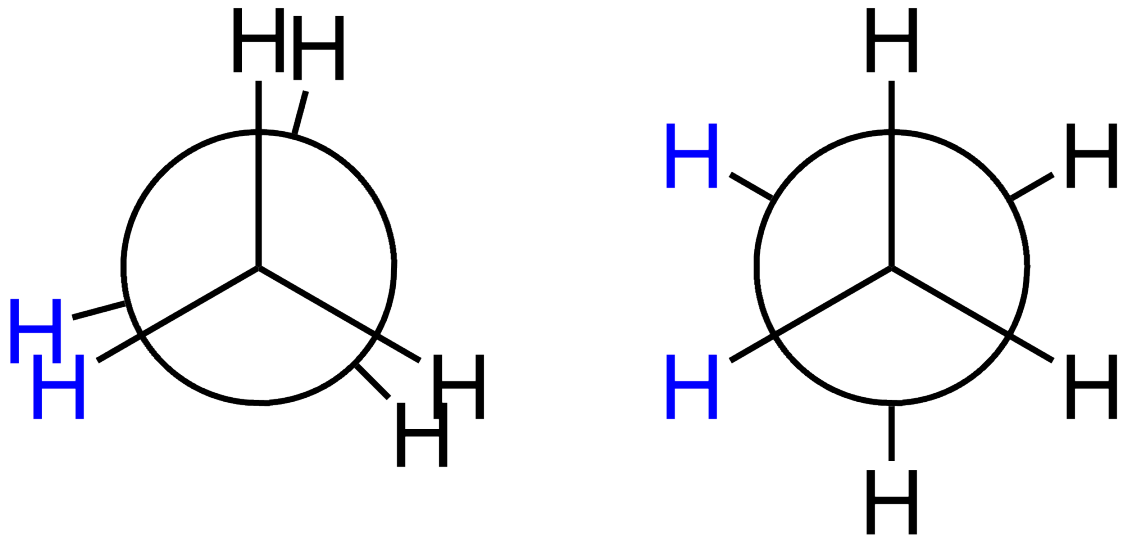


Figure 4.4. Newman projection of ethane: eclipsed (left, higher energy — front and back C–H bonds aligned) and staggered (right, lower energy — bonds at 60° offset). ("Newman projection of ethane" by Aglarech, public domain, via Wikimedia Commons.)

Conformational Analysis

Bond rotation lets the same molecule adopt many different three-dimensional shapes without breaking any bonds. Unlike stereoisomers, different conformations interconvert freely at room temperature.

The Chair Conformation

A flat, hexagonal cyclohexane ring would suffer from angle strain (its bond angles would be forced to 120°, away from the preferred 109.5°) and eclipsing interactions between neighboring hydrogens. Puckering the ring into a chair relieves both problems: every bond angle relaxes to near 109.5°, and every neighboring pair of hydrogens becomes staggered. The chair is the most stable conformation of cyclohexane.

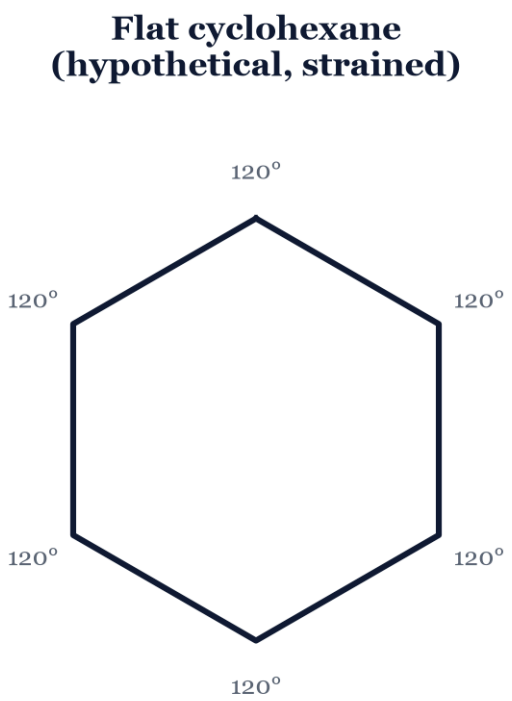


Figure 4.5. Flat cyclohexane (left) forces 120° bond angles — angle strain. ("Flat cyclohexane" — original figure for this handbook.)

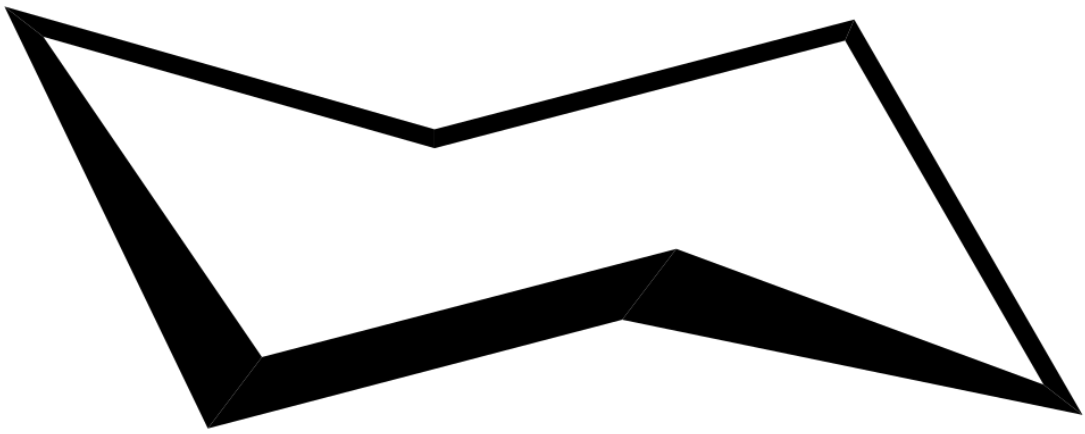


Figure 4.6. Puckering into the chair relaxes every bond angle to near the tetrahedral 109.5°, relieving the angle strain the flat ring would have. ("Chair conformation of cyclohexane" by ChemSim, public domain, via Wikimedia Commons.)

Axial and Equatorial Positions

Each carbon of the chair holds two positions, pointing in different directions:

Axial — perpendicular to the average plane of the ring, alternating up and down around the ring.
Equatorial — roughly in the plane of the ring, pointing outward.

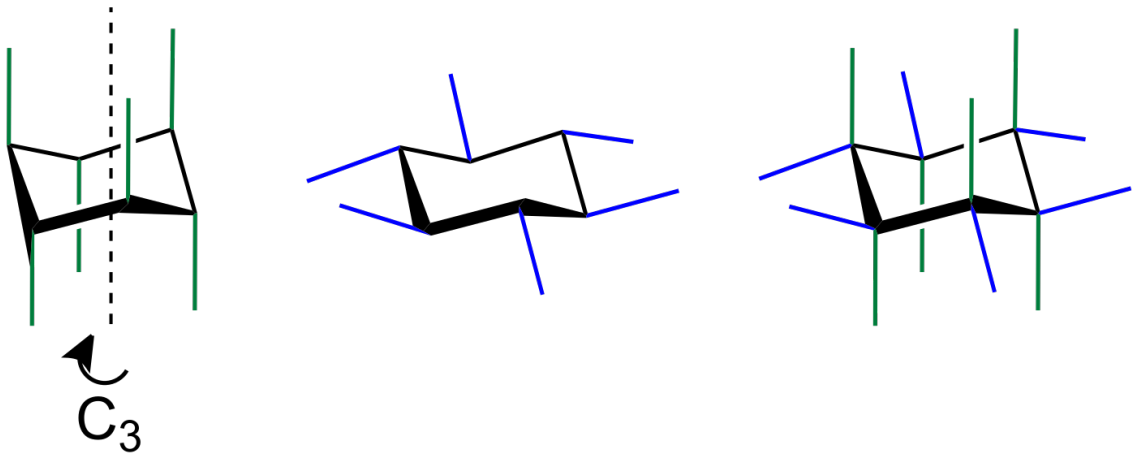


Figure 4.7. Axial (vertical, alternating up/down) versus equatorial (outward, roughly in the ring's plane) bonds at each carbon of the chair. ("Axial & equatorial bonds at cyclohexane" by Jü, public domain, via Wikimedia Commons.)

Ring Flipping

A chair can invert into another chair through a continuous rotation of its bonds — a ring flip. Ring flipping converts every axial position into an equatorial position and every equatorial position into an axial one, but it does not break bonds or change configuration at any stereocenter.

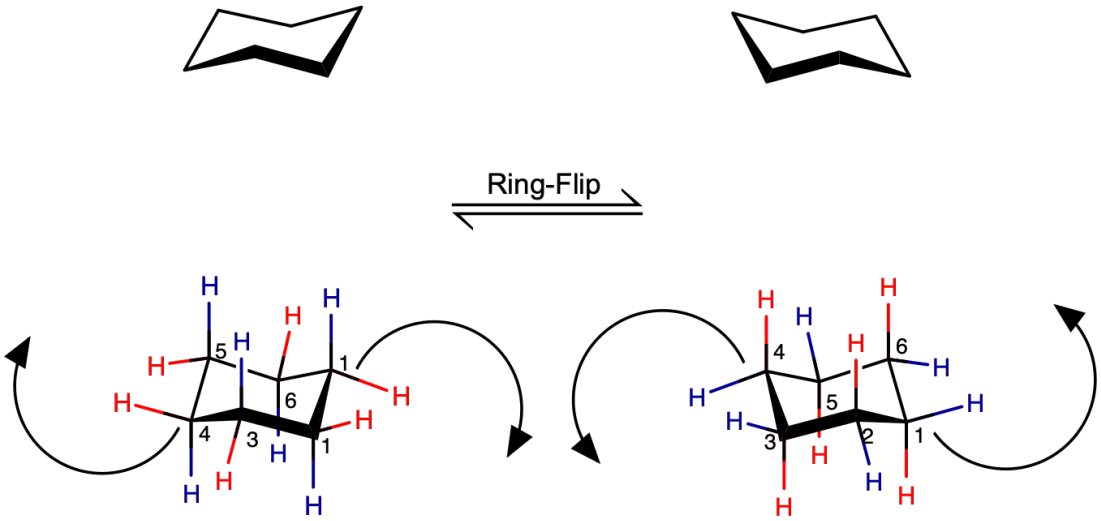


Figure 4.8. A ring flip interconverts the two chair forms: every substituent that was axial becomes equatorial, and vice versa — no bonds break, and no stereocenter's configuration changes. ("Ring flip of cyclohexane" by Naturwiki, public domain, via Wikimedia Commons.)

Why Equatorial Is Preferred

An axial substituent points toward the axial hydrogens two carbons away on the same face of the ring. These 1,3-diaxial interactions are a steric strain that grows with the size of the substituent. Because ring flipping is fast and reversible, a substituted cyclohexane exists as an equilibrium between two chairs, and the chair that places the larger substituent equatorial is generally favored.

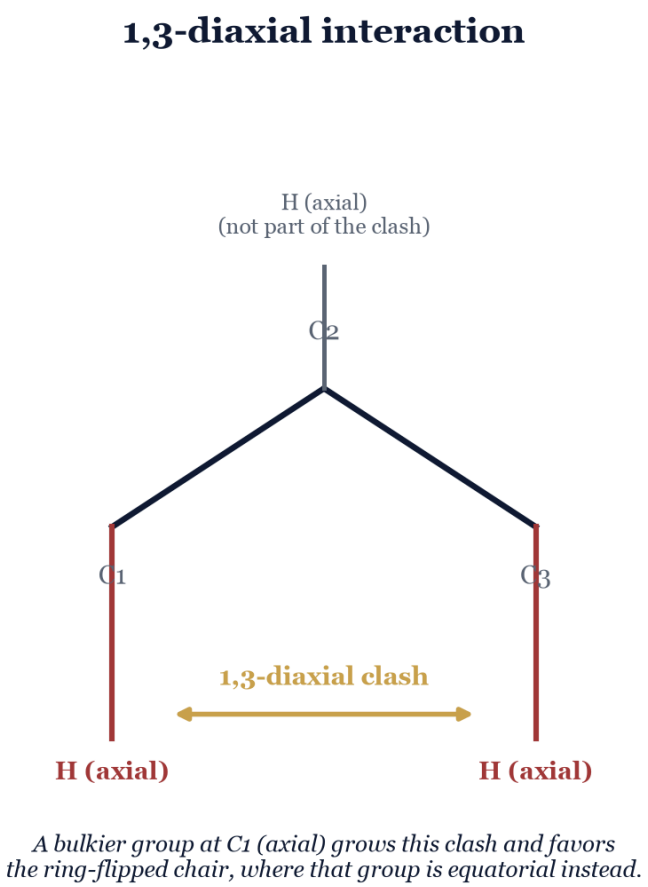


Figure 4.9. 1,3-diaxial interaction: a substituent placed axial at C1 points toward the axial hydrogens at C3 and C5, on the same face of the ring — the resulting steric clash grows with the substituent's size and favors the equatorial chair instead.

Visual Thinking

Stereochemistry is inherently visual.
Students benefit greatly from:

- drawing structures,
- using model kits,
- rotating molecules,
- and practicing repeatedly.

Gentle Exercises

Identify:

- chiral centers,
- enantiomeric pairs,
- molecules possessing symmetry.

Draw:

- a cyclohexane chair conformation with axial and equatorial positions labeled,

- the result of a ring flip on a substituted cyclohexane.

Common Mistakes

Trying to Visualize Everything Mentally

Better approach:
Draw structures. Use molecular models.

Confusing Conformations with Configurations

Better approach:
Bond rotation and ring flipping change conformation, not configuration. No bonds break, and stereocenters are unaffected.

Self-Assessment

I can:
- ☐ Recognize chiral centers.
- ☐ Distinguish enantiomers from diastereomers.
- ☐ Appreciate the importance of molecular shape.
- ☐ Understand the value of molecular models.
- ☐ Draw a cyclohexane chair and identify axial and equatorial positions.
- ☐ Explain why bulkier substituents favor the equatorial position.

Further Study

Reading

LibreTexts Organic Chemistry — Ch. 5, Stereochemistry at Tetrahedral Centers — Chirality; stereochemistry; conformations.

Videos

Organic Chemistry Tutor — Chirality; R/S configuration; chair conformations.
Khan Academy — Organic Chemistry — Chirality; stereoisomers.

Supplementary

Master Organic Chemistry — Chirality; stereochemistry.

Looking Ahead

Shape influences chemistry.
But reactions themselves are governed by the movement of electrons.
The next chapter introduces electron flow and mechanistic thinking.

Chapter 5: Electron Flow

Following the Electrons

Introduction

Organic chemistry is often described as the study of reactions and transformations.

Underlying these processes is the movement of electrons.

Electrons determine:

- how bonds form,
- how bonds break,
- and how molecules interact.

Learning to follow electrons is one of the most important skills in organic chemistry.

Although reactions may initially appear diverse and complicated, many can be understood by recognizing recurring patterns of electron movement.

Throughout this chapter, the emphasis is not on memorizing reactions but on understanding how electrons behave and how their movement explains chemical change.

Why Electron Flow Matters

Electrons govern:

- bonding,
- reactivity,
- stability,
- and molecular structure.

Understanding electron flow helps connect many of the ideas encountered in earlier chapters, including:

- functional groups,
- resonance,
- acids and bases,
- and stereochemistry.

Electron movement provides a framework for understanding how these concepts influence chemical behavior.

Curved Arrows

Organic chemists use curved arrows to represent the movement of electrons.

Curved arrows do not indicate the movement of atoms.

Instead, they show how electrons are redistributed during chemical processes.

Learning to interpret curved arrows is similar to learning the grammar and syntax of a new language.

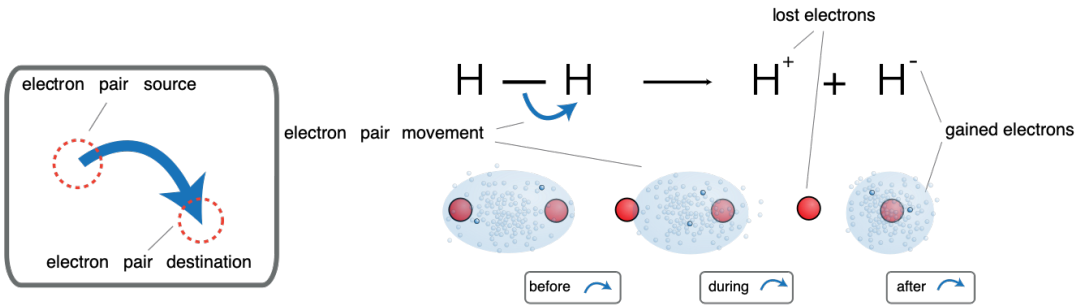


Figure 5.1. Curved arrow anatomy: the tail sits at the electron-pair source, the head points to the electron-pair destination. Worked example: heterolysis of H–H into H^+ (lost its electron pair) and H^- (gained the electron pair). ("Curved arrow electron pair" by Jkwchui, public domain, via Wikimedia Commons.)

Electron-Rich and Electron-Poor Regions

Electrons are not distributed uniformly within molecules.

Some regions possess relatively high electron density.

Others are relatively electron deficient.

These differences help explain why molecules interact with one another and why certain reactions occur.

Understanding electron density provides insight into:

- polarity,
- reactivity,
- and stability.

Nucleophiles and Electrophiles

Many reactions involve interactions between electron-rich and electron-poor species.

Nucleophiles

Nucleophiles donate electrons.

Common examples include:

- hydroxide,
- water,
- ammonia,
- and molecules possessing lone pairs.

Electrophiles

Electrophiles accept electrons.

Common examples include:

- carbocations,
- positively charged species,
- and polarized atoms within molecules.

These interactions appear repeatedly throughout organic chemistry.

Bond Formation and Bond Breaking

Chemical reactions involve changes in bonding.

New bonds form when electrons are shared.

Existing bonds break when electrons are redistributed.

Understanding how electrons move during these processes provides a foundation for understanding more complicated reactions.

Simple Examples of Electron Flow

Many familiar processes involve electron movement.

Examples include:

Proton Transfer

Acid-base reactions involve the transfer of protons and accompanying electron movement.

Lewis Acid-Base Interactions

Electron pairs are donated and accepted.

Simple Additions

Electron-rich species interact with electron-poor regions.

Although these examples are simple, they illustrate patterns that reappear throughout organic chemistry.

Themes That Reappear

Throughout organic chemistry, several ideas repeatedly influence electron movement:

- resonance,
- acidity and basicity,
- electronegativity,
- charge,
- and stability.

These principles help explain why electrons move in particular ways.

Common Mistakes

Following Atoms Instead of Electrons

Better approach:

Focus on electron movement.

Memorizing Reactions Without Understanding Electron Flow

Better approach:

Learn to recognize recurring patterns.

Treating Curved Arrows as Decorations

Better approach:

Interpret curved arrows as descriptions of electron movement.

Self-Assessment

I can:

☐ Interpret curved arrows.
☐ Recognize electron-rich and electron-poor regions.
☐ Distinguish nucleophiles from electrophiles.
☐ Understand how bonds form and break.
☐ Appreciate the importance of electron movement in organic chemistry.

Further Study

Reading

LibreTexts Organic Chemistry — Ch. 6, An Overview of Organic Reactions — Reaction mechanisms; curved-arrow notation.

Videos

Khan Academy — Resonance and Acid-Base Chemistry — Curved arrows; electron-pushing.

Continue practicing:

- resonance structures,
- acid-base reactions,
- and curved-arrow notation.

These ideas provide the foundation for understanding reaction mechanisms.

Looking Ahead

Electrons determine how molecules interact.

The next part explores how these interactions combine to produce chemical transformations.

Reaction mechanisms provide a framework for understanding how molecules change and why particular reaction pathways are favored.

IV

Part IV: Mechanistic Thinking

Recognizing Reaction Patterns

The previous sections introduced the foundational concepts that govern organic chemistry.

Functional groups provided vocabulary. **Resonance** explained electron distribution and stability. **Acids and bases** supplied logic. **Stereochemistry** emphasized the importance of shape. **Electron flow** introduced the movement of electrons.

These ideas now come together in the study of reaction mechanisms.

Mechanisms describe how molecules are transformed.

At first, the number of reactions encountered in Organic Chemistry I can seem overwhelming.

Fortunately, most reactions belong to a relatively small number of recurring families.

Throughout this part, the emphasis is not on memorizing isolated products.

Instead, the goal is to develop a framework for understanding why reactions occur and how different reaction pathways are related.

Three Reaction Families

Three major reaction families dominate much of Organic Chemistry I:

Substitution Reactions

One group replaces another.

Elimination Reactions

Atoms are removed to form multiple bonds.

Addition Reactions

Atoms are added across multiple bonds.

Although these reactions may initially appear distinct, they are deeply interconnected.

They share common principles:

- electron flow,
- stability,
- resonance,
- acids and bases,
- steric effects,
- and functional group transformations.

As familiarity grows, these mechanisms become less like isolated facts and more like recurring patterns.

Ultimately, mechanistic thinking reduces the need for memorization and helps students reason through unfamiliar problems.

The chapters that follow explore these reaction families and the patterns that unite them.

By the end of this part, the reader should begin to recognize that organic chemistry is not a collection of hundreds of unrelated reactions.

Rather, it is a coherent system governed by a surprisingly small number of principles.

Chapter 6: Introduction to Mechanisms

Learning to Follow the Electrons

Introduction

Reaction mechanisms describe how molecules are transformed.

Rather than simply identifying reactants and products, mechanisms explain:

- how molecules change,
- how bonds are broken,
- how bonds are formed,
- and how electrons move throughout a reaction.

Understanding mechanisms helps transform organic chemistry from a collection of isolated reactions into a coherent system.

Although many different reactions exist, the principles governing electron movement are remarkably consistent.

Learning to interpret mechanisms is therefore one of the most important goals of Organic Chemistry I.

Throughout this chapter, the emphasis is not on memorizing products, but on understanding how and why reactions occur.

As familiarity grows, mechanisms become less like sequences to memorize and more like patterns that can be recognized and understood.

What Is a Reaction Mechanism?

A reaction mechanism provides a step-by-step description of how molecules are transformed.

Mechanisms explain:

- how molecules change,
- which bonds break,
- which bonds form,
- how electrons move,
- and which intermediates may appear along the way.

Mechanisms provide explanations rather than isolated facts.

They allow chemists to understand why a particular reaction occurs and why one pathway may be favored over another.

Although mechanisms can initially seem intimidating, many are built upon a surprisingly small number of recurring ideas.

These ideas include:

- electron-rich species and electron-poor species,
- stability,
- resonance,
- acids and bases,
- and the tendency of systems to move toward lower-energy arrangements.

Understanding these principles reduces the need for memorization and helps organize what might otherwise appear to be a large collection of unrelated reactions.

Ultimately, mechanisms provide a framework for thinking rather than a list of facts to memorize.

Curved Arrows, Applied to Mechanisms

Chapter 5 introduced curved arrows: the notation for showing where electrons come from and where they go, never where atoms move.

Mechanisms are where that notation earns its keep. Every step in the reactions ahead is a curved arrow — or a small set of them — connecting a source of electron density to a destination.

The Major Participants

Several recurring actors appear throughout organic chemistry.

Nucleophiles

Electron-rich species that donate electrons.

Examples include:

- hydroxide ions,
- water,
- ammonia,
- and many molecules possessing lone pairs.

Electrophiles

Electron-poor species that accept electrons.

Examples include:

- carbocations,
- carbonyl carbons,
- and positively charged species.

Leaving Groups

Atoms or groups that depart during reactions.

Good leaving groups stabilize the electrons they take with them.

Intermediates

Temporary species formed during reaction pathways.

Examples include:

- carbocations,
- carbanions,
- radicals.

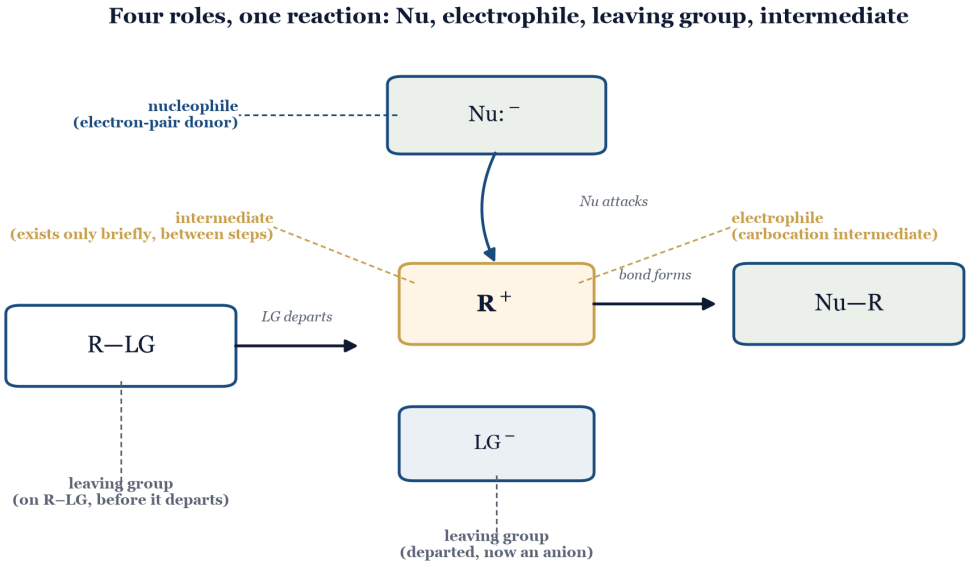


Figure 6.1. All four roles in one generic reaction: a leaving group departs from R–LG, leaving behind a carbocation intermediate that is simultaneously the electrophile, which a nucleophile ($Nu:^-$) then attacks.

Stability Governs Reactivity

Much of organic chemistry can be understood through a simple principle:

Stable species are favored.

Stability is influenced by:

- resonance,
- electronegativity,
- hybridization,
- steric effects,
- and charge distribution.

These factors influence:

- electron density,
- the stability of intermediates,
- the likelihood of reaction pathways,
- and the products that ultimately form.

Rather than memorizing isolated reactions, chemists repeatedly ask:

- Which species is most stable?
- Which pathway is favored?
- How are electrons distributed?
- How does structure influence reactivity?

The Major Reaction Families

Most reactions encountered in Organic Chemistry I belong to one of three families:

Substitution Reactions

One group replaces another.

Elimination Reactions

Atoms are removed to form multiple bonds.

Addition Reactions

Atoms are added across double or triple bonds.

Although many variations exist, these broad patterns account for much of the chemistry encountered in the first semester.

Thinking Mechanistically

Beginning students often ask:

"What product should I memorize?"

Experienced chemists ask:

- Where are the electrons?
- Which species is electron-rich?
- Which species is electron-poor?
- Which pathway leads to the most stable outcome?

Mechanistic thinking emphasizes understanding rather than memorization.

Gentle Exercises

Identify:

- nucleophiles,
- electrophiles,
- leaving groups,
- likely sites of electron movement.

Practice interpreting curved arrows.

Common Mistakes

Drawing Curved Arrows in the Wrong Direction

Better approach:

Curved arrows always originate at the source of electrons and point toward where they are going — from lone pairs or π bonds toward positive charges, empty orbitals, or electronegative atoms. Reversing the direction of an arrow describes the opposite of what is happening.

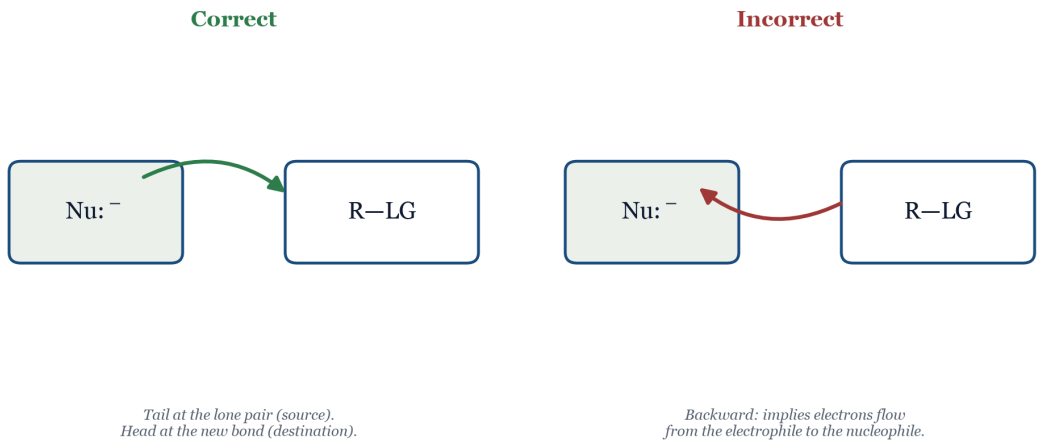


Figure 6.2. Same nucleophilic attack, drawn two ways: correct (tail at the lone pair, head at the new bond) versus incorrect (reversed, implying electrons flow from the electrophile to the nucleophile).

Ignoring Stability

Better approach:
Ask why one pathway is favored over another.

Viewing Reactions as Unrelated

Better approach:
Recognize recurring patterns.

Self-Assessment

I can:

- ☐ Understand the purpose of mechanisms.
- ☐ Recognize nucleophiles.
- ☐ Recognize electrophiles.
- ☐ Understand curved arrows.
- ☐ Appreciate the importance of stability.
- ☐ Distinguish substitution, elimination, and addition reactions.

Further Study

Reading

MIT OpenCourseWare — Lecture Handouts — Mechanisms; nucleophiles; electrophiles.
LibreTexts Organic Chemistry — Ch. 6, An Overview of Organic Reactions — Mechanisms; nucleophiles; electrophiles.

Videos

Organic Chemistry Tutor — Reaction mechanisms; curved arrows.
Khan Academy — Organic Chemistry — Reaction mechanisms.

Supplementary

Master Organic Chemistry — Curved arrows; nucleophiles and electrophiles; mechanisms.

Looking Ahead

The first major reaction family encountered in Organic Chemistry I is substitution.

These reactions illustrate how one functional group may be replaced by another and introduce two important mechanisms: SN1 and SN2.

Understanding the similarities and differences between these reactions forms one of the central themes of Organic Chemistry I.

Chapter 7: Substitution Reactions

Replacing One Group with Another

Introduction

Substitution reactions are among the first major reaction families encountered in Organic Chemistry I.
In these reactions, one atom or group is replaced by another.
Although many variations exist, two mechanisms dominate:

- SN2
- SN1

Understanding the differences between these mechanisms represents one of the most important milestones in the course.

The Big Idea

Both SN1 and SN2 accomplish the same overall transformation:
One group leaves. Another group takes its place.
The difference lies in how the replacement occurs.

SN2 Reactions

A Concerted Mechanism

In an SN2 reaction, bond formation and bond breaking occur simultaneously. There are no intermediates.

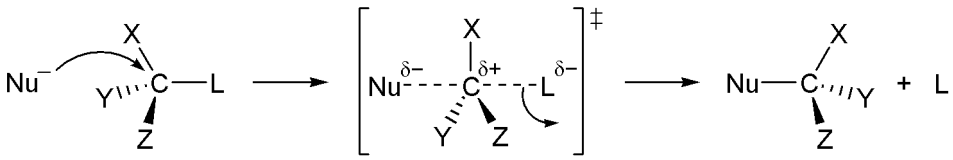


Figure 7.1. SN2 mechanism: the nucleophile attacks from the side opposite the leaving group, passing through a trigonal bipyramidal transition state, which inverts the configuration at carbon. ("SN2 reaction mechanism" by Calvero, public domain, via Wikimedia Commons.)

Characteristics

- One-step mechanism.
- Strong nucleophiles favored.
- Polar aprotic solvents preferred.
- Inversion of stereochemistry.
- Sensitive to steric hindrance.

Preferred Substrates

Best: methyl, primary. Possible: secondary. Poor: tertiary.

Why It Happens

Steric crowding affects the ability of the nucleophile to approach the reactive carbon.

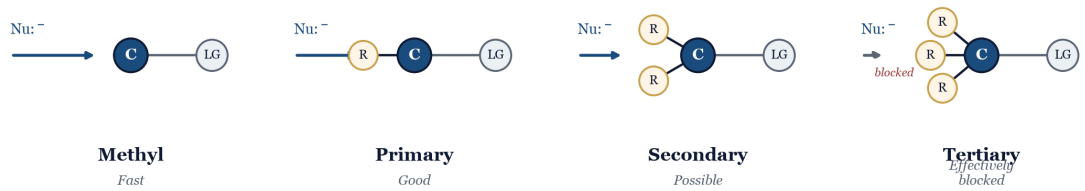


Figure 7.2. As alkyl substitution at the reactive carbon increases (methyl → primary → secondary → tertiary), the nucleophile's backside approach becomes progressively more obstructed, and the SN2 rate falls accordingly.

SN1 Reactions

A Stepwise Mechanism

The leaving group departs first. A carbocation intermediate forms. The nucleophile attacks afterward.

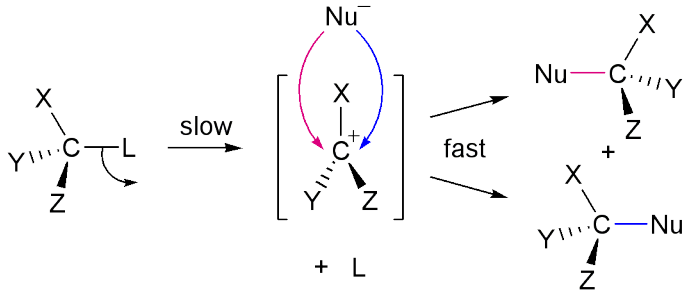


Figure 7.3. SN1 mechanism: the leaving group departs first (slow step) to form a planar carbocation intermediate, which the nucleophile then attacks from either face (fast step) — producing a mixture of stereochemical outcomes. ("SN1 reaction mechanism" by Calvero, public domain, via Wikimedia Commons.)

Characteristics

- Two-step mechanism.
- Weak nucleophiles acceptable.
- Polar protic solvents favored.
- Carbocation intermediate.
- Racemization possible.

Preferred Substrates

Best: tertiary. Possible: secondary. Poor: methyl, primary.

Why It Happens

Carbocation stability determines whether the reaction is favorable.

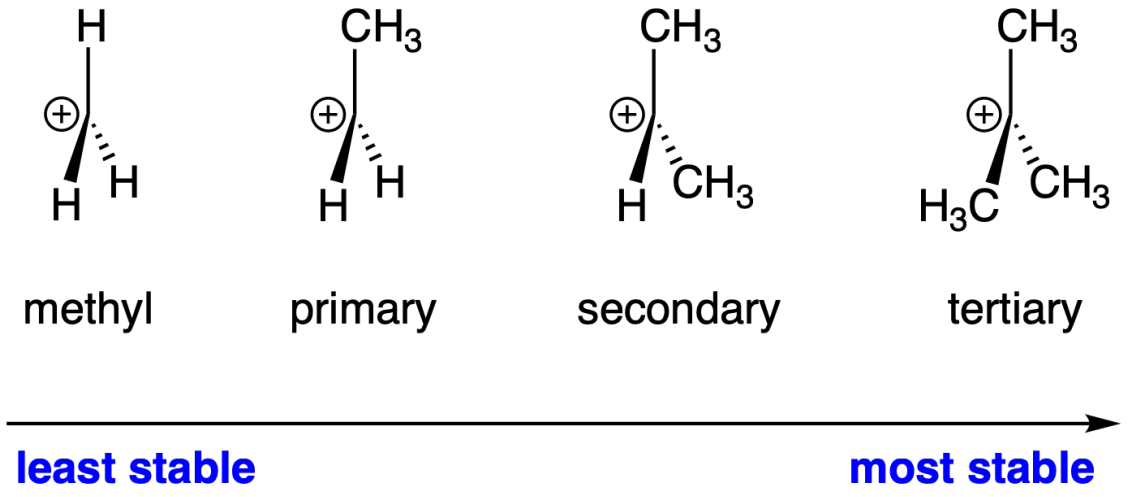


Figure 7.4. Carbocation stability increases from methyl to primary to secondary to tertiary, as more alkyl groups donate electron density toward the positively charged carbon. ("Series showing increasing stability of alkyl carbocations" via LibreTexts Chemistry (Morsch et al.), CC BY 4.0, via Wikimedia Commons.)

Comparing SN1 and SN2

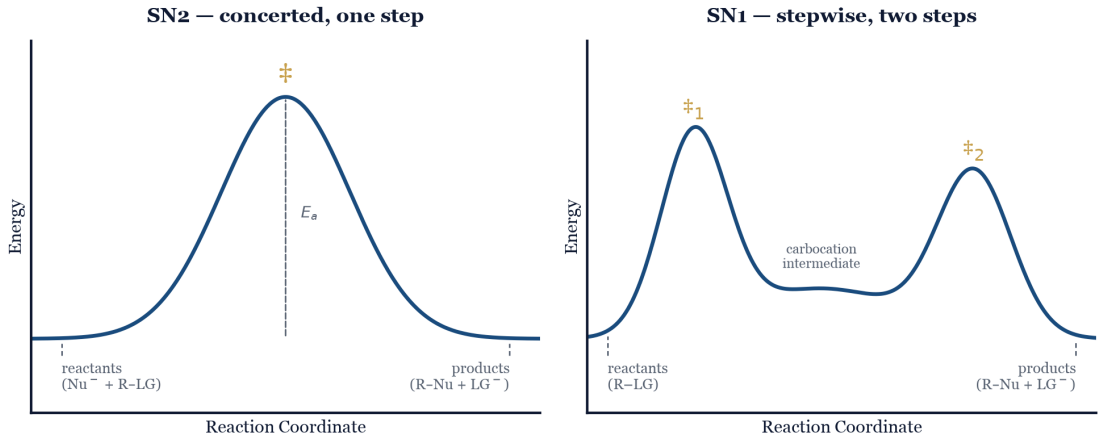


Figure 7.5. SN2 proceeds through a single transition state, while SN1 proceeds through two transition states separated by a carbocation intermediate.

Feature	SN2	SN1
Mechanism	One-step	Two-step
Intermediate	None	Carbocation
Nucleophile	Strong	Weak acceptable
Solvent	Polar aprotic	Polar protic
Preferred substrate	Primary	Tertiary
Stereochemistry	Inversion	Racemization (often partial)

Thinking About Substitution

Helpful questions include:

- How crowded is the reactive carbon?
- Is a carbocation stable?
- How strong is the nucleophile?
- What solvent is present?

Gentle Exercises

Identify: nucleophile, leaving group, substrate type.
Predict: whether SN1 or SN2 is more likely.

Common Mistakes

Memorizing Tables

Better approach:
Understand steric effects and carbocation stability.

Ignoring Solvents

Better approach:
Consider the reaction environment.

Overlooking Stereochemical Consequences

Better approach:
SN2 reactions invert configuration at the reaction center. SN1 reactions typically produce racemization, though often partial rather than complete — ion pairing between the carbocation and the departed leaving group can bias attack toward one face before the two fully separate. Predicting the correct product requires tracking stereochemistry, not just connectivity — two molecules with identical bonds but different spatial arrangement are different compounds.

Self-Assessment

I can:
☐ Distinguish SN1 and SN2.
☐ Explain carbocation stability.
☐ Appreciate steric hindrance.
☐ Understand stereochemical consequences.

Further Study

Reading

LibreTexts Organic Chemistry — Ch. 11, Substitution and Elimination — SN1 and SN2 mechanisms.

Videos

Organic Chemistry Tutor — SN1 vs. SN2 comparisons.

Supplementary

Master Organic Chemistry — Comparing the SN1 and SN2 Reactions — Substrate, nucleophile, and solvent effects on mechanism.

Looking Ahead

Substitution reactions replace groups. Another major reaction family removes groups entirely.

These elimination reactions introduce E1 and E2 mechanisms and lead to the formation of multiple bonds.

Chapter 8: Elimination Reactions

Building Double Bonds

Introduction

Elimination reactions remove atoms or groups from molecules and create double bonds.
These reactions are closely related to substitution reactions and often compete with them.
Two mechanisms dominate:

- E2
- E1

Understanding their similarities and differences helps organize much of Organic Chemistry I.

The Big Idea

Instead of replacing one group with another, elimination reactions remove atoms and generate π bonds.

E2 Reactions

A Concerted Mechanism

Bond formation and bond breaking occur simultaneously. No intermediates are formed.

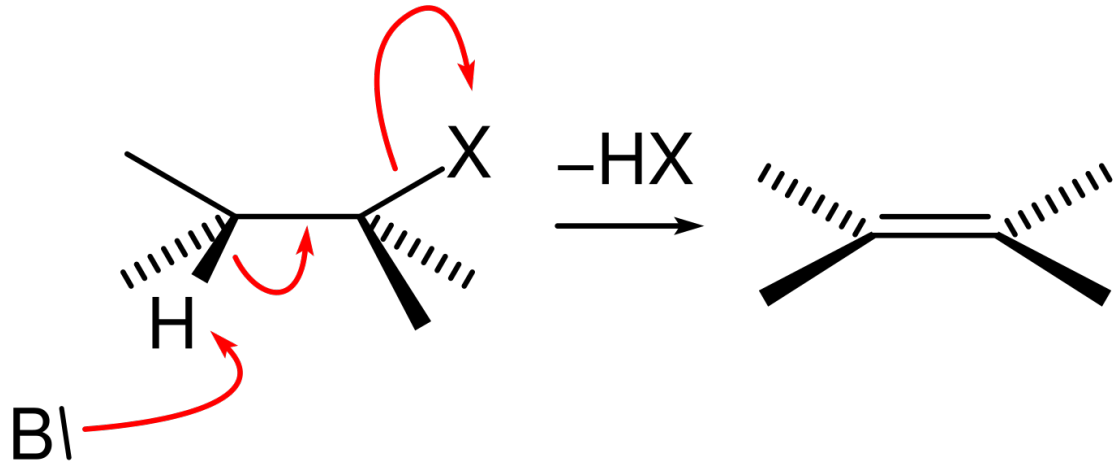


Figure 8.1. E2 mechanism: a base removes a β-hydrogen while the leaving group departs simultaneously, forming the new π bond in a single step. ("E2-mechanism" by Matthias M., public domain, via Wikimedia Commons.)

Characteristics

- One-step mechanism.
- Strong bases required.
- No carbocation intermediate.
- Anti-periplanar geometry important.

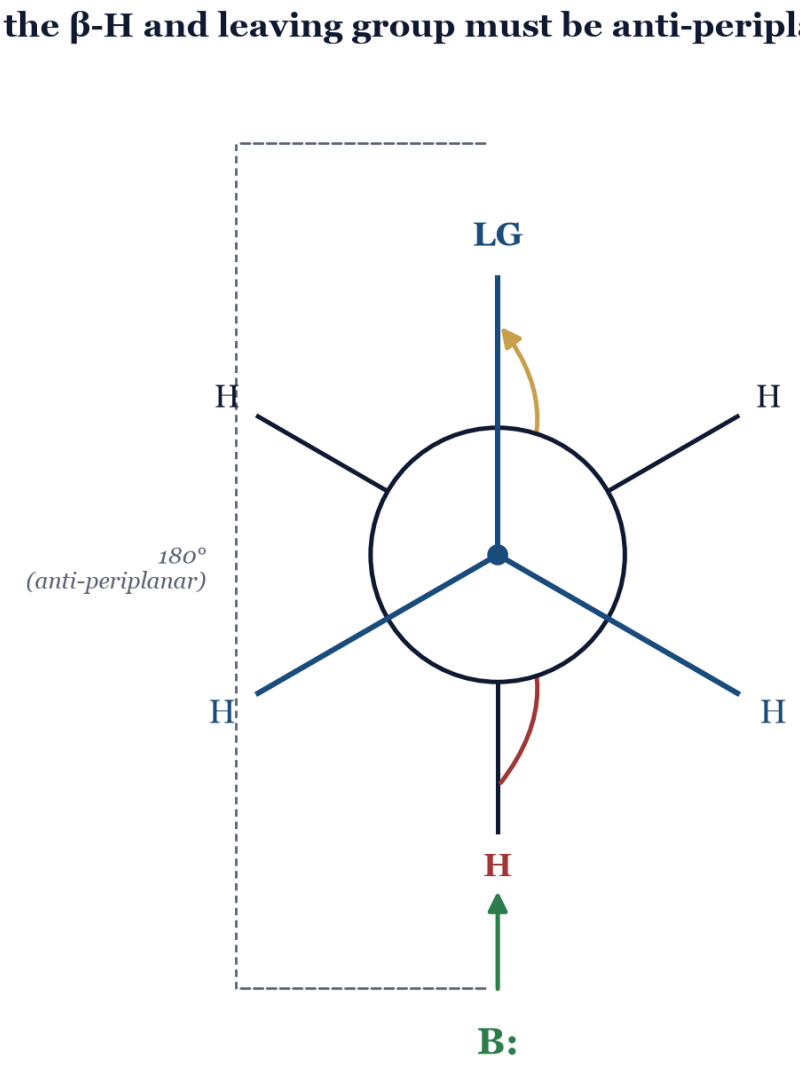


Figure 8.2. Newman projection sighting down the C–C bond: the β-hydrogen and leaving group must be anti-periplanar (180° apart) for E2 to proceed. The base removes the anti H as the leaving group departs, forming the new π bond in between.

Preferred Substrates

Best: tertiary, secondary. Possible: primary (with a bulky, non-nucleophilic base such as tert-butoxide, which favors elimination over SN2).

Why It Happens

Strong bases remove protons while leaving groups depart.

E1 Reactions

A Stepwise Mechanism

The leaving group departs first. A carbocation intermediate forms. Elimination occurs afterward.

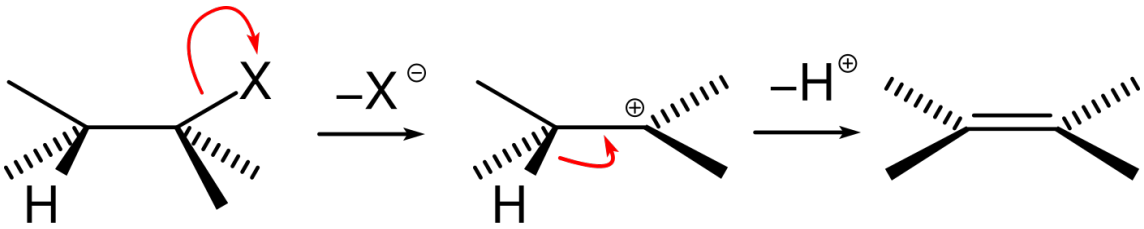


Figure 8.3. E1 mechanism: the leaving group departs first to form a carbocation intermediate, then a base removes a β-hydrogen to form the π bond. ("E1-mechanism" by Matthias M., public domain, via Wikimedia Commons.)

Characteristics

- Two-step mechanism.
- Weak bases acceptable.
- Carbocation intermediate.
- Rearrangements possible.

Preferred Substrates

Best: tertiary. Possible: secondary.

Similarity to SN1

E1 and SN1 reactions share carbocation intermediates and often occur under similar conditions.

Comparing E1 and E2

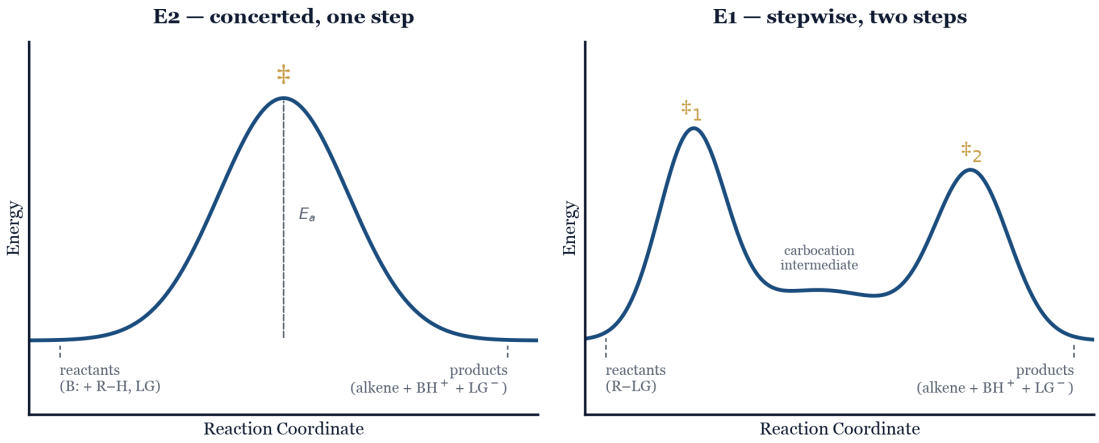


Figure 8.4. E2 proceeds through a single transition state, while E1 proceeds through two transition states separated by a carbocation intermediate.

Feature	E2	E1
Mechanism	One-step	Two-step
Intermediate	None	Carbocation
Base	Strong	Weak acceptable
Rearrangements	No	Possible

Feature	E2	E1
Preferred substrate	Secondary and tertiary	Tertiary

Competition Between Pathways

Many reactions can proceed through substitution, elimination, or mixtures of both.

The outcome depends upon:

- substrate structure,
- nucleophile strength,
- base strength,
- solvent,
- temperature.

Understanding this competition is one of the central themes of Organic Chemistry I.

Thinking About Elimination

Helpful questions include:

- Is a strong base present?
- Can a carbocation form?
- Is elimination favored over substitution?

Gentle Exercises

Determine: whether E1 or E2 is favored; whether substitution may compete.

Common Mistakes

Treating E1 and E2 as Isolated Reactions

Better approach:

Compare them to SN1 and SN2.

Forgetting the Geometric Requirements of E2

Better approach:

E2 elimination requires the departing hydrogen and the leaving group to be anti-periplanar — positioned on opposite sides of the molecule in the same plane. When a molecule cannot achieve this geometry due to its conformation, E2 is disfavored regardless of other conditions. Conformation matters.

Self-Assessment

I can:

☐ Distinguish E1 and E2.
☐ Understand carbocation intermediates.
☐ Appreciate the importance of strong bases.
☐ Understand competition with substitution.

Further Study

Reading

LibreTexts Organic Chemistry — Ch. 11, Substitution and Elimination — E1 and E2 mechanisms.

Videos

Organic Chemistry Tutor — E1 vs. E2 comparisons.

Looking Ahead

Elimination reactions create double bonds. These double bonds become sites of reactivity and give rise to addition reactions.

Chapter 9: Addition Reactions

Transforming Multiple Bonds

Introduction

Alkenes and alkynes are more reactive than alkanes because their π bonds are relatively easy to break.

Addition reactions convert multiple bonds into new single bonds while introducing additional atoms into molecules.

These reactions form an important bridge between Organic Chemistry I and Organic Chemistry II.

The Big Idea

Substitution replaces groups. Elimination forms multiple bonds. Addition reactions consume multiple bonds and create new functional groups.

Why Addition Reactions Matter

Addition reactions allow chemists to transform relatively simple molecules into more complex ones.

They make possible the synthesis of:

- alcohols,
- halides,
- carbonyl compounds,
- and many other functional groups.

Common Addition Reactions

Hydrogenation

Addition of hydrogen.

Hydrohalogenation

Addition of HX.

Hydration

Addition of water.

Halogenation

Addition of halogens.

Carbocations and Stability

Many addition reactions involve carbocation intermediates.

Consequently, ideas from earlier chapters remain important:

- resonance,
- stability,
- acids and bases,

- electron flow.

Organic chemistry repeatedly revisits the same foundational principles.

Regiochemistry

Not all additions occur in the same way.

When an electrophile adds to an unsymmetrical alkene, the two carbons of the double bond are not equivalent, and addition can proceed through two different carbocation intermediates. The pathway that forms the more stable intermediate is strongly preferred, because a more stable intermediate corresponds to a lower-energy transition state and a faster reaction.

Carbocation stability increases with the number of attached alkyl groups, so the more-substituted carbon is better able to stabilize a positive charge. As a result, hydrogen tends to add to the less-substituted carbon, leaving the more-substituted carbon to accept the other group. This outcome is known as Markovnikov's rule — but it is not an independent rule to memorize. It is a direct consequence of reasoning through intermediate stability.

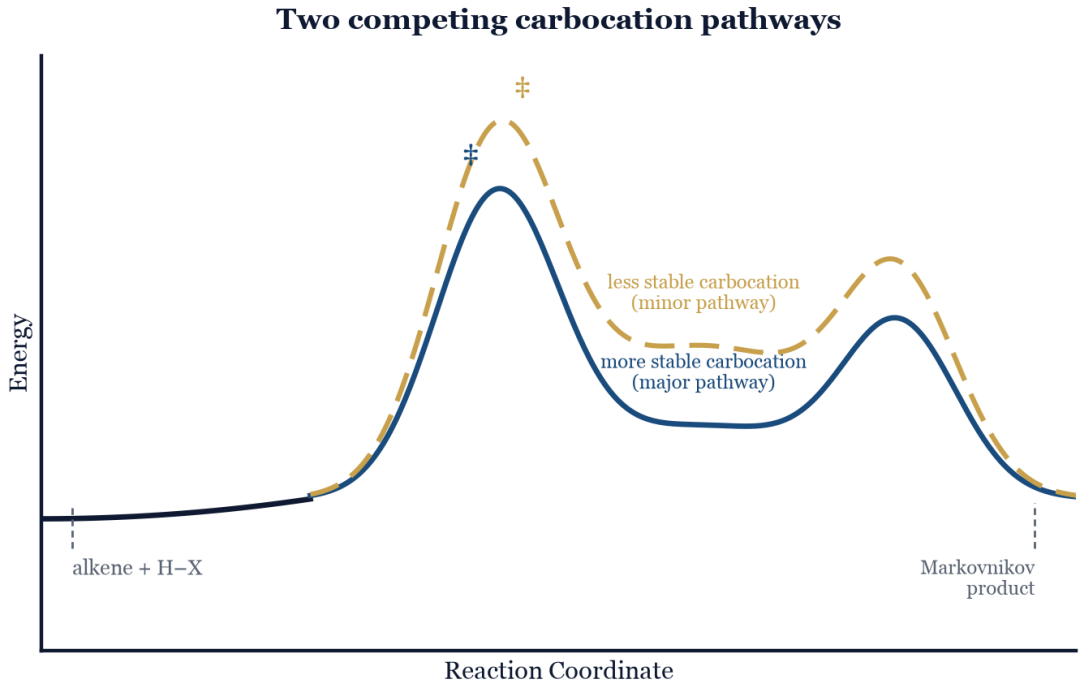


Figure 9.1. The two possible carbocation intermediates compete: the pathway through the more-substituted (more stable) carbocation has the lower-energy transition state and dominates, which is why Markovnikov's rule holds.

Important questions include:

- Which carbon receives hydrogen?
- Which carbon receives another group?
- Which pathway leads to the most stable intermediate?

Answering the third question answers the first two.

Thinking About Addition

Helpful questions include:

- Where are the π electrons?

- Which atom is electron-poor?
- Which intermediate is most stable?

Gentle Exercises

Identify: π bonds, electrophiles, nucleophiles.

Predict: where additions are likely to occur.

Predict: for an unsymmetrical alkene, which carbon ends up with the new group, by comparing the stability of the two possible carbocation intermediates.

Common Mistakes

Applying Addition Reactions to Aromatic Rings

Better approach:

Aromatic compounds strongly resist addition because addition would destroy aromatic stabilization. When a double bond is part of a benzene ring, substitution — not addition — is the expected pathway.

Predicting Regiochemistry Without Reasoning Through Intermediate Stability

Better approach:

When an electrophile adds to an unsymmetrical alkene, the intermediate carbocation forms preferentially at the more substituted carbon — the more stable one. Identifying the more stable intermediate predicts the major product. This principle underlies Markovnikov's rule.

Self-Assessment

I can:

☐ Recognize addition reactions.
☐ Understand why π bonds are reactive.
☐ Appreciate carbocation stability.
☐ Predict regiochemistry by comparing carbocation intermediates (Markovnikov's rule).
☐ Recognize common addition patterns.

Further Study

Reading

LibreTexts Organic Chemistry — Ch. 7, Alkenes: Structure and Reactivity — Electrophilic addition; Markovnikov's rule; carbocation stability.

Videos

Khan Academy — Alkenes and Alkynes — Addition reactions.

Looking Ahead

Although individual reactions are useful, experienced chemists rarely memorize isolated mechanisms.

Instead, they compare patterns and develop intuition.

The next chapter explores the relationships among substitution, elimination, and addition reactions.

Chapter 10: Comparing Reaction Families

Seeing the Patterns

Introduction

By this point, students have encountered three major reaction families: substitution, elimination, and addition.

At first, these reactions may appear to be independent topics.

Experienced chemists, however, rarely think about them separately.

Instead, they recognize recurring patterns and relationships.

Learning to see these relationships greatly reduces the amount of memorization required and helps transform organic chemistry into a coherent subject.

The Big Picture

Organic reactions can often be understood as different ways of changing functional groups.

Substitution

One group is replaced by another.

Elimination

Atoms are removed to create multiple bonds.

Addition

Atoms are added across multiple bonds.

Together, these three families account for much of Organic Chemistry I.

Reaction Families as Opposites

Certain reactions naturally complement one another.

Elimination

Produces π bonds.

Addition

Consumes π bonds.

Substitution

Changes functional groups without altering the number of π bonds.

Thinking about these relationships provides a useful framework for organizing reactions.

Similar Mechanisms

Many apparently different reactions share common features.

SN1 and E1

Both involve: carbocation intermediates, stepwise mechanisms, polar protic solvents, and tertiary substrates.

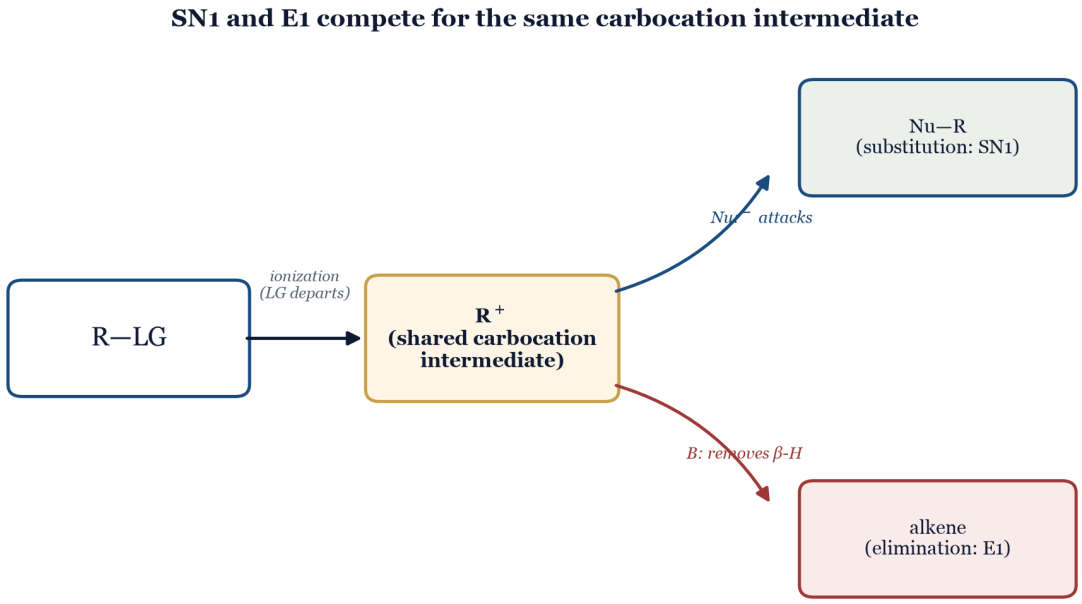


Figure 10.1. SN1 and E1 arise from the same carbocation intermediate: once the leaving group departs, a nucleophile can attack (substitution) or a base can remove a β-hydrogen (elimination) — the two pathways compete rather than occurring in isolation.

SN2 and E2

Both involve: concerted mechanisms, one-step processes, and strong nucleophiles or bases.

Recognizing these similarities helps explain why certain reactions compete with one another.

Stability Is the Unifying Principle

Throughout organic chemistry, one idea repeatedly appears:

Stable species are favored.

Stability is influenced by resonance, electronegativity, hybridization, steric effects, and charge distribution.

These factors determine which intermediates form, which pathways are favored, and which products predominate.

Questions Experienced Chemists Ask

Beginning students often ask: "What reaction do I memorize?"

Experienced chemists are more likely to ask:

Is a carbocation involved?

Is a strong base present?

Is the substrate crowded?

Is resonance important?

Which pathway produces the most stable intermediate?

Which pathway is fastest?

These questions provide a framework for reasoning through unfamiliar problems.

A Decision Framework

The questions above can be organized into a definite order. Working through them in sequence resolves most substitution and elimination problems.

First: Look at the Substrate

A methyl or primary carbon cannot support a carbocation, so SN1 and E1 are ruled out immediately. SN2 is favored — unless the base is bulky, which can force E2 even on a primary substrate.

A tertiary carbon cannot be attacked from the back side, so SN2 is ruled out immediately. SN1 or E1 become likely with a weak nucleophile or base; E2 becomes likely with a strong one.

Second: Look at the Nucleophile or Base

Strong and unhindered favors the concerted pathways — SN2 where the carbon is accessible, E2 otherwise.

Weak, or simply the solvent itself, favors the stepwise pathways that go through a carbocation — SN1 or E1.

Third: Look at the Solvent

A polar protic solvent stabilizes the carbocation intermediate that SN1 and E1 require. A polar aprotic solvent does the opposite: it leaves a nucleophile unsolvated and unusually reactive, favoring SN2.

Why This Order Matters

Checking the substrate first rules out entire pathways before any reagent details are considered — there is no need to weigh nucleophile strength once a tertiary carbon has already eliminated SN2 as a possibility. Reasoning in this order avoids the common mistake of jumping straight to the reagent and missing what the substrate has already decided.

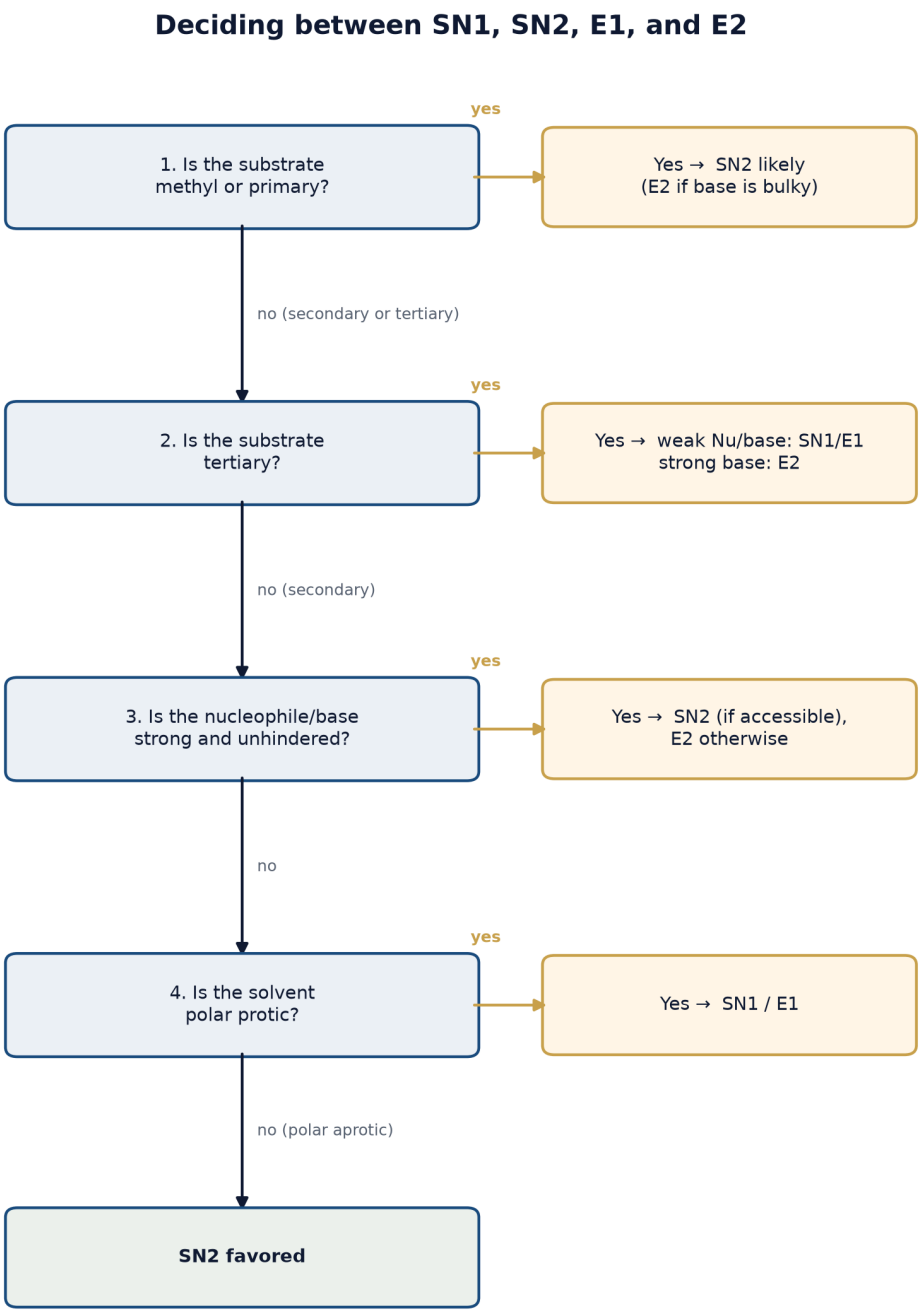


Figure 10.2. Deciding between SN1, SN2, E1, and E2 by working through the substrate, then the nucleophile/base, then the solvent, in that order.

A condensed, table form of this same reasoning is available in Appendix C for quick review.

Patterns Worth Recognizing

Strong Nucleophile + Primary Carbon

Often favors SN2.

Strong Base + Heat

Often favors E2.

Stable Carbocation

May favor SN1 or E1.

π Bonds Present

Often leads to addition reactions.

Although exceptions exist, recognizing these broad trends makes the subject considerably easier.

From Memorization to Pattern Recognition

Beginning students often feel overwhelmed because reactions appear unrelated.

With experience, however, patterns begin to emerge.

Instead of memorizing dozens of reactions individually, chemists recognize:

- recurring intermediates,
- recurring mechanisms,
- and recurring principles.

This shift from memorization to pattern recognition represents one of the most important developments in learning organic chemistry.

Gentle Exercises

Compare: SN1 and E1; SN2 and E2; elimination and addition.

Identify: similarities, differences, and competing pathways.

Apply: work through the substrate → nucleophile/base → solvent framework on a few substitution/elimination substrates and predict the likely pathway.

Common Mistakes

Treating Every Reaction as Unique

Better approach: Search for common patterns.

Memorizing Tables Without Understanding

Better approach: Focus on stability and electron flow.

Ignoring Competition Between Pathways

Better approach: Recognize that multiple mechanisms are often possible.

Self-Assessment

I can:

☐ Distinguish substitution, elimination, and addition.

☐ Recognize similarities between SN1 and E1.

☐ Recognize similarities between SN2 and E2.

☐ Understand that stability influences mechanisms.

☐ Appreciate the importance of pattern recognition.

☐ Work through the substrate → nucleophile/base → solvent decision framework on an unfamiliar problem.

Further Study

Reading

LibreTexts Organic Chemistry — Ch. 11, Substitution and Elimination — Reaction mechanisms; substitution; elimination; addition reactions.

Videos

Organic Chemistry Tutor — SN1 vs. SN2; E1 vs. E2.
Khan Academy — Organic Chemistry — Substitution and elimination reactions.

Supplementary

Master Organic Chemistry — Deciding SN1/SN2/E1/E2: The Substrate and **Wrapup** — SN1 versus SN2; E1 versus E2; reaction mechanisms.

Looking Ahead

As students gain experience, reactions begin to feel less like isolated facts and more like variations on familiar themes.

The final chapter of this part explores how chemists develop intuition and why repeated exposure is often more valuable than memorization.

Chapter 11: Developing Intuition

Learning to Think Like a Chemist

Introduction

By this point, students have encountered functional groups, resonance, acids and bases, stereochemistry, electron flow, and the major reaction families.

At first, these topics may have seemed overwhelming.

Yet experienced chemists rarely think of organic chemistry as a collection of isolated facts.

Instead, they rely upon intuition developed through repeated exposure to recurring patterns.

Developing this intuition is one of the central goals of studying organic chemistry.

What Intuition Really Means

Intuition is not magic. It is not innate talent. It is familiarity.

Experienced chemists have simply encountered the same ideas many times and learned to recognize patterns.

Over time, questions that once required deliberate effort become increasingly automatic.

Pattern Recognition

Beginning students often see many reactions, many structures, and many mechanisms.

Experienced chemists see:

- familiar functional groups,
- recurring intermediates,
- common patterns of electron movement,
- and stable versus unstable arrangements.

Much of expertise consists of recognizing these recurring themes.

Stability Explains Much of Organic Chemistry

Throughout the subject, one principle repeatedly appears:

Stable species are favored.

Resonance, electronegativity, hybridization, steric effects, and charge distribution all influence stability.

Understanding stability often reduces the need for memorization.

Asking Better Questions

Beginning students frequently ask: “What product do I memorize?”

Experienced chemists often ask:

- Where are the electrons?
- Where do they want to go?
- Which pathway produces the most stable intermediate?
- Which species is electron-rich?
- Which species is electron-poor?
- Which mechanism is most reasonable?

Learning to ask these questions gradually transforms the way problems are approached.

Drawing Is Essential

Organic chemistry is a visual subject. Reading alone is rarely sufficient.

Students benefit from:

- drawing structures,
- drawing mechanisms,
- using graph paper,
- using model kits,
- and revisiting ideas repeatedly.

Understanding often develops through the act of drawing.

Repetition Beats Cramming

Organic chemistry resembles language acquisition more than memorization.

Short, consistent study sessions are generally more effective than marathon sessions.

Repeated exposure allows patterns to become increasingly familiar.

Confusion during early encounters is normal. Clarity often emerges gradually.

Confusion Is Normal

Few students understand new concepts immediately.

Many ideas become clearer only after they have been encountered several times.

Struggling with difficult material is not evidence of inability. It is part of the learning process.

Experts Still Use Principles

Experienced chemists do not memorize every reaction.

Instead, they repeatedly rely upon functional groups, resonance, acids and bases, stereochemistry, and electron flow.

The same ideas introduced in earlier chapters continue to guide increasingly complex chemistry.

Organic Chemistry as a Language

Functional groups are vocabulary. Resonance provides grammar. Acids and bases supply logic. Stereochemistry introduces shape. Mechanisms describe motion.

As familiarity grows, the subject begins to feel less like memorization and more like learning a language.

Fluency develops gradually.

Gentle Exercises

Reflect on:

- Which concepts feel familiar?
- Which concepts still feel difficult?
- Which patterns have become easier to recognize?

Revisit earlier chapters and notice how ideas connect.

Common Mistakes

Expecting Instant Understanding

Better approach: Allow understanding to develop gradually.

Memorizing Without Understanding

Better approach: Focus on patterns and principles.

Comparing Progress to Other Students

Better approach: Measure progress against past understanding, not against other students.

Self-Assessment

I can:

- ☐ Appreciate the importance of pattern recognition.
- ☐ Understand that intuition develops gradually.
- ☐ Recognize the role of stability.
- ☐ Appreciate the value of repetition.
- ☐ Understand why drawing structures is important.
- ☐ View organic chemistry as a coherent system rather than isolated facts.

Further Study

Continue revisiting: functional groups, resonance, acids and bases, stereochemistry, and electron flow.

These ideas remain central throughout both semesters.

Looking Ahead

The first semester of organic chemistry focuses largely on foundational principles and major reaction patterns.

The second semester expands these ideas into richer and more sophisticated chemistry.

Carbonyl compounds, aromatic systems, spectroscopy, and synthetic strategy all rely upon the same principles introduced thus far.

The next part explores carbonyl chemistry, one of the most important and intellectually satisfying areas of organic chemistry.

V

Part V: Carbonyl Chemistry

The Heart of Organic Chemistry II

Carbonyl compounds occupy a central position in organic chemistry.

They are found throughout biological molecules, pharmaceuticals, polymers, and industrial chemistry.

In many ways, carbonyl chemistry represents the culmination of the ideas developed earlier in the handbook.

Resonance explains electron distribution.

Acids and bases influence reactivity.

Electron flow governs mechanisms.

Nucleophiles and electrophiles determine how reactions occur.

Although numerous reactions are encountered, many follow a surprisingly small number of recurring patterns.

Understanding these patterns transforms carbonyl chemistry from a collection of facts into an interconnected and highly logical subject.

Chapters in This Part

The chapters in this part explore:

- carbonyl compounds and nucleophilic addition,
- carboxylic acids and their derivatives,
- and the chemistry of enols and enolates.

Together, these topics form much of the conceptual core of Organic Chemistry II.

This handbook's primary focus is preparing for Organic Chemistry I, so the chapters from here through the end move faster and go less deep than Parts III–IV did. Treat them as a conceptual preview — a map of what's ahead — rather than a complete substitute for a full Organic Chemistry II course or textbook.

Chapter 12: Carbonyl Compounds and Nucleophilic Addition

The Electrophilic Carbon

Introduction

Among all functional groups encountered in organic chemistry, carbonyl compounds are among the most important.

The carbonyl group appears in:

- aldehydes,
- ketones,
- carboxylic acids,
- esters,
- amides,
- and many biological molecules.

Understanding carbonyl chemistry begins with understanding the nature of the carbonyl bond itself.

Why Carbonyl Groups Matter

The carbon-oxygen double bond is polarized.

Oxygen attracts electron density, leaving the carbon partially positive.

As a result:

- oxygen behaves relatively electron-rich,
- carbon behaves relatively electron-poor.

This polarization makes carbonyl carbons electrophilic and therefore susceptible to nucleophilic attack.

Aldehydes and Ketones

These compounds represent the simplest carbonyl-containing functional groups.

Aldehydes

Contain terminal carbonyl groups. Generally more reactive.

Ketones

Contain internal carbonyl groups. Usually somewhat less reactive.

Nucleophilic Addition

Many reactions of aldehydes and ketones involve nucleophilic addition.

The general pattern is:

1. Nucleophile attacks carbonyl carbon.
2. Electrons shift toward oxygen.
3. Proton transfer restores neutrality.

Although many specific reactions exist, this pattern appears repeatedly throughout Organic Chemistry II.

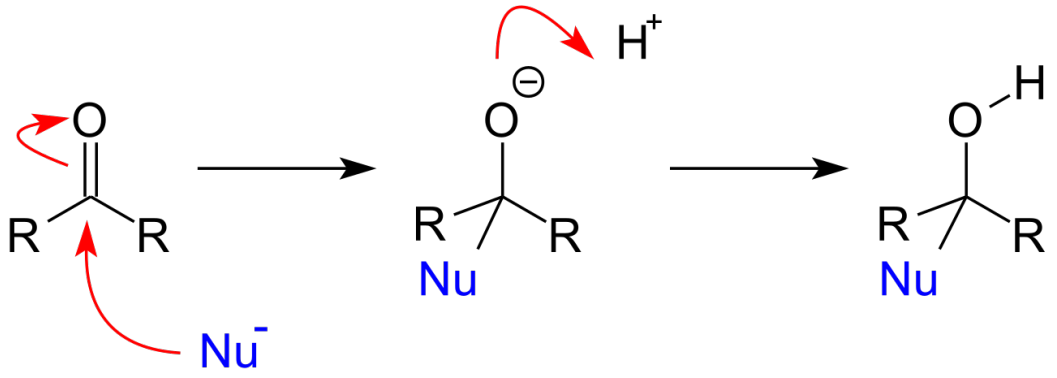


Figure 12.1. General nucleophilic addition mechanism: a nucleophile (Nu^-) attacks the carbonyl carbon, pushing the π electrons onto oxygen to give a tetrahedral alkoxide intermediate, which is then protonated to give the neutral alcohol product. ("Nucleophilic additions to carbonyls" by V8rik, public domain, via Wikimedia Commons.)

Common Examples

Hydration

Addition of water.

Alcohol Formation

Reduction reactions.

Hemiacetals and Acetals

Important in carbohydrate chemistry.

Thinking About Carbonyl Reactions

Helpful questions include:

- Where is the electrophilic center?
- Which species acts as the nucleophile?
- How does resonance influence stability?
- Which intermediates are formed?

Common Mistakes

Memorizing Products

Better approach: Follow electron flow.

Ignoring Polarity

Better approach: Recognize the electrophilic carbon.

Self-Assessment

I can:

☐ Explain why the carbonyl carbon is electrophilic.

☐ Describe the general nucleophilic addition pattern.

☐ Distinguish aldehydes from ketones by relative reactivity.

☐ Recognize hydration, reduction, and hemiacetal/acetal formation as examples of nucleophilic addition.

Looking Ahead

Not all carbonyl compounds behave identically.

The next chapter explores carboxylic acids and their derivatives, where substitution rather than addition becomes the dominant theme.

Chapter 13: Carboxylic Acids and Their Derivatives

Substitution at the Carbonyl

Introduction

Carboxylic acids and their derivatives represent another major family of carbonyl compounds.
These include:

- carboxylic acids,
- esters,
- amides,
- acid chlorides,
- and anhydrides.

Although these compounds differ in structure and reactivity, they share many common features.

Relative Reactivity

Some carbonyl compounds are more reactive than others.
In general:
Acid chlorides → Anhydrides → Esters → Amides
Understanding this trend helps explain many reaction pathways.

Nucleophilic Acyl Substitution

Unlike aldehydes and ketones, many carboxylic acid derivatives undergo substitution rather than simple addition.
The general pattern is:

1. Nucleophilic attack.
2. Formation of a tetrahedral intermediate.
3. Departure of a leaving group.

This mechanism appears repeatedly throughout Organic Chemistry II.

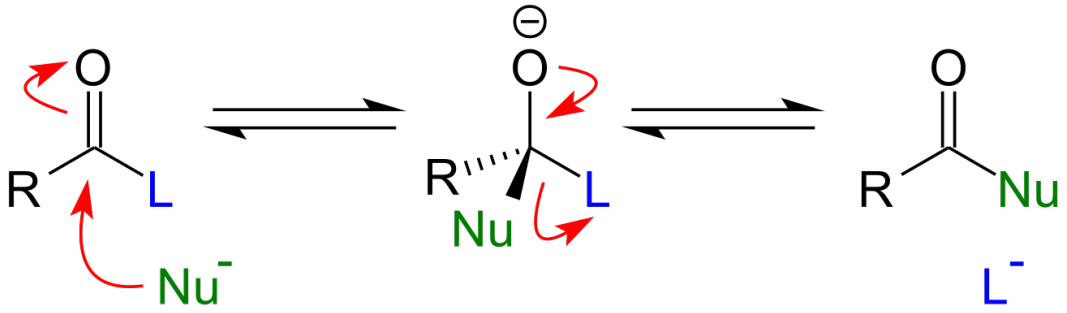


Figure 13.1. Nucleophilic acyl substitution: the same first step as Ch.12's addition mechanism — a nucleophile attacks the carbonyl carbon to give a tetrahedral intermediate — but here a leaving group (L) is present, so the intermediate collapses by re-forming the C=O and ejecting L^- rather than being protonated. ("Nucleophilic acyl substitution" by V8rik, public domain, via Wikimedia Commons.)

Biological Importance

These functional groups are widespread:

Esters

Lipids and fats.

Amides

Proteins and peptides.

Carboxylic Acids

Fatty acids and metabolism.

Thinking About Reactivity

Helpful questions include:

- How good is the leaving group?
- Which derivative is more reactive?
- Which pathway is favored?

Common Mistakes

Treating All Carbonyl Compounds Equally

Better approach: Recognize differences in reactivity.

Ignoring Leaving Groups

Better approach: Think mechanistically.

Self-Assessment

I can:

☐ Rank acid chlorides, anhydrides, esters, and amides by relative reactivity.
☐ Distinguish nucleophilic acyl substitution from nucleophilic addition.
☐ Describe the tetrahedral intermediate and leaving-group departure.
☐ Connect carboxylic acid derivatives to biological roles (esters in lipids, amides in proteins).

Looking Ahead

Carbonyl chemistry becomes even richer when reactions occur adjacent to the carbonyl group. This introduces the chemistry of enols and enolates.

Chapter 14: Enols, Enolates, and Carbon–Carbon Bond Formation

Building Larger Molecules

Introduction

Many important organic reactions involve atoms adjacent to carbonyl groups.

These positions possess unusual acidity and can give rise to highly useful intermediates known as enols and enolates.

These species make possible the formation of new carbon-carbon bonds.

Keto-Enol Tautomerism

Carbonyl compounds may exist in equilibrium with enol forms.

Although keto forms are usually favored, both structures play important roles in reactivity.

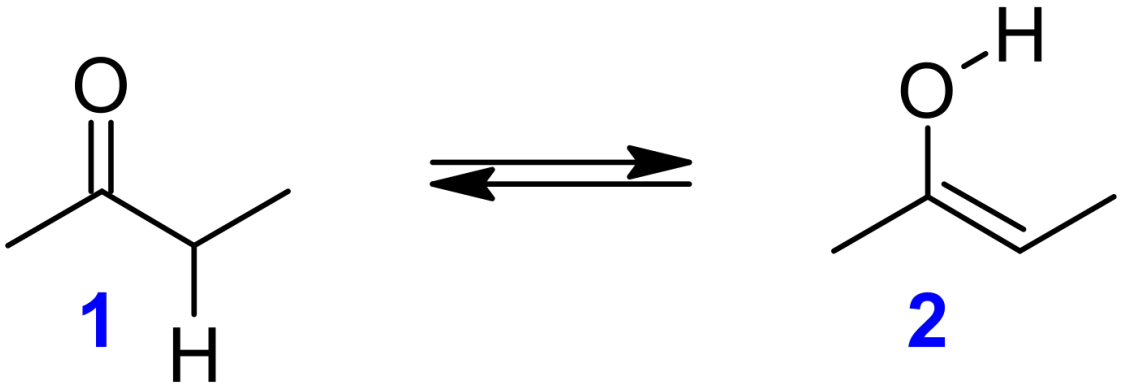


Figure 14.1. Keto (1) and enol (2) tautomers of butan-2-one, in equilibrium — the keto form is normally favored, but the enol form is what actually reacts in enolate chemistry. ("Keto-enol tautomerism" by Pen1234567, CC BY 3.0, via Wikimedia Commons.)

Enolates

Removal of an α-hydrogen produces an enolate.

Enolates are stabilized by resonance and serve as powerful nucleophiles.

Carbon–Carbon Bond Formation

One of the most important goals of organic synthesis is constructing larger molecules.

Enolates enable this through reactions such as:

Aldol Reactions

Formation of β-hydroxy carbonyl compounds.

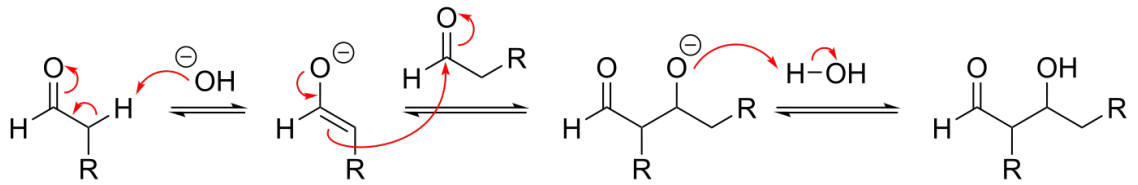


Figure 14.2. The aldol mechanism: base removes an α-hydrogen to form an enolate, which attacks the carbonyl carbon of a second aldehyde molecule to form the new C–C bond, giving a β-hydroxy carbonyl (aldol) product after protonation. ("Base-catalyzed aldol addition" by Pillsmarch, CC BY 4.0, via Wikimedia Commons.)

Claisen Condensations

Formation of β-keto esters.

These reactions represent important examples of carbon-carbon bond formation.

Themes That Reappear

Throughout carbonyl chemistry, familiar ideas continue to dominate:

- resonance,
- acids and bases,
- nucleophiles,
- electrophiles,
- stability,
- and electron flow.

Organic Chemistry II repeatedly revisits the principles established in earlier chapters.

Common Mistakes

Viewing Reactions Independently

Better approach: Recognize recurring mechanistic themes.

Overlooking Which Proton Is Most Acidic

Better approach:

Not all C–H bonds in a molecule are equally acidic. Alpha protons — those on carbons directly adjacent to the carbonyl group — are unusually acidic because their removal produces a resonance-stabilized enolate. Identifying the alpha position correctly is the essential first step in enolate chemistry.

Self-Assessment

I can:

☐ Explain keto-enol tautomerism.
☐ Identify the alpha position and explain why it is unusually acidic.
☐ Recognize an enolate as a resonance-stabilized nucleophile.
☐ Recognize aldol reactions and Claisen condensations as carbon–carbon bond-forming reactions.

Looking Ahead

Carbonyl chemistry demonstrates the remarkable power of resonance and electron flow.

The next part explores another extraordinary consequence of electron delocalization: aromaticity.

Benzene and related compounds possess unusual stability and exhibit their own distinctive patterns of reactivity.

VI Part VI: Aromatic Chemistry

Stability and Special Reactivity

Few molecules have influenced the development of organic chemistry more than benzene.

Although benzene contains multiple double bonds, it behaves very differently from ordinary alkenes.

Its unusual stability and distinctive patterns of reactivity arise from electron delocalization and aromaticity.

Understanding aromatic compounds represents one of the most elegant applications of resonance in organic chemistry.

The same ideas encountered throughout the handbook continue to appear:

- resonance,
- stability,
- electron flow,
- electrophiles,
- and functional group transformations.

Chapters in This Part

The chapters in this part explore:

- aromaticity,
- electrophilic aromatic substitution,
- and the effects of substituents on aromatic reactivity.

Together, these concepts explain the chemistry of many biologically and industrially important compounds.

Chapter 15: Benzene and Aromaticity

Extraordinary Stability

Introduction

At first glance, benzene appears to be a molecule containing three ordinary carbon-carbon double bonds.
However, its properties differ significantly from those of typical alkenes.
Benzene exhibits unusual stability and undergoes reactions that preserve its aromatic system.
Understanding this behavior requires a deeper appreciation of resonance and electron delocalization.

Resonance and Delocalization

The electrons within benzene are distributed over the entire ring.
No single resonance structure completely describes the molecule.
Instead, benzene exists as a resonance hybrid.
Electron delocalization lowers energy and contributes to remarkable stability.

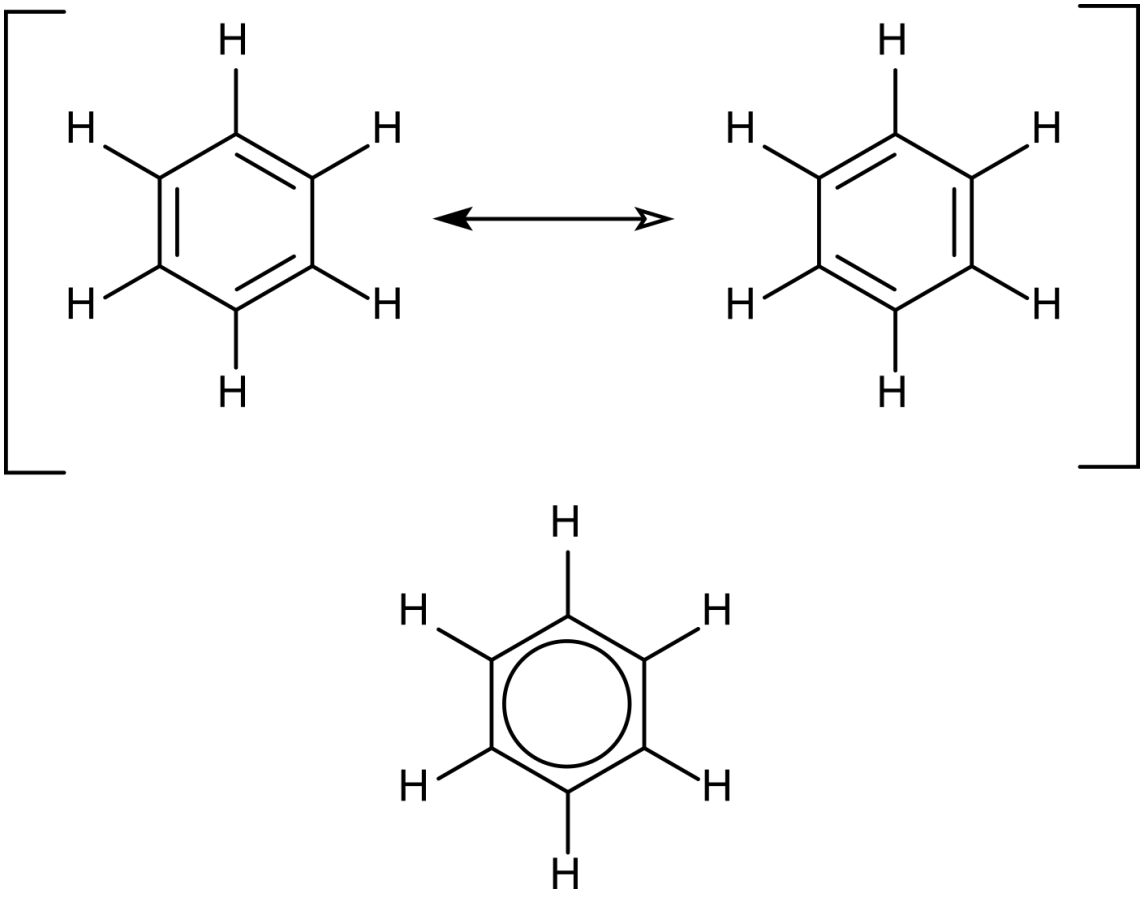


Figure 15.1. Benzene's two equivalent Kekulé resonance structures (top) and the delocalized-ring shorthand that represents their hybrid (bottom) — no single structure with alternating single and double bonds is correct on its own. ("Benzene resonance structures" by Edgar181, public domain, via Wikimedia Commons.)

Aromaticity

Certain cyclic molecules possess exceptional stability. These compounds are described as aromatic.

Aromatic systems typically exhibit:

- cyclic structures,
- conjugation,
- planarity,
- and characteristic electron counts.

The electron-count requirement is Hückel's rule: a cyclic, planar, fully conjugated system is aromatic when it contains $4n+2$ π electrons, where n = 0, 1, 2, 3, and so on — giving 2, 6, 10, 14 π electrons. Benzene's six π electrons (n = 1) satisfy this rule.

Why Aromaticity Matters

Aromaticity influences:

- stability,
- reactivity,
- acidity,
- and biological activity.

Many important compounds contain aromatic rings, including amino acids, pharmaceuticals, dyes, and polymers.

Thinking About Aromatic Systems

Helpful questions include:

- Is the ring conjugated?
- Is the structure planar?
- Does resonance stabilize the system?
- Will the reaction preserve aromaticity?

Common Mistakes

Treating Benzene Like an Alkene

Better approach: Recognize that aromatic stabilization changes reactivity.

Viewing Resonance Structures as Separate Molecules

Better approach: Think in terms of electron delocalization.

Self-Assessment

I can:

☐ Explain why benzene is unusually stable compared to a typical alkene.
☐ Recognize the criteria for aromaticity (cyclic, conjugated, planar, appropriate electron count).
☐ Describe benzene as a resonance hybrid rather than a set of separate structures.
☐ Predict that aromatic rings resist addition reactions.

Looking Ahead

Although aromatic compounds are highly stable, they are not inert.

Their most characteristic reactions involve substitution rather than addition.

Chapter 16: Electrophilic Aromatic Substitution

Preserving Aromaticity

Introduction

Unlike ordinary alkenes, aromatic compounds generally avoid addition reactions.
Addition would destroy aromatic stabilization.
Instead, aromatic compounds typically undergo substitution reactions that preserve the aromatic ring.
These reactions are collectively known as electrophilic aromatic substitution.

The General Pattern

Electrophilic aromatic substitution follows a recurring sequence:

1. Formation of an electrophile.
2. Attack by the aromatic ring.
3. Temporary loss of aromaticity.
4. Restoration of aromatic stabilization.

Preservation of aromaticity is the driving theme behind these reactions.

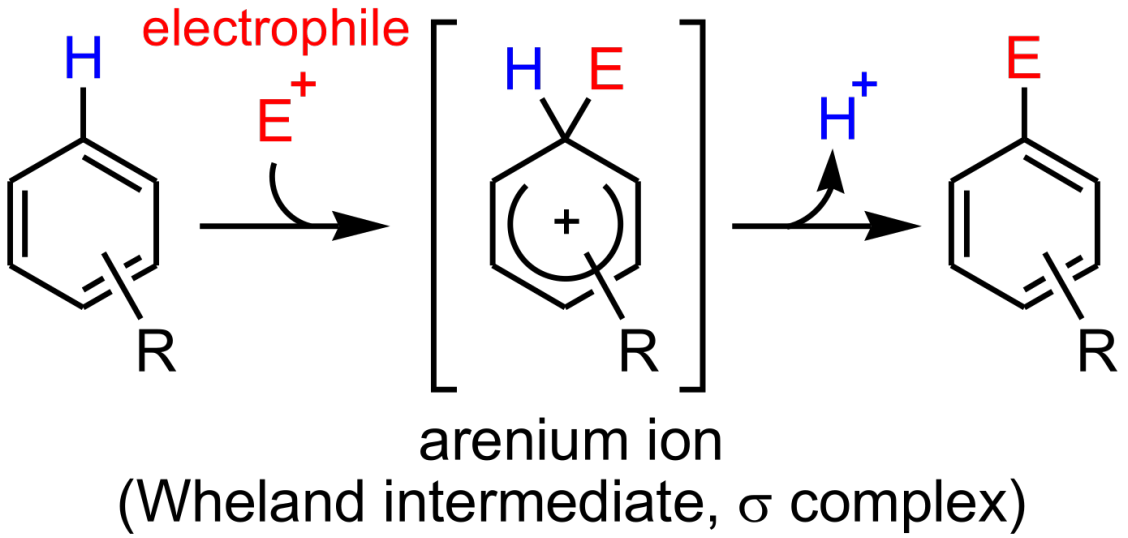


Figure 16.1. The arenium-ion (Wheland intermediate) mechanism: an electrophile (E^+) attacks the ring, temporarily breaking aromaticity and delocalizing the positive charge over three carbons, then loss of H^+ restores the aromatic ring with E in place of one H. ("Arenium ion mechanism" by Su-no-G, public domain, via Wikimedia Commons.)

Common Reactions

Halogenation

Introduction of halogens.

Nitration

Introduction of nitro groups.

Sulfonation

Introduction of sulfonic acids.

Friedel-Crafts Reactions

Formation of carbon-carbon bonds.

Thinking About Aromatic Reactions

Helpful questions include:

- Which species is the electrophile?
- How is aromaticity temporarily disrupted?
- How is aromaticity restored?

Common Mistakes

Treating Aromatic Reactions Like Alkene Reactions

Better approach: Recognize the importance of preserving aromatic stabilization.

Forgetting to Identify the Electrophile First

Better approach:

Electrophilic aromatic substitution begins with formation of an activated electrophile, which is often generated in a preparatory step from the reagent. The identity and source of that electrophile determines what type of EAS reaction is occurring — halogenation, nitration, sulfonation, or Friedel-Crafts.

Self-Assessment

I can:

☐ Explain why aromatic rings undergo substitution rather than addition.

☐ Walk through the general EAS mechanism: electrophile formation, ring attack, temporary loss and restoration of aromaticity.

☐ Identify halogenation, nitration, sulfonation, and Friedel-Crafts reactions as EAS.

☐ Recognize that identifying the electrophile is the first step in any EAS problem.

Looking Ahead

Not all aromatic compounds react identically.

Substituents already attached to the ring influence both reactivity and orientation.

Chapter 17: Substituent Effects and Aromatic Compounds

Directing Reactivity

Introduction

Substituents attached to aromatic rings influence where additional reactions occur.
Some groups increase reactivity, while others decrease it.
Some direct substitution toward ortho and para positions. Others favor the meta position.
Understanding these effects provides a framework for predicting aromatic substitution patterns.

Activating and Deactivating Groups

Substituents influence electron density through:

- resonance,
- induction,
- and charge distribution.

These effects alter the stability of reaction intermediates and therefore influence reactivity.

Activating groups donate electron density into the ring — most often by resonance, from a lone pair on the attached atom (–OH, $-NH_2$, –OR) — and make the ring more reactive toward electrophiles than benzene itself.

Deactivating groups withdraw electron density from the ring, either by resonance ($-NO_2$, –C=O, –CN, each pulling electron density toward themselves) or by induction alone (halogens), and make the ring less reactive than benzene.

Ortho, Meta, and Para Directors

Certain groups favor ortho substitution, para substitution, or meta substitution. The pattern follows from which ring positions best stabilize (or least destabilize) the positive charge of the arenium ion intermediate.

Ortho/para directors are, with one exception, also activating: a lone pair on the substituent donates directly into the ring at the ortho and para positions, stabilizing the intermediate there. Alkyl groups direct ortho/para as well, through hyperconjugation and induction rather than a lone pair.

Meta directors are electron-withdrawing groups with a positive or partial-positive atom adjacent to the ring ($-NO_2$, –C≡N, –C=O, $-SO_3H$). Substitution at the ortho or para position would place the arenium ion's positive charge directly next to that existing positive character — strongly destabilizing — so the meta position is favored instead, even though the ring is deactivated overall.

Halogens are the one exception worth remembering: they are deactivating (their electronegativity withdraws electron density inductively) but still ortho/para-directing (a lone pair still donates into the ring by resonance, just less effectively than for –OH or $-NH_2$).

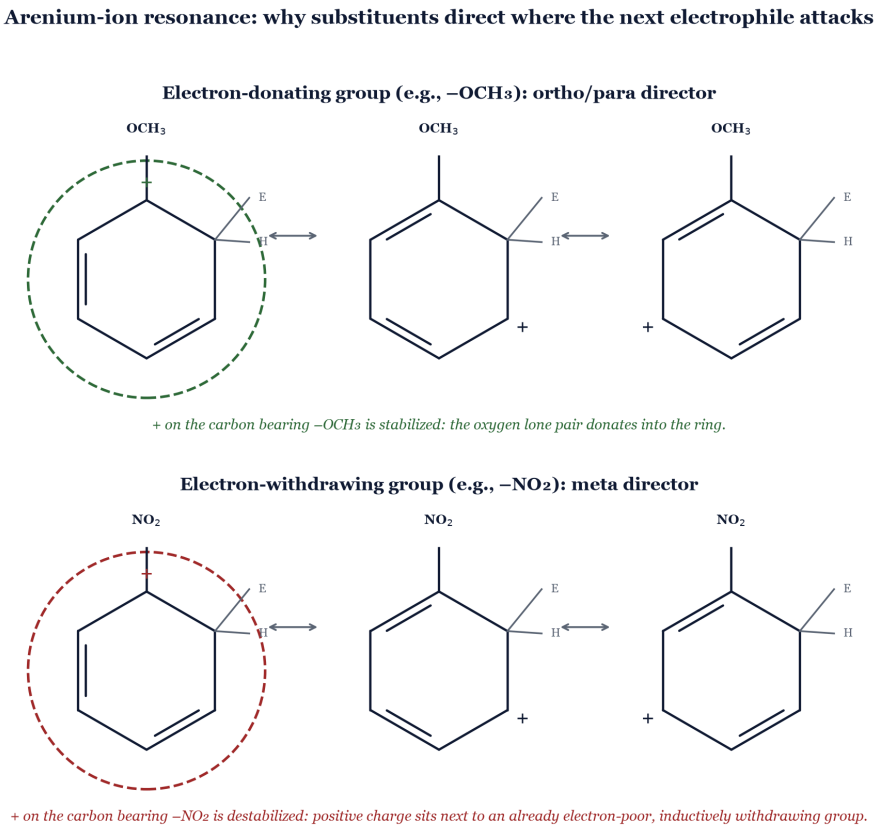


Figure 17.1. The three arenium-ion resonance structures for attack ortho to a ring substituent X, side by side for an electron-donating group (–OCH_3, left) and an electron-withdrawing group (–NO_2, right). In both cases one resonance structure places the + charge directly on the carbon bearing X — for –OCH_3 that structure is stabilized by oxygen lone-pair donation (hence ortho/para direction); for –NO_2 that same structure is destabilized by the adjacent electron-poor nitrogen (hence meta direction).

Phenols and Heterocycles

Not all aromatic compounds are simple benzene derivatives.

Other important aromatic systems include:

Phenols

Important in biological chemistry.

Heterocycles

Contain atoms such as nitrogen, oxygen, or sulfur within the ring.

These compounds are widespread in pharmaceuticals and biomolecules.

Themes That Reappear

Throughout aromatic chemistry, familiar principles continue to dominate:

- resonance,
- stability,
- electron flow,
- electrophiles,

- and pattern recognition.

Organic chemistry repeatedly revisits the same ideas in new contexts.

Common Mistakes

Memorizing Directing Effects Without Understanding

Better approach: Think about electron density and intermediate stability.

Viewing Aromatic Reactions Independently

Better approach: Recognize recurring mechanistic themes.

Self-Assessment

I can:

☐ Distinguish activating from deactivating substituents.
☐ Predict whether a substituent directs ortho/para or meta.
☐ Explain why halogens are deactivating yet ortho/para-directing.
☐ Recognize phenols and heterocycles as aromatic systems beyond simple benzene derivatives.

Looking Ahead

Understanding molecular structure requires more than recognizing functional groups and mechanisms.

Chemists must also determine what molecules actually are.

The next part explores spectroscopy, one of the most powerful tools available for revealing molecular structure.

VII Part VII: Spectroscopy

Seeing Molecules

Throughout organic chemistry, chemists seek to understand the structure and behavior of molecules.

Until now, the emphasis has largely been on explaining why molecules react and how transformations occur.

Spectroscopy introduces a complementary question:

How do chemists determine what molecules actually are?

Spectroscopic methods provide experimental evidence that allows chemists to infer molecular structure.

In many ways, spectroscopy represents the meeting point between theory and observation.

Chapters in This Part

The chapters in this part explore:

- infrared spectroscopy,
- nuclear magnetic resonance spectroscopy,
- mass spectrometry,
- and strategies for combining these techniques to determine molecular structure.

Together, these tools transform chemistry into a process of interpretation and problem-solving.

Chapter 18: Infrared Spectroscopy and Functional Group Identification

Recognizing Molecular Signatures

Introduction

Different chemical bonds vibrate in characteristic ways.

These vibrations interact with infrared radiation and produce distinctive absorption patterns.

Infrared spectroscopy allows chemists to identify functional groups and gain insight into molecular structure.

Although IR spectra may initially appear complicated, they often provide valuable clues about the presence or absence of specific functional groups.

Why Infrared Spectroscopy Matters

IR spectroscopy is especially useful for identifying:

- alcohols,
- carbonyl compounds,
- amines,
- alkenes,
- and other common functional groups.

Because many functional groups possess characteristic absorptions, IR spectra often serve as an important first step in structural analysis.

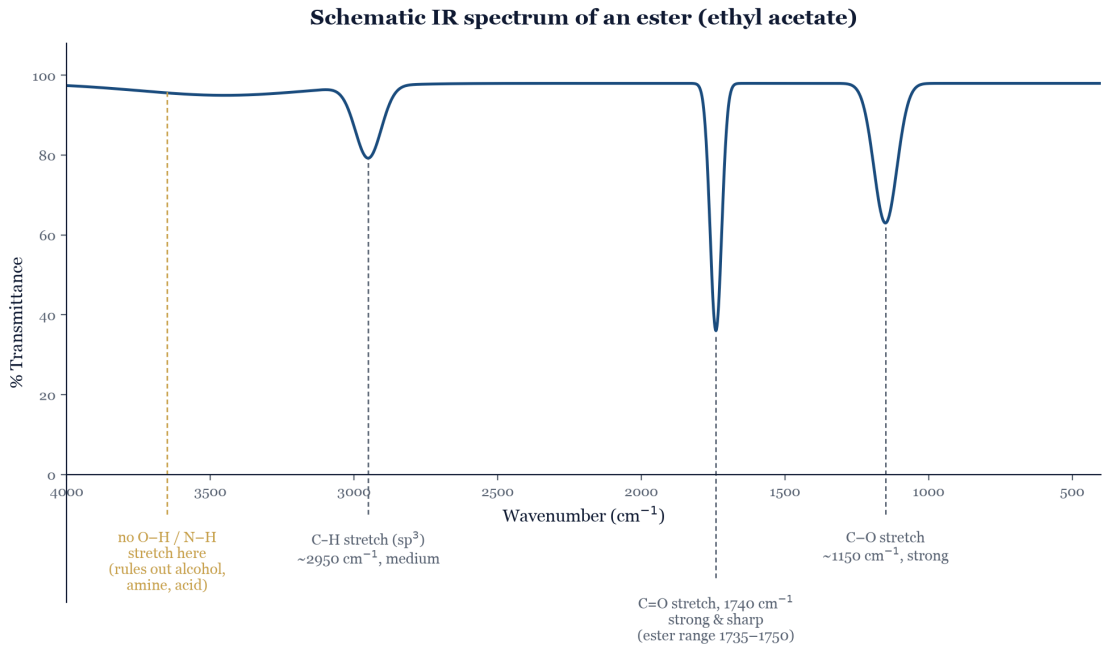


Figure 18.1. A schematic IR spectrum of an ester (ethyl acetate), showing the diagnostic C=O and C–O stretches, the ordinary C–H stretch, and — just as informative — the absence of any O–H or N–H stretch, which rules out alcohols, amines, and acids.

Functional Groups Revisited

Infrared spectroscopy highlights a recurring theme throughout organic chemistry: functional groups determine behavior.

Characteristic peaks correspond to familiar functional groups encountered earlier in the handbook.

Thus, spectroscopy reinforces the importance of functional group recognition.

Thinking About IR Spectra

Helpful questions include:

- Is a carbonyl present?
- Is an alcohol present?
- Are N–H or O–H bonds present?
- Which functional groups are absent?

Rather than providing complete answers, IR spectroscopy often narrows the possibilities.

Common Mistakes

Trying to Memorize Every Peak

Better approach: Focus on major functional groups.

Viewing IR as a Collection of Numbers

Better approach: Think about structure.

Self-Assessment

I can:

☐ Explain what an IR spectrum reveals about a molecule.

☐ Recognize characteristic absorptions for common functional groups.

☐ Use IR evidence to narrow down, rather than fully determine, molecular structure.

Looking Ahead

Infrared spectroscopy reveals functional groups.

Nuclear magnetic resonance spectroscopy provides even richer structural information.

Specific wavenumber ranges for the functional groups mentioned above are collected in Appendix D.

Chapter 19: Nuclear Magnetic Resonance Spectroscopy

Understanding Molecular Environments

Introduction

Nuclear magnetic resonance spectroscopy is one of the most powerful tools available for studying organic molecules.

Unlike infrared spectroscopy, which focuses primarily on bonds and functional groups, NMR provides information about the environments experienced by individual atoms.

NMR allows chemists to reconstruct molecular structures with remarkable precision.

Proton NMR

Proton NMR provides information about:

- chemical environments,
- neighboring atoms,
- and relative numbers of hydrogens.

Three ideas become especially important:

Chemical Shift

Where signals appear.

Integration

Relative numbers of hydrogens.

Splitting Patterns

Relationships between neighboring atoms.

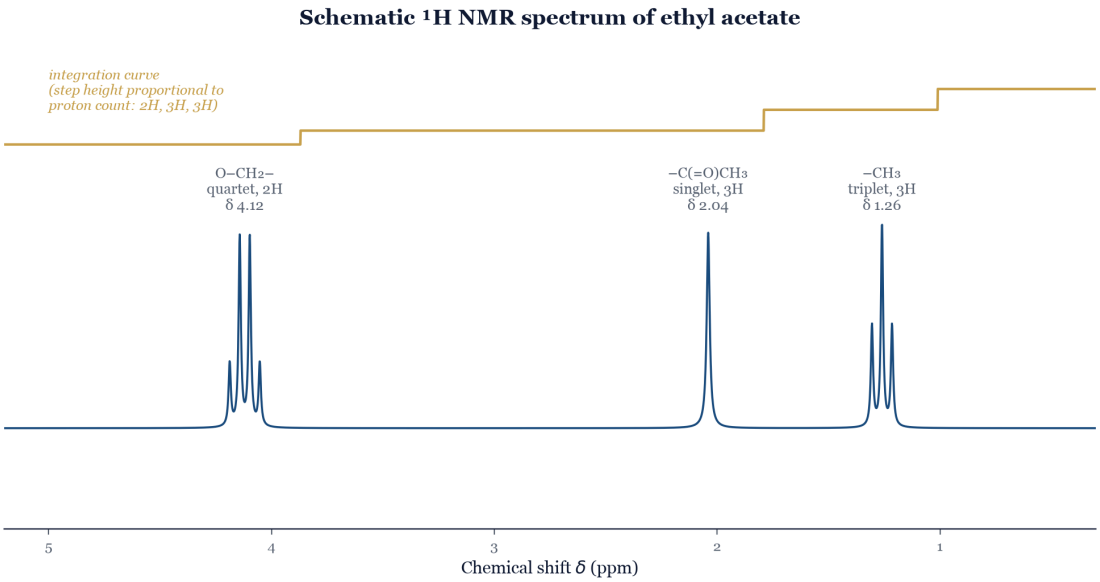


Figure 19.1. A schematic ¹H NMR spectrum of ethyl acetate, showing all three ideas at once: chemical shift (three signals at different δ values), integration (the gold step curve, rising by 2H, then 3H, then 3H), and splitting (quartet, singlet, and triplet — each multiplicity set by the number of neighboring protons).

Carbon NMR

Carbon-13 NMR complements proton NMR by providing information about carbon environments.

Together, proton and carbon NMR provide powerful structural insights.

Pattern Recognition

Interpreting NMR spectra involves recognizing recurring patterns.

As familiarity grows, spectra become increasingly meaningful.

Much of expertise develops through repeated exposure.

Thinking About NMR

Helpful questions include:

- How many unique environments exist?
- What do chemical shifts suggest?
- Which atoms are neighbors?
- Does the proposed structure fit the evidence?

Common Mistakes

Confusing Chemical Shift with Integration

Better approach:

Chemical shift and integration answer different questions. Chemical shift indicates the electronic environment of a hydrogen — how shielded or deshielded it is. Integration indicates how many hydrogens share that environment. Interpreting them separately before combining the information reduces confusion significantly.

Treating Signals Independently

Better approach: Look for relationships.

Self-Assessment

I can:

- ☐ Distinguish chemical shift, integration, and splitting as separate questions.
- ☐ Explain what carbon-13 NMR adds beyond proton NMR.
- ☐ Use neighboring-proton relationships to interpret splitting patterns.

Looking Ahead

Spectroscopy becomes even more powerful when multiple techniques are combined.

Representative chemical shift ranges and splitting patterns are collected in Appendix D.

Chapter 20: Mass Spectrometry and Structure Determination

Solving Molecular Puzzles

Introduction

Mass spectrometry provides information about molecular mass and fragmentation patterns.

Combined with infrared and NMR spectroscopy, mass spectrometry allows chemists to determine molecular structures.

The process resembles solving a puzzle in which multiple pieces of evidence must be integrated.

Molecular Mass

Mass spectrometry provides clues regarding:

- molecular weight,
- isotopic patterns,
- and fragmentation.

These features help narrow structural possibilities.

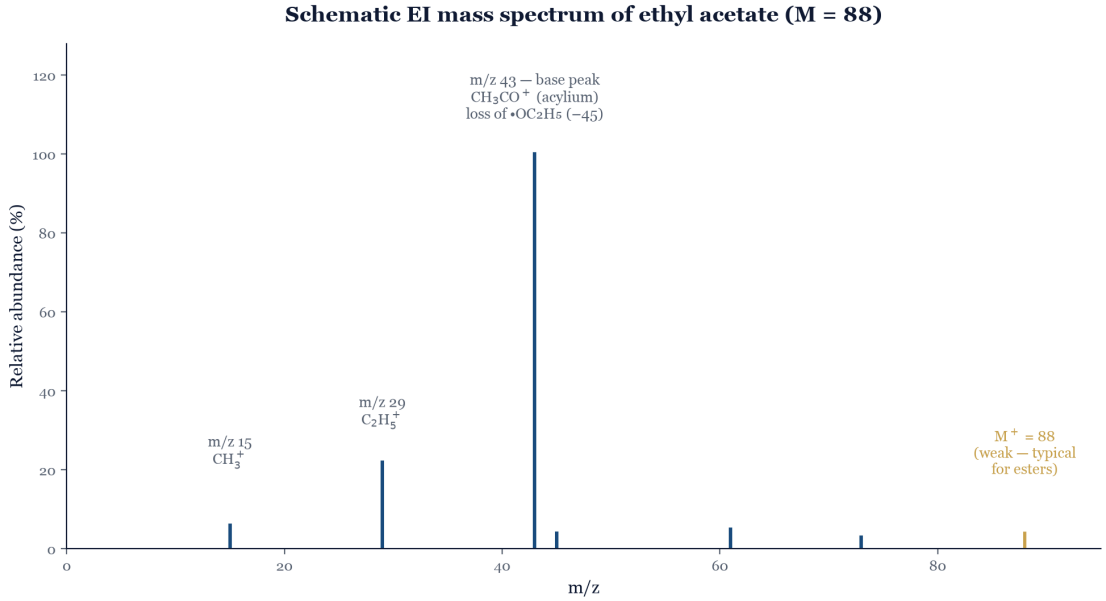


Figure 20.1. A schematic mass spectrum of ethyl acetate: the weak molecular ion (M^+ = 88) anchors the molecular weight, while the base peak at m/z 43 (the acylium ion CH_3CO^+, from loss of $\bullet OC_2H_5$) and the peak at m/z 29 ($C_2H_5^+$) are exactly the fragment losses catalogued in Appendix D.

Combining Evidence

Experienced chemists rarely rely upon a single technique.

Instead, they integrate:

Infrared Spectroscopy

Functional groups.

Proton NMR

Hydrogen environments.

Carbon NMR

Carbon environments.

Mass Spectrometry

Molecular mass and fragmentation.

Together, these methods provide a remarkably powerful framework for determining molecular structure.

Structure Determination

Beginning students often view spectroscopy as a collection of unrelated techniques.

Experienced chemists treat spectroscopy as a process of assembling evidence.

The goal is not memorization but interpretation.

Themes That Reappear

Throughout spectroscopy, familiar ideas continue to appear:

- functional groups,
- symmetry,
- structure,
- pattern recognition,
- and intuition.

Organic chemistry repeatedly revisits the same principles from new perspectives.

Common Mistakes

Treating Spectroscopic Techniques Separately

Better approach: Combine evidence.

Expecting Immediate Answers

Better approach: Approach structure determination as a puzzle.

Self-Assessment

I can:

☐ Explain what mass spectrometry reveals about a molecule.

☐ Recognize the role of fragmentation in structure determination.

☐ Combine IR, NMR, and MS evidence into a single structural proposal.

Looking Ahead

Spectroscopy reveals what molecules are.

The final part of the handbook explores how chemists decide what molecules should become.

This shift from analysis to design introduces retrosynthesis, strategy, and the art of molecular construction.

Common fragment losses and diagnostic ions are collected in Appendix D.

VIII Part VIII: Synthesis and Strategy

Bringing Everything Together

Organic chemistry ultimately becomes the art of designing molecules and understanding how transformations can be combined to achieve synthetic goals.

By this stage, many ideas encountered earlier in the handbook begin to converge.

Functional groups, resonance, acids and bases, electron flow, mechanisms, and pattern recognition all contribute to synthetic thinking.

The goal is no longer simply to explain reactions.

Instead, the challenge becomes deciding which reactions should be used and how they can be combined to achieve a desired outcome.

Chapters in This Part

The chapters in this part explore:

- retrosynthesis,
- multistep synthesis,
- common strategies,
- and the development of chemical intuition.

Ultimately, organic chemistry becomes an exercise in creativity guided by fundamental principles.

Chapter 21: Retrosynthesis and Multi-Step Synthesis

Working Backward

Introduction

Beginning students often view reactions individually.

Experienced chemists frequently think in reverse.

Instead of asking “What product will this reaction produce?” they ask “How might this product be constructed?”

This process, known as retrosynthesis, allows complex molecules to be broken into simpler pieces.

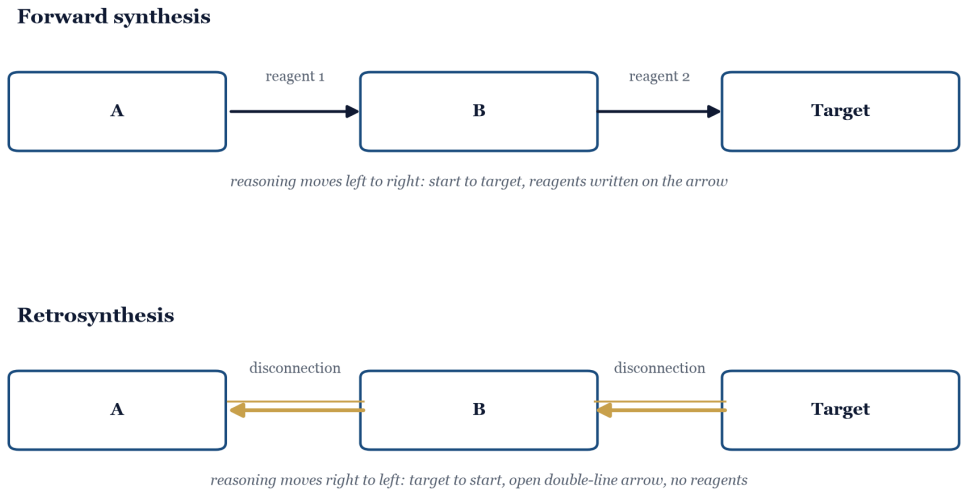


Figure 21.1. Forward synthesis reasons start-to-target with ordinary arrows carrying reagents; retrosynthesis reasons target-to-start with an open double-line arrow and no reagents — it records a disconnection, not a reaction.

Functional Group Transformations

Many syntheses rely upon converting one functional group into another.

Common transformations include:

- alcohols to carbonyl compounds,
- alkenes to alcohols,
- carboxylic acids to esters,
- and carbonyl compounds to alcohols.

Thinking in terms of transformations helps organize synthetic pathways.

Multi-Step Synthesis

Complex targets often require several reactions.
Planning these sequences requires attention to:

- order of reactions,
- functional group compatibility,
- selectivity,
- and efficiency.

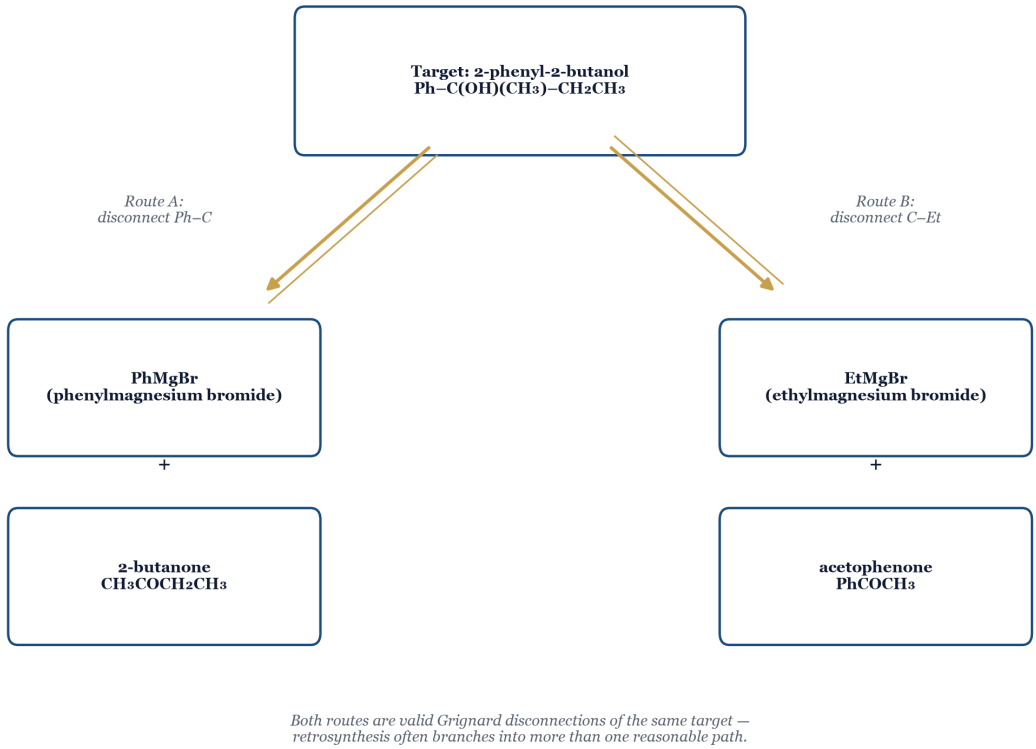


Figure 21.2. A worked retrosynthetic tree for the tertiary alcohol 2-phenyl-2-butanol: because a Grignard addition installs one new C–C bond at the alcohol carbon, the target admits two genuinely different disconnections — PhMgBr + 2-butanone, or EtMgBr + acetophenone. A single target often branches into more than one reasonable synthetic route.

Thinking Backward

Retrosynthesis emphasizes:

- simplifying structures,
- identifying useful intermediates,
- and recognizing familiar patterns.

The process resembles solving a puzzle in reverse.

Common Mistakes

Thinking Only Forward

Better approach: Learn to work backward.

Treating Reactions Independently

Better approach: Think in sequences.

Self-Assessment

I can:

- ☐ Explain the logic of working backward from a target molecule.
- ☐ Identify functional group interconversions useful in synthesis.
- ☐ Describe the considerations involved in planning a multi-step sequence.

Looking Ahead

Synthetic planning often relies upon recurring strategies and familiar reaction patterns.

Chapter 22: Named Reactions and Protecting Groups

Useful Tools and Strategies

Introduction

Organic chemistry contains many named reactions.

Although these reactions are traditionally memorized, they are often best understood as combinations of familiar mechanistic principles.

Similarly, protecting groups provide ways to temporarily control reactivity during multistep synthesis.

Named Reactions

Named reactions represent recurring patterns.

Examples include:

- Aldol reactions,
- Claisen condensations,
- Friedel-Crafts reactions,
- and many others.

Rather than isolated facts, these reactions are applications of concepts already encountered.

Protecting Groups

Sometimes molecules contain multiple reactive sites.

Protecting groups temporarily block one region while chemistry is performed elsewhere.

Afterward, the protecting group can be removed.

This strategy allows more complicated syntheses to become manageable.

Efficiency and Selectivity

Synthetic chemists seek:

- fewer steps,
- higher yields,
- greater selectivity,
- and simpler pathways.

These considerations influence how reactions are chosen.

Common Mistakes

Memorizing Named Reactions

Better approach: Understand mechanisms.

Ignoring Selectivity

Better approach: Think strategically.

Self-Assessment

I can:

- ☐ Recognize common named reactions as applications of familiar mechanisms.
- ☐ Explain the purpose of a protecting group.
- ☐ Weigh efficiency and selectivity when comparing synthetic routes.

Looking Ahead

As experience grows, reactions become less like isolated facts and more like familiar tools.

Chapter 23: Developing Synthetic Intuition

Thinking Like a Chemist

Introduction

The study of organic chemistry ultimately involves much more than memorizing reactions.
It involves learning to recognize patterns, evaluate possibilities, and design pathways.
Developing this intuition takes time and repeated exposure.

Expertise and Pattern Recognition

Experienced chemists do not memorize every possible reaction.
Instead, they rely upon:

- functional groups,
- resonance,
- acids and bases,
- stability,
- and mechanism.

These recurring ideas provide a framework for understanding unfamiliar situations.

Creativity and Constraints

Organic chemistry combines creativity with logic.
Many pathways may be possible. Choosing among them requires judgment and experience.
The process resembles solving puzzles or composing music more than memorizing facts.

Organic Chemistry Beyond the Classroom

Organic chemistry influences:

- medicine,
- biochemistry,
- materials science,
- pharmacology,
- and chemical engineering.

The principles encountered throughout this handbook continue to appear in many scientific disciplines.

Common Mistakes

Expecting Memorization to Be Enough

Better approach: Develop intuition and pattern recognition.

Viewing Chemistry as Isolated Reactions

Better approach: Focus on recurring principles.

Self-Assessment

I can:

- ☐ Appreciate the role of pattern recognition.
- ☐ Understand that intuition develops gradually.
- ☐ Recognize the importance of strategy.
- ☐ Appreciate the creative aspects of chemistry.
- ☐ View organic chemistry as an interconnected subject.

Further Study

Continue revisiting: mechanisms, functional group transformations, retrosynthesis, and spectroscopy. These ideas continue to deepen with experience.

Epilogue

Returning to the Beginning

At the beginning of this handbook, the emphasis was placed on:

- understanding rather than memorization,
- pattern recognition,
- and developing intuition.

These themes have reappeared throughout the study of organic chemistry.

Although the subject can initially appear overwhelming, it ultimately becomes increasingly coherent as familiarity grows.

Beginning students often encounter a large number of structures, reactions, and mechanisms.

Experienced chemists, however, frequently rely upon a surprisingly small collection of recurring ideas:

- functional groups,
- resonance,
- acids and bases,
- electron flow,
- stability,
- and pattern recognition.

These principles provide a framework for understanding increasingly sophisticated chemistry.

The journey through organic chemistry is not simply the accumulation of facts.

It is the gradual development of fluency.

Final Thoughts

Functional groups provide vocabulary.

Resonance provides grammar.

Acids and bases provide logic.

Mechanisms describe change.

Carbonyl chemistry reveals the power of electron flow.

Aromatic chemistry illustrates the remarkable consequences of resonance and stability.

Spectroscopy reveals structure.

Synthesis transforms understanding into design.

Organic chemistry is not merely the study of molecules.

It is the study of patterns, transformations, and the remarkable ways in which structure determines behavior.

Fluency develops gradually.

Understanding deepens with repetition.

And like any language, organic chemistry becomes more rewarding the longer one spends with it.

Appendices

A. Functional Group Atlas

This appendix collects the functional groups introduced in Chapter 1 into a single structured reference: identity, geometry, polarity, hybridization, and typical reactivity for each group, followed by a family tree and an interconversion map showing how groups transform into one another across the handbook.

A.1 How to Read an Entry

Each entry lists five things:

- **Structure** — the defining atoms and bonds, written in condensed form.
- **Hybridization** — the orbital hybridization of the key atom(s) in the group.
- **Geometry** — the approximate bond angle and shape around that atom.
- **Polarity** — whether the group is polar or nonpolar, and why.
- **Typical reactivity** — the kind of chemistry the group tends to undergo, in one or two sentences.

These five properties are the ones used repeatedly throughout the handbook to predict how an unfamiliar molecule will behave.

A.2 Hydrocarbons

A.2.0.1 Alkanes

Structure: C–C and C–H single bonds only (e.g., $CH_3CH_2CH_3$) **Hybridization:** sp^3 at carbon **Geometry:** Tetrahedral, ~109.5° **Polarity:** Nonpolar **Typical reactivity:** Low. Undergo radical halogenation and combustion but do not react with most common reagents. Function as the unreactive "scaffold" that other functional groups attach to.

A.2.0.2 Alkenes

Structure: C=C double bond (e.g., $CH_2{=}CH_2$) **Hybridization:** sp^2 at both alkene carbons **Geometry:** Trigonal planar, ~120° **Polarity:** Weakly polar; the π bond is polarizable and electron-rich **Typical reactivity:** The π electrons act as a nucleophile. Undergoes electrophilic addition (Chapter 9) — addition of HX, H_2O, X_2, and hydrogenation all convert the double bond into two new single bonds.

A.2.0.3 Alkynes

Structure: C≡C triple bond (e.g., CH≡CH) **Hybridization:** sp at both alkyne carbons **Geometry:** Linear, 180° **Polarity:** Weakly polar **Typical reactivity:** Similar to alkenes but with two π bonds available; undergoes one or two successive additions (Chapter 9). Terminal alkyne C–H is unusually acidic (Chapter 3) due to the high s-character of the sp carbon.

A.2.0.4 Arenes (Aromatic Rings)

Structure: Six-membered ring of sp^2 carbons with a delocalized, cyclic π system (benzene, C_6H_6, is the parent) **Hybridization:** sp^2 at every ring carbon **Geometry:** Planar hexagon, 120° internal angles **Polarity:** Nonpolar overall, though substituents can introduce a dipole **Typical reactivity:** The delocalized π system resists addition (which would break aromaticity) and instead undergoes electrophilic aromatic substitution (Chapter 16), preserving the ring.

A.3 Halogen-Containing Groups

A.3.0.1 Alkyl Halides

Structure: C–X, where X = F, Cl, Br, or I **Hybridization:** sp^3 at the carbon bearing the halogen **Geometry:** Tetrahedral, ~109.5° **Polarity:** Polar C–X bond (halogen is electronegative) **Typical reactivity:** The halogen is a good leaving group, so alkyl halides are the classic substrate for substitution (Chapter 7) and elimination (Chapter 8) reactions.

A.4 Oxygen-Containing Groups

A.4.0.1 Alcohols

Structure: C–O–H **Hybridization:** sp^3 at carbon and at oxygen **Geometry:** Tetrahedral at carbon; bent (~108–109°) at oxygen **Polarity:** Polar; hydrogen bond donor and acceptor **Typical reactivity:** Weakly acidic at O–H (Chapter 3); the oxygen is nucleophilic, and the hydroxyl can be converted into a leaving group for substitution or eliminated to form an alkene (Chapter 8).

A.4.0.2 Phenols

Structure: Ar–O–H (hydroxyl attached directly to an aromatic ring) **Hybridization:** sp^2 at the ring carbon bearing oxygen; oxygen lone pair conjugates into the ring **Geometry:** Planar at the point of attachment **Polarity:** Polar; hydrogen bond donor and acceptor **Typical reactivity:** More acidic than alcohols (Chapter 3) because the conjugate base (phenoxide) is resonance-stabilized by the ring. The ring is also activated toward electrophilic aromatic substitution (Chapter 17).

A.4.0.3 Ethers

Structure: C–O–C **Hybridization:** sp^3 at oxygen **Geometry:** Bent at oxygen, ~109.5° **Polarity:** Polar bonds, but no O–H means no hydrogen bond donation **Typical reactivity:** Relatively unreactive; commonly used as solvents rather than reactants. Lack a good leaving group under normal conditions.

A.4.0.4 Aldehydes

Structure: R–CHO (carbonyl carbon bonded to at least one hydrogen) **Hybridization:** sp^2 at the carbonyl carbon **Geometry:** Trigonal planar, ~120° **Polarity:** Strongly polar C=O dipole **Typical reactivity:** Carbonyl carbon is electrophilic and undergoes nucleophilic addition (Chapter 12). Less sterically hindered than ketones, so generally more reactive toward nucleophiles.

A.4.0.5 Ketones

Structure: R–CO–R′ (carbonyl carbon bonded to two carbon groups) **Hybridization:** sp^2 at the carbonyl carbon **Geometry:** Trigonal planar, ~120° **Polarity:** Strongly polar C=O dipole **Typical reactivity:** Undergoes nucleophilic addition (Chapter 12), generally somewhat slower than aldehydes due to greater steric bulk and electron donation from two alkyl groups.

A.5 Carboxylic Acids and Their Derivatives

These five groups share a carbonyl carbon attached to a heteroatom and undergo the same general reaction — nucleophilic acyl substitution (Chapter 13) — but differ enormously in reactivity depending on how good a leaving group that heteroatom provides. Plain –OH is a poor leaving group: a carboxylic acid typically needs activation (protonation, or conversion to an acid chloride) before it will undergo substitution as readily as the other four members of this family.

A.5.0.1 Carboxylic Acids

Structure: R–COOH **Hybridization:** sp^2 at the carbonyl carbon **Geometry:** Trigonal planar, ~120° **Polarity:** Highly polar; O–H allows hydrogen bonding (carboxylic acids often exist as dimers) **Typical reactivity:** Acidic at O–H (Chapter 3); the conjugate base (carboxylate) is resonance-stabilized across both oxygens. Converted to acid chlorides, esters, and amides via nucleophilic acyl substitution.

A.5.0.2 Acid Chlorides

Structure: R–COCl **Hybridization:** sp^2 at the carbonyl carbon **Geometry:** Trigonal planar, ~120° **Polarity:** Very polar **Typical reactivity:** The most reactive carboxylic acid derivative — chloride is an excellent leaving group. Reacts readily with water, alcohols, and amines to generate acids, esters, and amides.

A.5.0.3 Anhydrides

Structure: R–CO–O–CO–R′ **Hybridization:** sp^2 at both carbonyl carbons **Geometry:** Trigonal planar at each carbonyl **Polarity:** Polar **Typical reactivity:** Second most reactive derivative, behind acid chlorides. A carboxylate is a moderate leaving group, so anhydrides readily acylate alcohols and amines.

A.5.0.4 Esters

Structure: R–CO–O–R′ **Hybridization:** sp^2 at the carbonyl carbon **Geometry:** Trigonal planar, ~120° **Polarity:** Polar **Typical reactivity:** Moderately reactive; undergoes hydrolysis back to the carboxylic acid or transesterification, but requires more forcing conditions than acid chlorides or anhydrides. Often recognizable by pleasant, fruity odors.

A.5.0.5 Amides

Structure: R–CO–NR'_2 **Hybridization:** sp^2 at the carbonyl carbon; nitrogen lone pair delocalizes into the carbonyl, making nitrogen effectively sp^2 as well **Geometry:** Planar across the whole C(=O)–N unit **Polarity:** Highly polar, but nitrogen's lone pair is tied up in resonance **Typical reactivity:** The least reactive carboxylic acid derivative and the most stable — nitrogen is a poor leaving group because of resonance donation into the carbonyl. This same resonance makes amide nitrogen far less basic and less nucleophilic than amine nitrogen. Forms the peptide bond in proteins.

A.5.0.6 Acetals and Hemiacetals

Structure: Hemiacetal — a carbon bonded to one –OH and one –OR; Acetal — a carbon bonded to two –OR groups. Both form from addition of alcohol(s) to an aldehyde or ketone. **Hybridization:** sp^3 at the central carbon (contrast with the sp^2 parent carbonyl) **Geometry:** Tetrahedral, ~109.5° **Polarity:** Polar C–O bonds **Typical reactivity:** Formed and hydrolyzed reversibly under acid catalysis (Chapter 12). Acetals are stable to base and are used as protecting groups to temporarily mask a carbonyl during a synthesis.

A.6 Nitrogen-Containing Groups

A.6.0.1 Amines

Structure: C–NR_2 (R = H or alkyl/aryl) **Hybridization:** sp^3 at nitrogen (lone pair occupies the fourth position) **Geometry:** Trigonal pyramidal, ~107° **Polarity:** Polar; primary and secondary amines are hydrogen bond donors, and all amines are hydrogen bond acceptors **Typical reactivity:** The nitrogen lone pair is both basic (Chapter 3) and strongly nucleophilic — amines are common nucleophiles in substitution and acyl substitution reactions.

A.6.0.2 Amides

See **Carboxylic Acids and Their Derivatives**, above. Amides sit at the intersection of the oxygen- and nitrogen-containing families: the carbonyl places them among the acyl derivatives, while the nitrogen places them among biologically central nitrogen groups (proteins, peptides).

A.7 Aromatic Heterocycles

Structure: Aromatic rings containing one or more nitrogen, oxygen, or sulfur atoms in place of a ring carbon (e.g., pyridine, furan, pyrrole) **Hybridization:** sp^2 throughout the ring, maintaining the delocalized π system **Geometry:** Planar **Polarity:** Varies with the heteroatom; ring nitrogen lone pairs may or may not be part of the aromatic π system depending on whether they are conjugated into the ring **Typical reactivity:** Retains aromatic character and undergoes substitution rather than addition; the heteroatom strongly influences reactivity and where substitution occurs (Chapter 17). Widespread in pharmaceuticals and biomolecules.

A.8 Summary Table

Functional Group	Structure	Hybridization	Geometry	Polarity	Typical Reactivity
Alkane	C–C, C–H	sp^3	Tetrahedral (109.5°)	Nonpolar	Unreactive scaffold
Alkene	C=C	sp^2	Trigonal planar (120°)	Weakly polar	Electrophilic addition
Alkyne	C≡C	sp	Linear (180°)	Weakly polar	Addition; acidic terminal C–H
Arene	Delocalized ring	sp^2	Planar hexagon	Nonpolar	Electrophilic aromatic substitution
Alkyl halide	C–X	sp^3	Tetrahedral	Polar	Substitution, elimination
Alcohol	C–O–H	sp^3	Tetrahedral / bent at O	Polar	Weak acid; nucleophile; substrate for substitution/ elimination
Phenol	Ar–O–H	sp^2	Planar	Polar	More acidic than alcohols; activates ring toward EAS
Ether	C–O–C	sp^3	Bent at O	Polar bonds, no H-bond donor	Largely unreactive; common solvent
Aldehyde	R–CHO	sp^2	Trigonal planar	Strongly polar	Nucleophilic addition
Ketone	R–CO–R′	sp^2	Trigonal planar	Strongly polar	Nucleophilic addition
Carboxylic acid	R–COOH	sp^2	Trigonal planar	Highly polar	Acidic; acyl substitution
Acid chloride	R–COCl	sp^2	Trigonal planar	Very polar	Most reactive acyl substitution
Anhydride	R–CO–O–CO–R′	sp^2	Trigonal planar	Polar	Reactive acyl substitution
Ester	R–CO–O–R′	sp^2	Trigonal planar	Polar	Moderate acyl substitution; hydrolysis
Amide	R–CO–NR'_2	sp^2 (C and N)	Planar	Polar, N lone pair delocalized	Least reactive acyl derivative; very stable
Acetal/Hemiacetal	C(OR)(OR)/ C(OH)(OR)	sp^3	Tetrahedral	Polar	Reversible, acid-cat-

Functional Group	Structure	Hybridization	Geometry	Polarity	Typical Reactivity
					alyzed; protecting group
Amine	C–NR_2	sp^3	Trigonal pyramidal (~107°)	Polar	Basic; strongly nucleophilic
Aromatic heterocycle	Ring with N/O/S	sp^2	Planar	Variable	Substitution; heteroatom-directed reactivity

A.9 Functional Group Family Tree

- **Hydrocarbons** — carbon and hydrogen only
  - Alkanes (single bonds)
  - Alkenes (one or more C=C)
  - Alkynes (one or more C≡C)
  - Arenes (aromatic rings)
- **Halogen-containing**
  - Alkyl halides
- **Oxygen-containing**
  - Alcohols and phenols (C–OH)
  - Ethers (C–O–C)
  - Carbonyl-containing groups (C=O)
    - Aldehydes and ketones (simple carbonyls — undergo *addition*)
    - Carboxylic acid derivatives (carbonyl + heteroatom leaving group — undergo *substitution*)
      - Carboxylic acids
      - Acid chlorides
      - Anhydrides
      - Esters
      - Amides
    - Acetals and hemiacetals (carbonyl + alcohol addition products)
- **Nitrogen-containing**
  - Amines
  - Amides (also a carbonyl-containing group, above)
- **Aromatic heterocycles** — bridge the aromatic and heteroatom families

The single most useful split in this tree is between the **simple carbonyls** (aldehydes, ketones — no good leaving group, so they undergo addition) and the **acyl derivatives** (carboxylic acids and their relatives — a heteroatom leaving group is present, so they undergo substitution). This distinction, developed in Chapters 12 and 13, explains most of carbonyl chemistry.

A.10 Functional Group Interconversion Map

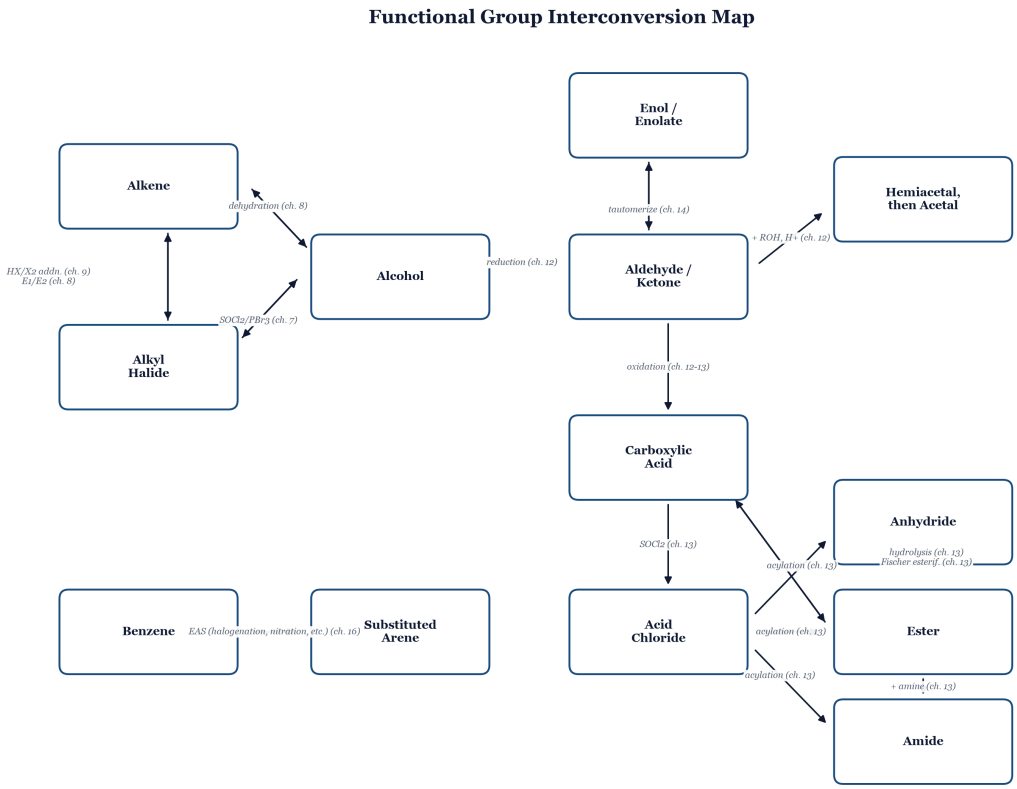


Figure A.1: **Figure A.1.** The interconversion table below, as a map: every arrow is one row of the table, labeled with the transformation and chapter.

Starting Group	Product	Typical Transformation	Chapter
Alkene	Alkyl halide	Electrophilic addition of HX or X_2	9
Alkyl halide	Alkene	Elimination (E1/E2)	8
Alkyl halide	Alcohol	Substitution (SN1/SN2) with water or hydroxide	7
Alcohol	Alkyl halide	Substitution with $SOCl_2$, PBr_3, or acid + halide	7
Alcohol	Alkene	Acid-catalyzed dehydration (E1)	8
Alkene	Alcohol	Acid-catalyzed hydration (Markovnikov addition)	9
Alcohol	Aldehyde or ketone	Oxidation	12

Starting Group	Product	Typical Transformation	Chapter
Aldehyde or ketone	Alcohol	Reduction, or addition of a nucleophile	12
Aldehyde	Carboxylic acid	Oxidation	12–13
Aldehyde/ketone + alcohol	Hemiacetal, then acetal	Acid-catalyzed addition	12
Carboxylic acid	Acid chloride	Reaction with $SOCl_2$	13
Acid chloride	Anhydride, ester, or amide	Nucleophilic acyl substitution	13
Ester	Carboxylic acid	Hydrolysis	13
Carboxylic acid + alcohol	Ester	Fischer esterification	13
Ester or acid chloride	Amide	Substitution with an amine	13
Ketone or aldehyde	Enol or enolate	Tautomerization, or deprotonation at the α-carbon	14
Benzene	Substituted arene	Electrophilic aromatic substitution (halogenation, nitration, sulfonation, Friedel-Crafts)	16

Reading this table both directions is a useful exercise: given a target molecule, work backward through the map to identify which starting material and reaction would produce it — the core skill developed in retrosynthetic analysis (Chapter 21).

A.11 Cross-References

- **Chapter 1 (Functional Groups)** — first introduction to each group and its role in the handbook.
- **Chapter 3 (Acids and Bases)** — pKa trends referenced throughout this atlas; see also **Appendix B (pKa Tables)**.
- **Chapters 7–9 (Substitution, Elimination, Addition)** — mechanisms behind the hydrocarbon and alkyl halide interconversions above.
- **Chapters 12–14 (Carbonyl Chemistry)** — mechanisms behind the carbonyl and acyl substitution interconversions above.
- **Chapters 15–17 (Aromaticity)** — mechanisms behind arene and heterocycle reactivity.
- **Appendix C (Reaction Summary Tables)** — condensed, exam-ready versions of the reactions referenced in the interconversion map.

B. pKa Tables

Chapter 3 makes a deliberate choice not to lead with numbers: the goal there is to understand *why* one acid is stronger than another by evaluating the stability of the conjugate base. This appendix is the reference that goes with that framework — a set of representative pKa values, organized by compound class, to consult once the underlying reasoning is in place.

A caution before using this appendix: the Common Mistake named in Chapter 3 is memorizing pKa values in place of understanding stability. Use this table to check reasoning and to calibrate intuition (is this acid stronger or weaker than water? than acetic acid?) — not as a list to memorize outright. Exact values also vary somewhat by source and solvent; what matters is the relative order and the structural reasoning behind it.

B.1 How to Read pKa

pKa = −log(Ka). A *lower* pKa means a *stronger* acid — it dissociates more completely.

Each unit of pKa represents a **factor of 10** in acid strength. An acid with pKa 5 is 10 times stronger than one with pKa 6, and 100,000 times stronger than one with pKa 10.

Basicity is the mirror image. The weaker the conjugate acid (higher its pKa, in the pKaH notation used for amines below), the stronger the base. There is no separate "pKb table" in this appendix — every base's strength is read from the pKa of its conjugate acid.

A functional group is a moderate acid, base, both, or neither, depending on which factor from Chapter 3 applies to it — resonance, electronegativity, induction, or hybridization. The tables below are grouped by compound class so those factors can be compared side by side.

B.2 Master Table — Representative pKa Values

Ordered from strongest acid to weakest.

Compound	Acidic Site	pKa (approx.)	Compound Class
HCl	H–Cl	−7	Mineral acid (reference point)
H_3O^+	$H–OH_2^+$	−1.7	Hydronium (reference point)
Trifluoroacetic acid	CF_3COOH	0.2	Carboxylic acid (heavily inductive)
Trichloroacetic acid	CCl_3COOH	0.7	Carboxylic acid (heavily inductive)
Dichloroacetic acid	$Cl_2CHCOOH$	1.3	Carboxylic acid
Chloroacetic acid	$ClCH_2COOH$	2.9	Carboxylic acid
Formic acid	HCOOH	3.8	Carboxylic acid
Benzoic acid	PhCOOH	4.2	Carboxylic acid
Anilinium ion	$PhNH_3^+$	4.6	Ammonium (conjugate acid of a weak amine)
Acetic acid	CH_3COOH	4.8	Carboxylic acid

Compound	Acidic Site	pKa (approx.)	Compound Class
Pyridinium ion	$C_5H_5NH^+$	5.2	Ammonium (aromatic amine)
p-Nitrophenol	4-O_2N–C_6H_4OH	7.2	Phenol (electron-poor ring)
Acetylacetone (pentane-2,4-dione)	–CH_2– between two C=O	~9	1,3-Dicarbonyl (doubly activated α-C–H)
Ammonium ion	NH_4^+	9.25	Ammonium
Phenol	C_6H_5OH	10.0	Phenol
Methylammonium ion	$CH_3NH_3^+$	10.6	Ammonium (alkyl amine)
Diethyl malonate	–CH_2– between two esters	~13	1,3-Dicarbonyl (doubly activated α-C–H)
Water	H_2O	15.7	Reference solvent
Ethanol	CH_3CH_2OH	16	Alcohol
tert-Butanol	$(CH_3)_3COH$	18	Alcohol (more hindered/less stabilized)
Acetone	CH_3–CO–CH_3, α-C–H	20	Ketone α-carbon
Terminal alkyne	HC≡CH, C–H	25	Hydrocarbon (sp C–H)
Ethyl acetate	CH_3CO–OEt, α-C–H	25	Ester α-carbon
Ammonia	NH_3	38	Reference (as an acid, not a base)
Ethylene	$H_2C=CH_2$, C–H	44	Hydrocarbon (sp^2 C–H)
Ethane	CH_3CH_3, C–H	50	Hydrocarbon (sp^3 C–H)

B.3 Carboxylic Acids

Compound	pKa	Structural Note
Trifluoroacetic acid	0.2	Three highly electronegative F atoms pull electron density from the carboxylate
Trichloroacetic acid	0.7	Three inductively withdrawing Cl atoms
Chloroacetic acid	2.9	One inductively withdrawing Cl atom
Formic acid	3.8	No alkyl group donating electron density
Benzoic acid	4.2	Aromatic ring is mildly electron-withdrawing relative to alkyl

Compound	pKa	Structural Note
Acetic acid	4.8	Simple alkyl carboxylic acid — the typical reference value

Why carboxylic acids are acidic at all: deprotonation gives a carboxylate ion whose negative charge is delocalized equally over both oxygens by resonance. This is the same reasoning developed in Chapter 3′s Gentle Exercise ("why are carboxylic acids stronger acids than alcohols?") — an alkoxide has nowhere to delocalize its charge, while a carboxylate does.

Why the halogenated acids are so much stronger: induction, not resonance. Electronegative halogens near the carboxyl group pull electron density through the sigma bonds, stabilizing the negative charge on the carboxylate. This effect drops off quickly with distance — a halogen on the carbon adjacent to the carboxyl (α) has a much larger effect than one further away.

B.4 Phenols

Compound	pKa	Structural Note
p-Nitrophenol	7.2	The nitro group is strongly electron-withdrawing and conjugated directly into the ring
Phenol	10.0	Reference value

Why phenols are more acidic than alcohols (compare phenol, pKa 10, to ethanol, pKa 16): the phenoxide ion delocalizes its negative charge into the aromatic ring by resonance, spreading it onto the ortho and para carbons. An alkoxide has no comparable delocalization pathway. This is the same resonance argument used for carboxylate, applied to a different scaffold — see Appendix A's entry on phenols and Chapter 17 for how ring substituents shift this value further.

Why electron-withdrawing ring substituents increase acidity further: a para-nitro group can accept negative charge directly by resonance (the charge can be drawn all the way onto the nitro oxygens), which is why p-nitrophenol is nearly 1,000 times more acidic than phenol itself. Electron-donating substituents (e.g., para-methoxy) have the opposite effect.

B.5 Alcohols and Water

Compound	pKa	Structural Note
Water	15.7	Reference solvent
Ethanol	16	Typical primary/secondary alcohol
tert-Butanol	18	Bulkier alkoxide is less well solvated/stabilized

Alcohols and water are only weakly acidic — their conjugate bases (alkoxide, hydroxide) carry a full negative charge with no resonance delocalization. Alkoxide is nonetheless a strong enough base to be useful synthetically (e.g., in E2 eliminations, Chapter 8), precisely because it is not resonance-stabilized.

B.6 Ammonium Ions and Amine Basicity

Amines themselves are not usually discussed by "pKa" directly — instead, chemists report the pKa of the **conjugate acid** (the ammonium ion), often written pKaH. A **higher** pKaH means a **more basic** amine, because its conjugate acid holds onto the proton more tightly.

Amine	Conjugate Acid	pKaH	Basicity Note
Aniline	Anilinium ion	4.6	Weakly basic — nitrogen lone pair is delocal-

Amine	Conjugate Acid	pKaH	Basicity Note
			ized into the aromatic ring, less available to accept a proton
Pyridine	Pyridinium ion	5.2	Weakly basic — lone pair sits in an sp^2 orbital in the ring plane, not part of the aromatic system, but still less basic than an alkyl amine
Ammonia	Ammonium ion	9.25	Reference value
Methylamine	Methylammonium ion	10.6	More basic than ammonia — the alkyl group donates electron density to nitrogen

Why aromatic amines are weaker bases than alkyl amines: in aniline, the nitrogen lone pair is conjugated into the ring (the same resonance that makes aniline nitrogen a weaker nucleophile — see Appendix A's note on amide resonance for the analogous effect on amides, which is far more extreme). That lone pair is less available to accept a proton, so aniline is a much weaker base than cyclohexylamine, its non-aromatic analog.

B.7 C–H Acids and Hybridization

Compound	pKa	Hybridization at Carbon
Ethane	50	sp^3
Ethylene	44	sp^2
Terminal alkyne (acetylene)	25	sp

Why hybridization affects C–H acidity: an sp orbital has more s-character (50%) than sp^2 (33%) or sp^3 (25%). Electrons in an orbital with more s-character sit closer to the nucleus, so the conjugate base (a carbanion) is more stable when the negative charge sits in an sp orbital. This is why a terminal alkyne C–H (Chapter 9) is acidic enough to be deprotonated by strong bases such as sodium amide, while an alkane or alkene C–H is not.

B.8 Carbonyl α-Carbons and Enolates

Compound	pKa	Structural Note
Ethyl acetate (ester α-C–H)	25	One carbonyl stabilizes the enolate by resonance
Acetone (ketone α-C–H)	20	One carbonyl stabilizes the enolate by resonance; ketones are somewhat more acidic than esters at the α-position
Diethyl malonate (1,3-diester α-C–H)	~13	Two carbonyls both stabilize the same enolate — resonance delocalizes the negative charge onto two separate carbonyl oxygens
Acetylacetone (1,3-diketone α-C–H)	~9	Two carbonyls, same doubly-stabilized effect, and ketone car-

Compound	pKa	Structural Note
		bonyls stabilize slightly better than ester carbonyls

Why α-carbons are acidic at all: deprotonating a C–H adjacent to a carbonyl generates an enolate, whose negative charge is resonance-delocalized onto the carbonyl oxygen rather than sitting on carbon alone (Chapter 14). This is the same stability principle as carboxylate and phenoxide — resonance delocalization of the conjugate base — applied to a carbanion instead of an alkoxide.

Why 1,3-dicarbonyls are dramatically more acidic: with two carbonyls flanking the same C–H, the single resulting enolate can delocalize onto *either* carbonyl oxygen, effectively doubling the resonance stabilization. This is why diethyl malonate and acetylacetone are common starting materials for enolate alkylation chemistry (Chapter 14) — their α-protons are acidic enough to be removed by moderate bases like alkoxide, rather than requiring the very strong bases needed for a simple ketone or ester.

B.9 The Four Stability Factors, Revisited

Chapter 3 introduces four factors that stabilize a conjugate base, sometimes remembered by the mnemonic **ARIO** — **A**tom, **R**esonance, **I**nduction, **O**rbital (hybridization). Every trend in this appendix is an example of one of these four:

Factor	What It Means	Example From This Appendix
Atom	More electronegative atoms (further right on the periodic table) or larger atoms (further down the periodic table) stabilize negative charge better — electronegativity dominates across a period, size dominates down a group	Underlies why O–H is more acidic than N–H (electronegativity); not heavily featured in this course's scope otherwise
Resonance	Delocalizing charge across multiple atoms lowers its energy	Carboxylic acids, phenols, and enolates are all far more acidic than their non-delocalized counterparts (alcohols, alkanes)
Induction	Nearby electronegative atoms withdraw electron density through sigma bonds, stabilizing adjacent charge	Trifluoroacetic acid vs. acetic acid; chloroacetic acid vs. acetic acid
Orbital (hybridization)	More s-character holds electrons closer to the nucleus, stabilizing negative charge	Terminal alkyne C–H (sp) vs. alkene C–H (sp^2) vs. alkane C–H (sp^3)

When comparing two acids, working through these four factors in order — is one atom more electronegative, can the charge resonate, is there an inductive effect nearby, does hybridization differ — will explain nearly every pKa trend in this table without needing to memorize the numbers directly.

B.10 Cross-References

- **Chapter 3 (Acids and Bases)** — the conceptual framework (stability of the conjugate base) that this appendix supplies values for.
- **Chapter 8 (Elimination)** — alkoxide and other strong, non-resonance-stabilized bases as the reagents that drive E2 elimination.
- **Chapter 9 (Addition)** — terminal alkyne acidity and its use in alkylation chemistry.
- **Chapter 14 (Enols and Enolates)** — the mechanism behind α-carbon acidity and enolate resonance in full detail.
- **Chapter 17 (Substituent Effects)** — how ring substituents shift phenol and aniline acid/base strength.

- **Appendix A (Functional Group Atlas)** — polarity and reactivity notes for each compound class referenced here.

C. Reaction Summary Tables

The main chapters deliberately favor patterns and mechanisms over reagent lists — the Common Mistakes sections in Chapters 7–17 repeatedly warn against memorizing tables in place of understanding *why* a reaction happens. This appendix is the reagent-level reference that goes with that reasoning: once a mechanism is understood, these tables are where to look up which specific reagents accomplish it.

How to use this appendix: each table gives the reaction name, typical reagents/conditions, the product, the key mechanistic pattern (which should already be familiar from the chapter body), and a common pitfall. Use it for exam review, not first-pass learning.

C.1 Substitution and Elimination (SN1, SN2, E1, E2)

Reaction	Typical Reagents/ Conditions	Substrate	Mechanism	Product / Stereochemistry	Common Pitfall
SN2	Strong nucleophile (e.g., NaOH, NaOR, NaCN, NaN_3, thiolate); polar aprotic solvent (DMSO, DMF, acetone)	Methyl, primary (secondary possible)	One step, concerted, backside attack	Inversion of configuration at the reactive carbon	Attempting SN2 on a tertiary substrate — sterics make backside attack impossible
SN1	Weak nucleophile, often the solvent itself (H_2O, ROH); polar protic solvent	Tertiary (secondary possible)	Two steps via carbocation intermediate	Racemization (attack from either face of the planar carbocation)	Forgetting that carbocation rearrangements (hydride/alkyl shifts) can change the constitution of the product
E2	Strong, often bulky base (e.g., NaOEt, KOtBu, DBU) + heat	Primary, secondary, tertiary	One step, concerted; requires anti-periplanar H and leaving group	Alkene; Zaitsev (more substituted) product usually favored unless the base is bulky	Ignoring the conformational requirement — if no anti-periplanar H is accessible, E2 cannot proceed from that conformation
E1	Weak base, polar protic solvent, heat	Tertiary (secondary possible)	Two steps via carbocation intermediate	Alkene; Zaitsev product favored; rearrangements possible	Assuming E1 and SN1 don't compete — they arise from the same carbocation

Reaction	Typical Reagents/ Conditions	Substrate	Mechanism	Product / Stereochemistry	Common Pitfall
					and typically occur together

C.1.1 Decision Framework

Reasoning through these four questions, in order, resolves most substitution/elimination problems:

1. **Is the substrate methyl or primary?** → SN2 is likely (unless the base/nucleophile is bulky, which favors E2 even on primary substrates).
2. **Is the substrate tertiary?** → SN1/E1 are likely if the nucleophile/base is weak; E2 is likely if the base is strong.
3. **Is the nucleophile/base strong and unhindered?** → Favors the concerted pathways (SN2 on unhindered carbons, E2 otherwise).
4. **Is the solvent polar protic?** → Favors the stepwise, carbocation pathways (SN1/E1).

See Chapter 10 for the underlying reasoning; this table is the condensed version for quick lookup.

C.2 Addition to Alkenes and Alkynes

Reaction	Typical Reagents/ Conditions	Mechanism	Product / Regiochemistry	Common Pitfall
Hydrogenation	H_2, Pd or Pt catalyst	Syn addition across a metal surface	Alkane; both H atoms add to the same face	Forgetting that a catalyst is required — H_2 does not add to alkenes uncatalyzed
Hydrohalogenation	HX (HCl, HBr, HI)	Carbocation intermediate	Markovnikov addition — H adds to the less substituted carbon, X to the more substituted (more stable carbocation) carbon	Placing the halogen on the wrong carbon by not identifying the more stable carbocation first
Acid-catalyzed hydration	H_3O^+ / H_2O	Carbocation intermediate	Markovnikov addition — OH ends up on the more substituted carbon; rearrangements possible	Forgetting that this pathway can rearrange, unlike the anti-Markovnikov alternative below
Hydroboration–oxidation	BH_3 (or BH_3·THF), then H_2O_2/NaOH	Concerted, single-step addition (no carbocation)	Anti-Markovnikov addition — OH ends up on the less substituted carbon; syn addition; no rearrangement	Confusing this with acid-catalyzed hydration — same overall transformation (alkene → alcohol), opposite regiochemistry
Halogenation	X_2 (Cl_2, Br_2)	Bridged halonium ion intermediate	Vicinal dihalide; anti addition	Predicting syn addition — the bridged interme-

Reaction	Typical Reagents/ Conditions	Mechanism	Product / Regiochemistry	Common Pitfall
				diate forces the second halogen to attack from the opposite face

Regiochemistry note: the Markovnikov vs. anti-Markovnikov contrast above is the classic example of the regiochemistry reasoning introduced in Chapter 9 — identifying which pathway proceeds through the more stable intermediate (a carbocation, for Markovnikov addition) versus which pathway avoids a carbocation altogether (hydroboration).

Aromatic rings do not undergo these reactions — see Electrophilic Aromatic Substitution, below, and the Chapter 9 Common Mistake on this point.

C.3 Nucleophilic Addition to Aldehydes and Ketones

Reaction	Typical Reagents/Conditions	Product	Common Pitfall
Hydration	H_2O	Geminal diol (hydrate)	Assuming this equilibrium always favors the hydrate — for most ketones, the carbonyl form is favored
Reduction	$NaBH_4$ or $LiAlH_4$, then aqueous workup	Alcohol	Using the same reagent for reducing a carboxylic acid derivative — $NaBH_4$ is generally too weak for esters/amides, while $LiAlH_4$ is strong enough to reduce those as well
Organometallic addition	Grignard reagent (RMgX) or organolithium (RLi), then aqueous workup	New C–C bond; alcohol	Forgetting that these are strong bases as well as strong nucleophiles — they are incompatible with acidic protons (O–H, N–H) elsewhere in the molecule
Hemiacetal/acetal formation	Alcohol (ROH), acid catalyst	Hemiacetal (1 equiv. ROH) or acetal (2 equiv. ROH, water removed)	Forgetting that this is reversible — acetals hydrolyze back to the carbonyl under aqueous acid, which is exactly why they are useful as protecting groups

Every reaction in this table follows the same general pattern introduced in Chapter 12: a nucleophile attacks the electrophilic carbonyl carbon, electron density shifts onto oxygen, and (where applicable) a proton transfer restores neutrality.

C.4 Nucleophilic Acyl Substitution (Carboxylic Acid Derivatives)

Unlike aldehydes and ketones, carboxylic acid derivatives have a leaving group attached to the carbonyl carbon. The tetrahedral intermediate formed by nucleophilic attack collapses by ejecting that leaving

group and reforming the C=O — substitution, not addition. This is the central distinction developed in Chapter 13.

Relative reactivity: Acid chlorides → Anhydrides → Esters → Amides (most to least reactive), tracking how good a leaving group each derivative provides.

Starting Material	Typical Reagents/Conditions	Product	Common Pitfall
Carboxylic acid	$SOCl_2$	Acid chloride	Forgetting this is usually the first step needed before making an anhydride, ester, or amide from a carboxylic acid directly
Carboxylic acid	Alcohol (ROH), acid catalyst (Fischer esterification)	Ester	Assuming this reaction goes to completion — Fischer esterification is an equilibrium and usually needs excess alcohol or water removal to favor the ester
Acid chloride or anhydride	H_2O	Carboxylic acid	—
Acid chloride or anhydride	Alcohol (ROH)	Ester	—
Acid chloride or anhydride	Amine (R_2NH)	Amide	—
Ester	H_3O^+ or NaOH (saponification), H_2O	Carboxylic acid (or carboxylate, if base)	Confusing acid- and base-mediated hydrolysis — base-mediated hydrolysis (saponification) is irreversible because the carboxylate product is unreactive toward further attack
Ester	Amine (R_2NH)	Amide	Requires more forcing conditions than starting from an acid chloride, since alkoxide is a worse leaving group than chloride

Reading this table as a cascade: acid chlorides and anhydrides are reactive enough to be converted directly into acids, esters, or amides by choosing the nucleophile (water, alcohol, or amine, respectively) — the same substitution mechanism, three different nucleophiles.

C.5 Enols, Enolates, and Carbon–Carbon Bond Formation

Reaction	Typical Reagents/ Conditions	Product	Mechanistic Note	Common Pitfall
Enolate alkylation	Strong, non-nucleophilic base (e.g., LDA) to form the eno-	New C–C bond at the α-carbon	Enolate acts as a nucleophile toward the alkyl halide's elec-	Using a nucleophilic base (e.g., NaOH) instead of LDA — a nucle-

Reaction	Typical Reagents/ Conditions	Product	Mechanistic Note	Common Pitfall
	late, then an alkyl halide		trophilic carbon (an SN2-like step)	ophilic base can attack the alkyl halide itself instead of just deprotonating
Aldol reaction	Base (e.g., NaOH) or acid catalyst	β-hydroxy carbonyl compound	Enolate (or enol) attacks the carbonyl carbon of a second molecule	Forgetting to identify the α-carbon correctly before drawing the enolate nucleophile
Aldol condensation	Aldol product, heat (or the same conditions, driven further)	α,β-unsaturated carbonyl compound	Dehydration of the β-hydroxy group, favored by conjugation with the carbonyl	Stopping analysis at the aldol product when the question asks for the condensation (dehydrated) product
Claisen condensation	Alkoxide base (e.g., NaOEt)	β-keto ester	Ester enolate attacks the carbonyl carbon of a second ester molecule, expelling alkoxide (acyl substitution, not simple addition)	Confusing this with the aldol reaction — Claisen requires an ester (a leaving group is needed for the substitution step that follows addition)

See Chapter 14 for the acidity argument (enolate resonance stabilization) and Appendix B's section on carbonyl α-carbons for representative pKa values.

C.6 Electrophilic Aromatic Substitution

Reaction	Typical Reagents/Conditions	Electrophile Generated	Product
Halogenation	X_2, FeX_3 (Lewis acid catalyst)	X^+ (halogenium, activated by the Lewis acid)	Aryl halide
Nitration	HNO_3, H_2SO_4	NO_2^+ (nitronium ion)	Nitrobenzene derivative
Sulfonation	SO_3, H_2SO_4 (fuming sulfuric acid)	SO_3 (electrophilic sulfur)	Benzenesulfonic acid (reversible — can be removed later by treatment with dilute aqueous acid)
Friedel-Crafts alkylation	R–X, $AlCl_3$	R^+ (carbocation, or a polarized complex)	Alkylbenzene; carbocation rearrangements possible; over-alkylation possible since the product is more

Reaction	Typical Reagents/Conditions	Electrophile Generated	Product
			electron-rich than the starting arene
Friedel-Crafts acylation	R–COCl, $AlCl_3$	Acylium ion ($R–C{\equiv}O^+$)	Aryl ketone; no rearrangement (acylium is resonance-stabilized); no over-acylation (the ketone product deactivates the ring)

C.6.1 Directing and Activating Effects (Chapter 17)

Substituent Type	Examples	Effect on Reactivity	Directs To
Strong activators	–OH, $–NH_2$, –OR	Strongly activating (lone pair donates into the ring by resonance)	Ortho/para
Weak activators	Alkyl groups ($–CH_3$, etc.)	Mildly activating (inductive electron donation, hyperconjugation)	Ortho/para
Deactivating, o/p-directing	Halogens (–F, –Cl, –Br, –I)	Deactivating overall (inductively electron-withdrawing) but still ortho/para-directing (lone pairs can still donate by resonance)	Ortho/para
Deactivating, meta-directing	$–NO_2$, –C≡N, –COOH, –CHO, –C(=O)R, $–SO_3H$	Strongly deactivating (withdraw electron density by resonance and induction, with no lone pair to donate back)	Meta

Why halogens are the exception to the activating/directing correlation: halogens withdraw electron density inductively (deactivating the ring overall) but still possess lone pairs that can donate into the ring by resonance at the ortho/para positions specifically — enough to direct substitution there, even though the net effect on the ring is deactivating. See Chapter 17 for the full resonance argument.

C.7 Addition vs. Substitution at Carbonyls — A Direct Comparison

This is one of the most frequently confused pairs in Organic Chemistry II. Both reactions begin identically — a nucleophile attacks the electrophilic carbonyl carbon, forming a tetrahedral intermediate — but what happens next depends entirely on what else is attached to that carbon.

	Aldehydes/Ketones (Chapter 12)	Carboxylic Acid Derivatives (Chapter 13)
Leaving group on carbonyl carbon?	No (only H or R groups)	Yes (Cl, OR, OCOR, NR_2)
Fate of the tetrahedral intermediate	Protonated to give a stable alcohol (or hemiacetal)	Collapses, ejecting the leaving group and reforming C=O

	Aldehydes/Ketones (Chapter 12)	Carboxylic Acid Derivatives (Chapter 13)
Net transformation	Addition (C=O becomes C–OH, no atoms lost)	Substitution (one heteroatom group replaces another)

Reasoning through this table only requires one question: **is there a leaving group already attached to the carbonyl carbon?** If not, addition is the outcome; if so, substitution is.

C.8 Cross-References

- **Chapters 7–10 (Substitution, Elimination, Addition, Comparing Reactions)** — the mechanistic reasoning behind the first two tables.
- **Chapters 12–14 (Carbonyl Chemistry)** — the mechanistic reasoning behind the carbonyl, acyl substitution, and enolate tables.
- **Chapters 16–17 (Aromaticity)** — the mechanistic reasoning behind electrophilic aromatic substitution and directing effects.
- **Appendix A (Functional Group Atlas)** — the interconversion map that this appendix supplies specific reagents for.
- **Appendix B (pKa Tables)** — acidity values referenced in the enolate and acyl substitution discussions above.
- **Chapter 21 (Retrosynthesis)** — using these tables in reverse to plan a synthetic route.

D. Spectroscopy Reference

Chapters 18–20 deliberately teach spectroscopy as a process of reasoning — narrowing down structural possibilities by combining evidence — rather than a set of numbers to memorize. This appendix is the numeric companion to that process: representative IR absorptions, NMR chemical shifts, splitting patterns, and mass spectrometry fragmentation patterns, organized for lookup once a spectrum is at hand.

How to use this appendix: treat every value as a typical range, not an exact cutoff — real spectra vary with the rest of the molecule. The Chapter 18 Common Mistake applies here too: the goal is to recognize a handful of diagnostic signals, not to memorize the entire table.

D.1 Infrared (IR) Absorption Table

Functional Group	Bond	Wavenumber Range (cm^{-1})	Intensity / Shape
Alcohol, phenol	O–H	3200–3550	Strong, broad
Carboxylic acid	O–H	2500–3300	Strong, very broad (often overlaps with C–H stretches)
Primary amine	N–H	3300–3500	Medium; two bands (asymmetric + symmetric stretch)
Secondary amine	N–H	3300–3500	Medium; one band
Alkane	C–H (sp^3)	2850–2960	Medium
Alkene, arene	C–H (sp^2)	3000–3100	Medium
Alkyne	C–H (sp)	~3300	Sharp, medium–strong
Aldehyde	C–H (of C(=O)H)	2720 and 2820	Two weak bands, diagnostic alongside the C=O stretch
Alkyne	C≡C	2100–2260	Weak (can be absent if the alkyne is symmetric)
Ether	C–O	1050–1150	Strong
Alkene, arene	C=C	1450–1680	Medium; aromatic rings often show several bands in this range

D.1.1 Carbonyl (C=O) Stretch by Compound Class

The carbonyl stretch is one of the most diagnostic IR signals, and its exact position tracks the same reactivity/resonance trend developed in Chapters 12–13 and Appendix C: the more a heteroatom lone pair donates into the carbonyl (lowering its double-bond character), the lower the stretching frequency.

Compound Class	C=O Range (cm^{-1})	Note
Acid chloride	1790–1815	Highest frequency — chlorine's lone pairs overlap poorly with

Compound Class	C=O Range (cm^{-1})	Note
		the carbonyl carbon (weak resonance donation), while its electronegativity withdraws electron density inductively; the net effect is high double-bond character and most electrophilic carbon (matches its position at the top of the reactivity order in Appendix C)
Anhydride	1750 and 1820	Two bands (asymmetric + symmetric stretch of the two carbonyls)
Ester	1735–1750	—
Aldehyde	1720–1740	Paired with the diagnostic 2720/2820 C–H doublet above
Ketone	1705–1725	—
Carboxylic acid	1710–1760	Broadened/shifted by hydrogen bonding (acids often exist as dimers)
Amide	1630–1695	Lowest frequency — nitrogen's lone pair donates most effectively into the carbonyl, reducing its double-bond character (same resonance argument as amide's low reactivity and low nitrogen basicity, Appendix A)

D.2 ^{1}H NMR Chemical Shift Table

All values in δ (ppm), referenced to tetramethylsilane (TMS, δ = 0).

Proton Environment	Typical δ Range	Note
Alkyl C–H, not adjacent to a functional group	0.9–1.5	Baseline aliphatic region
C–H adjacent to C=O, C=C, or aromatic ring (allylic/benzylic)	2.0–2.5	Slightly deshielded by the adjacent π system
C–H adjacent to a halogen	3.0–4.0	Deshielded by the electronegative halogen
O–CH_2/O–CH_3 (ether or ester alkyl group)	3.3–4.5	Deshielded by the adjacent oxygen
Alcohol O–H	1–5 (variable)	Broad; position shifts with concentration and hydrogen bonding; exchangeable
Vinyl C–H (alkene)	4.5–6.5	—
Aromatic C–H	6.5–8.5	Deshielded by the aromatic ring current
Amine N–H	1–5 (variable)	Broad; exchangeable

Proton Environment	Typical δ Range	Note
Amide N–H	5–8 (variable)	Broad; exchangeable
Aldehyde C–H	9.5–10.0	Highly diagnostic — appears in no other common environment
Carboxylic acid O–H	10–13	Broad; exchangeable; one of the most downfield common signals

Exchangeable protons (O–H, N–H) vary in position and often appear broadened; they can be confirmed by shaking the sample with D_2O, which causes the signal to disappear (Chapter 19).

D.3 ^{13}C NMR Chemical Shift Table

Carbon Environment	Typical δ Range	Note
Alkyl carbon (sp^3), not adjacent to a heteroatom	0–40	Baseline aliphatic region
Carbon attached to a halogen	0–70	Range depends heavily on which halogen
Carbon attached to oxygen or nitrogen (C–O, C–N)	50–90	—
Alkyne carbon (sp)	65–90	—
Alkene and aromatic carbon (sp^2)	100–150	—
Carboxylic acid, ester, and amide carbonyl carbon	160–185	Shifted upfield relative to ketones/aldehydes by resonance donation from the attached heteroatom (same reasoning as the IR C=O trend above)
Aldehyde carbonyl carbon	190–205	—
Ketone carbonyl carbon	205–220	Furthest downfield — no adjacent heteroatom lone pair to donate into the carbonyl and reduce its electron deficiency

Reading the carbonyl region as a shortcut: a signal above 190 ppm signals an aldehyde or ketone; a signal in the 160–185 range signals an acyl derivative with an attached heteroatom (acid, ester, or amide) — the same addition-vs-substitution distinction from Appendix C shows up directly in the carbon shift.

D.4 Splitting Patterns (^{1}H NMR)

Splitting follows the **n + 1 rule**: a proton with *n* neighboring protons — equivalent to each other, but non-equivalent to the observed proton — is split into *n + 1* peaks. When neighboring protons belong to more than one non-equivalent set, the result is a more complex multiplet (e.g., a doublet of doublets), not a simple n + 1 pattern.

Neighboring Protons (n)	Multiplicity	Peaks
0	Singlet	1
1	Doublet	2
2	Triplet	3
3	Quartet	4

Neighboring Protons (n)	Multiplicity	Peaks
4	Quintet	5

D.4.1 Representative Coupling Constants (J, in Hz)

Relationship	Typical J (Hz)
Vicinal, freely rotating sp^3–sp^3 (^3J)	6–8
Vicinal, alkene, cis	6–12
Vicinal, alkene, trans	12–18
Geminal, alkene (same carbon)	0–3
Aromatic, ortho	7–10
Aromatic, meta	1–3
Aromatic, para	0–1

Why trans coupling exceeds cis coupling on an alkene: this is a geometric/orbital overlap effect, not something to derive from first principles at this stage — but it is worth recognizing as a diagnostic tool: a large vicinal J (12–18 Hz) across a double bond indicates a trans (E) relationship, while a smaller one (6–12 Hz) indicates cis (Z), directly connecting an NMR spectrum to the E/Z nomenclature in Appendix E.

D.5 Mass Spectrometry: Common Fragment Losses

Mass Lost	Fragment	Suggests
15	$\bullet CH_3$	Methyl group present
17	$\bullet OH$	Alcohol
18	H_2O	Alcohol (dehydration in the mass spectrometer)
28	CO or C_2H_4	Carbonyl compound (loss of CO) or an ethyl/alkene fragment
29	$\bullet CHO$ or $\bullet C_2H_5$	Aldehyde (loss of CHO) or an ethyl group
43	$C_3H_7^+$ or CH_3CO^+ (acylium)	Propyl fragment, or a methyl ketone (acylium ion is often a strong, diagnostic peak)
45	$\bullet COOH$	Carboxylic acid
57	$C_4H_9^+$ or $C_2H_5CO^+$ (acylium)	Butyl fragment, or an ethyl ketone
77	$C_6H_5^+$ (phenyl cation)	Monosubstituted benzene ring

Acylium ions ($R–C{\equiv}O^+$, the same cationic species that drives Friedel-Crafts acylation in Appendix C) are common, stabilized fragments from ketones and aldehydes, which is why losses corresponding to $R–CO^+$ (43, 57, and similar) are frequently prominent peaks.

The molecular ion (M^+) — the unfragmented, ionized starting molecule — gives the molecular weight directly and is the anchor point for interpreting every fragment loss above it (Chapter 20).

D.6 Cross-References

- **Chapter 18 (Infrared Spectroscopy)** — the conceptual role of IR as a first-pass functional group screen.
- **Chapter 19 (NMR Spectroscopy)** — chemical shift, integration, and splitting as three separate, complementary questions.
- **Chapter 20 (Mass Spectrometry)** — combining IR, NMR, and MS evidence into a single structural proposal.
- **Appendix A (Functional Group Atlas)** — polarity and structural notes that explain many of the IR and NMR trends above.
- **Appendix C (Reaction Summary Tables)** — the reactivity order (acid chloride → anhydride → ester → amide) that the carbonyl IR/^{13}C trends directly parallel.
- **Appendix E (IUPAC Nomenclature Reference)** — E/Z geometry, referenced above in the coupling constant discussion.

E. IUPAC Nomenclature Reference

This appendix provides a working reference for IUPAC organic nomenclature at the level needed for Organic Chemistry I and II. It is designed to be used alongside Chapter 1 (Functional Groups) and returned to throughout the course as new compound classes are introduced. It is not exhaustive — the full IUPAC system includes preferred names, retained names, and additional rules beyond this handbook's scope (see "A Note on Ambiguity" below).

E.1 The Logic of IUPAC Nomenclature

The IUPAC system is designed so that a compound's name and structure determine each other unambiguously. The name encodes three things:

1. **The length of the parent chain** (how many carbons)
2. **The principal functional group** (what kind of compound it is)
3. **The location and identity of all substituents** (what is attached, and where)

Given a name, a trained chemist can reconstruct the structure. Given a structure, a trained chemist can derive the name. The goal for students is to move comfortably in both directions for the compound classes covered in Organic Chemistry I and II.

E.2 Step-by-Step Naming Procedure

E.2.1 Step 1 — Identify the principal functional group

The suffix is determined by the highest-priority functional group present. Use the priority order in the table below. If the molecule contains only carbon and hydrogen single bonds, it is an alkane.

E.2.2 Step 2 — Find the parent chain

Identify the longest continuous carbon chain that includes the principal functional group. For aldehydes and carboxylic acids, the carbonyl carbon is always carbon 1 and must be included in the chain.

E.2.3 Step 3 — Number the chain

Number from the end that gives the principal functional group the lowest possible locant. If there is a tie, number from the end that gives substituents the lowest locants.

E.2.4 Step 4 — Name substituents

Identify all groups attached to the parent chain that are not the principal functional group. Name them as prefixes using the substituent table below.

E.2.5 Step 5 — Assemble the name

List substituents alphabetically (ignoring multiplying prefixes such as di-, tri-), include locants for all substituents and the principal functional group, and add the suffix.

Format: locant(s)-substituent(s) + parent chain prefix + locant-suffix

E.3 Parent Chain Prefixes

Carbons	Prefix	Carbons	Prefix
1	meth-	6	hex-
2	eth-	7	hept-
3	prop-	8	oct-
4	but-	9	non-
5	pent-	10	dec-

For chains longer than 10 carbons: undec- (11), dodec- (12), tridec- (13), tetradec- (14), pentadec- (15).

E.4 Functional Group Priority and Suffixes

When multiple functional groups are present, the one with the highest priority (lowest number in this table) determines the suffix. All lower-priority groups are expressed as prefixes.

Priority	Functional Group	Suffix	Prefix (when not principal)
1	Carboxylic acid	-oic acid	carboxy-
2	Ester	-oate	(alkoxy-carbonyl-)
3	Amide	-amide	carbamoyl-
4	Aldehyde	-al	oxo- (on terminal carbon)
5	Ketone	-one	oxo-
6	Alcohol	-ol	hydroxy-
7	Amine	-amine	amino-
8	Alkyne	-yne	—
9	Alkene	-ene	—
10	Alkane	-ane	—

Note on aldehydes: The carbonyl carbon of an aldehyde is always C-1, so no locant is needed in the name (e.g., propanal, not propan-1-al).

Note on carboxylic acids: Similarly, the carboxyl carbon is always C-1.

E.5 Common Substituent Names

Substituent	Structure	Name
Methyl	$-CH_3$	methyl–
Ethyl	$-CH_2CH_3$	ethyl–
Propyl	$-CH_2CH_2CH_3$	propyl–
Isopropyl	$-CH(CH_3)_2$	isopropyl– (or 1-methylethyl–)
Butyl	$-CH_2CH_2CH_2CH_3$	butyl–
tert-Butyl	$-C(CH_3)_3$	tert-butyl– (or 1,1-dimethylethyl–)
Phenyl	$-C_6H_5$	phenyl–
Benzyl	$-CH_2C_6H_5$	benzyl–

Substituent	Structure	Name
Fluoro	–F	fluoro–
Chloro	–Cl	chloro–
Bromo	–Br	bromo–
Iodo	–I	iodo–
Hydroxy	–OH	hydroxy–
Methoxy	$-OCH_3$	methoxy–
Amino	$-NH_2$	amino–
Nitro	$-NO_2$	nitro–
Oxo	=O	oxo–

E.6 Multiplying Prefixes

When the same substituent appears more than once, use a multiplying prefix. These are not alphabetized — alphabetize by the substituent name itself.

Count	Prefix
2	di–
3	tri–
4	tetra–
5	penta–
6	hexa–

Example: 2,3-dimethylbutane (two methyl groups, not dimethyl for alphabetization purposes).

E.7 Alkenes and Alkynes

E.7.1 Locants

The double or triple bond position is given the lowest possible locant. The locant refers to the lower-numbered carbon of the multiple bond.

Example: but-1-ene (double bond between C1 and C2), but-2-ene (double bond between C2 and C3).

E.7.2 E/Z Geometry

When a double bond has two different groups on each carbon, it can exist as E or Z isomers.

Z (zusammen) — higher-priority groups on the same side of the double bond.

E (entgegen) — higher-priority groups on opposite sides.

Priority is assigned by atomic number (Cahn–Ingold–Prelog rules): higher atomic number = higher priority. When the attached atoms are the same, move outward along the chain until a difference is found.

Cis/trans is an older convention still used for simple cases: cis = same side, trans = opposite side. E/Z is unambiguous and applies to all cases.

E.8 Ring Systems

E.8.1 Cycloalkanes

Add the prefix **cyclo–** before the parent chain name.

Structure	Name
3-carbon ring	cyclopropane
4-carbon ring	cyclobutane
5-carbon ring	cyclopentane
6-carbon ring	cyclohexane

For substituted cycloalkanes, number the ring to give substituents the lowest locants. If one substituent is present, it is at C-1 (no locant needed).

E.8.2 Benzene

Benzene is named as its own parent. Monosubstituted benzenes are named as benzene derivatives (e.g., chlorobenzene, nitrobenzene). For disubstituted benzenes, three arrangements are possible:

- **ortho (o–)** — substituents at positions 1 and 2
- **meta (m–)** — substituents at positions 1 and 3
- **para (p–)** — substituents at positions 1 and 4

The ortho/meta/para prefix system is widely used alongside IUPAC locants.

When benzene is a substituent rather than the parent, it is named **phenyl–**.

E.9 Worked Examples

E.9.1 Example 1 — Aldehyde

Structure: $CH_3CH_2CH_2CHO$ (four-carbon chain, terminal aldehyde)

1. Principal functional group: aldehyde → suffix **-al**
2. Parent chain: 4 carbons → **but-**
3. Aldehyde carbon is C-1; no other substituents
4. **Name: butanal**

E.9.2 Example 2 — Alcohol with substituent

Structure: $CH_3CH(OH)CH_2CH_3$ (four-carbon chain, hydroxyl on C-2)

1. Principal functional group: alcohol → suffix **-ol**
2. Parent chain: 4 carbons → **but-**
3. Number from the end closest to the OH: hydroxyl at C-2
4. No other substituents
5. **Name: butan-2-ol**

E.9.3 Example 3 — Ketone

Structure: $CH_3COCH_2CH_2CH_3$ (five-carbon chain, carbonyl at C-2)

1. Principal functional group: ketone → suffix **-one**
2. Parent chain: 5 carbons → **pent-**
3. Number from the end closest to the carbonyl: C-2
4. **Name: pentan-2-one**

E.9.4 Example 4 — Alkene with substituent

Structure: $CH_3CH{=}C(CH_3)CH_2CH_3$ (five-carbon chain with a double bond and a methyl branch)

1. Principal functional group: alkene → suffix **-ene**
2. Parent chain: 5 carbons → **pent-**
3. Double bond at C-2 (lower locant from left end)
4. Methyl substituent at C-3
5. **Name: 3-methylpent-2-ene**

E.9.5 Example 5 — Carboxylic acid

Structure: CH_3CH_2COOH (three-carbon chain, carboxylic acid)

1. Principal functional group: carboxylic acid → suffix **-oic acid**
2. Parent chain: 3 carbons → **prop-**
3. Carboxyl carbon is C-1; no locant needed
4. **Name: propanoic acid**

E.10 Common Name ↔ IUPAC Name Table

Common Name	IUPAC Name	Functional Group
Formaldehyde	methanal	aldehyde
Acetaldehyde	ethanal	aldehyde
Acetone	propan-2-one	ketone
Acetic acid	ethanoic acid	carboxylic acid
Formic acid	methanoic acid	carboxylic acid
Propionic acid	propanoic acid	carboxylic acid
Butyric acid	butanoic acid	carboxylic acid
Ethanol	ethanol	alcohol
Isopropanol	propan-2-ol	alcohol
Glycerol	propane-1,2,3-triol	polyol
Chloroform	trichloromethane	haloalkane
Ethylene	ethene	alkene
Acetylene	ethyne	alkyne
Aniline	benzenamine (or aminobenzene)	amine
Toluene	methylbenzene	aromatic
Phenol	phenol	aromatic alcohol

E.11 A Note on Ambiguity

The IUPAC system is updated periodically, and two valid IUPAC names sometimes exist for the same compound (particularly for alcohols, where both propan-1-ol and 1-propanol appear in the literature). Either form is generally accepted in coursework unless an instructor specifies otherwise.

Common names remain in widespread use in industry, biochemistry, and pharmacology. Developing fluency with both systems is a practical skill that continues to matter well beyond the introductory course.

F. Recommended Resources

This appendix consolidates the resources referenced throughout the handbook into a single reference. All resources listed here are freely available online. No single resource is required — the goal is to provide options so that each reader can find the explanation style that works best for them.

F.1 Core Resources

F.1.1 Khan Academy — Organic Chemistry

Main page: khanacademy.org/science/organic-chemistry

Khan Academy provides structured video lessons covering most topics in Organic Chemistry I and II, as well as general chemistry review. The organic chemistry section is particularly strong on foundational topics including functional groups, resonance, acids and bases, and reaction mechanisms. Topics are organized into units with videos, articles, and practice exercises.

Best used for: Initial exposure to a topic, foundational concept review, and acid-base chemistry.

F.1.2 Organic Chemistry Tutor

YouTube channel: The Organic Chemistry Tutor

An extensive library of problem-focused videos covering nearly every topic in both semesters of organic chemistry. Particularly useful for worked examples and visual walkthroughs of mechanisms.

Best used for: Mechanism walkthroughs, SN1/SN2/E1/E2 comparisons, stereochemistry, and spectroscopy interpretation.

F.1.3 Professor Dave Explains

YouTube channel: Professor Dave Explains

Organic Chemistry playlist: Organic Chemistry — Professor Dave Explains

Clear, conversational explanations of organic chemistry topics in short videos. Strong coverage of nomenclature, functional groups, and spectroscopy.

Best used for: Quick introductions, nomenclature, NMR and IR fundamentals.

F.1.4 Master Organic Chemistry

Main page: masterorganicchemistry.com

A well-organized website designed specifically for organic chemistry students. Offers concise articles on most major topics, an extensive pKa table, and focused explanations of common problem areas. The articles go deeper than most videos and are especially strong on reasoning through mechanisms rather than memorizing them.

Best used for: Targeted topic review, pKa reference, understanding acidity trends, and troubleshooting difficult concepts.

F.1.5 LibreTexts Organic Chemistry

Main page: Organic Chemistry (Morsch et al.) — LibreTexts

A comprehensive open-access organic chemistry textbook. Useful as a primary reading source when a more thorough explanation is needed than a video provides. Covers the full two-semester sequence.

Best used for: In-depth reading on any topic, as a supplement to or replacement for a commercial textbook.

F.1.6 MIT OpenCourseWare — 5.12 Organic Chemistry I

Main page: MIT OCW 5.12 Organic Chemistry I
Lecture handouts: Lecture Handouts
Problem sets: Assignments
Exams: Exams
Free course materials from MIT's undergraduate organic chemistry sequence. Includes lecture notes, problem sets with solutions, and exams with answer keys.
Best used for: Practice problems, exam preparation, and seeing how an advanced course presents the material.

F.1.7 OpenStax Chemistry 2e

Main page: openstax.org/books/chemistry-2e
A comprehensive general chemistry textbook. Recommended specifically for the general chemistry review in Part II.
Best used for: Reviewing atomic structure, bonding, molecular geometry, hybridization, acids and bases, and equilibrium before the organic chemistry course begins.

F.2 Resources by Topic

F.2.1 General Chemistry Review

Topic	Recommended Resources
Atomic structure and periodic trends	OpenStax Ch. 6; Khan Academy — Atomic Structure
Chemical bonding	OpenStax Ch. 7; Khan Academy — Structure and Bonding
Lewis structures and formal charge	OpenStax Ch. 7; Khan Academy — Structure and Bonding
Molecular geometry (VSEPR)	OpenStax Ch. 7; Khan Academy — Structure and Bonding
Hybridization	OpenStax Ch. 8; Khan Academy — Structure and Bonding
Acids and bases, pKa	OpenStax Ch. 14; Khan Academy — Acids and Bases
Equilibrium	OpenStax Ch. 13; Khan Academy — Acids and Bases

F.2.2 Foundational Organic Chemistry

Topic	Recommended Resources
Functional groups	Khan Academy — Organic Chemistry; LibreTexts Ch. 3 — Alkanes and Functional Groups; Organic Chemistry Tutor
Resonance	Khan Academy — Resonance and Acid-Base; LibreTexts Ch. 2 — Resonance (§2.3–2.5); Master Organic Chemistry — Intro to Resonance; Master Organic Chemistry — Evaluating Resonance Structures

Topic	Recommended Resources
Acids and bases (organic)	Khan Academy — Resonance and Acid-Base; LibreTexts Ch. 2 — Polar Bonds and Acids/Bases
Stereochemistry and chirality	Khan Academy — Organic Chemistry; LibreTexts Ch. 5 — Stereochemistry; Organic Chemistry Tutor
Electron flow and curved arrows	Khan Academy — Resonance and Acid-Base; LibreTexts Ch. 6 — Overview of Organic Reactions

F.2.3 Reaction Mechanisms

Topic	Recommended Resources
Introduction to mechanisms	LibreTexts Ch. 6 — Overview of Organic Reactions; Organic Chemistry Tutor
SN1 and SN2 substitution	LibreTexts Ch. 11 — Substitution and Elimination; Master Organic Chemistry — SN1 vs. SN2; Organic Chemistry Tutor
E1 and E2 elimination	LibreTexts Ch. 11 — Substitution and Elimination; Organic Chemistry Tutor
Addition reactions	Khan Academy — Alkenes and Alkynes; LibreTexts Ch. 7 — Alkene Reactivity
Comparing SN1/SN2/E1/E2	Master Organic Chemistry — Deciding SN1/SN2/E1/E2: Substrate; Master Organic Chemistry — SN1/SN2/E1/E2 Wrapup

F.2.4 Carbonyl Chemistry

Topic	Recommended Resources
Aldehydes and ketones	LibreTexts Ch. 19 — Aldehydes and Ketones; Organic Chemistry Tutor
Carboxylic acids and derivatives	LibreTexts Ch. 20 — Carboxylic Acids; LibreTexts Ch. 21 — Acyl Substitution
Enols and enolates	LibreTexts Ch. 22 — Carbonyl Alpha-Substitution; Organic Chemistry Tutor
Aldol and Claisen reactions	LibreTexts Ch. 23 — Carbonyl Condensation; Organic Chemistry Tutor

F.2.5 Aromatic Chemistry

Topic	Recommended Resources
Aromaticity and benzene	Khan Academy — Aromatic Compounds; LibreTexts Ch. 15 — Benzene and Aromaticity; Professor Dave Explains
Electrophilic aromatic substitution	Khan Academy — Aromatic Compounds; LibreTexts Ch. 16 — EAS; Organic Chemistry Tutor

Topic	Recommended Resources
Substituent effects	Khan Academy — Aromatic Compounds; LibreTexts Ch. 16 — EAS

F.2.6 Spectroscopy

Topic	Recommended Resources
Infrared spectroscopy	LibreTexts Ch. 12 — MS and IR; Professor Dave Explains; Organic Chemistry Tutor
Proton NMR	LibreTexts Ch. 13 — NMR; Professor Dave Explains; Organic Chemistry Tutor
Carbon-13 NMR	LibreTexts Ch. 13 — NMR; Organic Chemistry Tutor
Mass spectrometry	LibreTexts Ch. 12 — MS and IR; Professor Dave Explains
Combined structure determination	MIT OCW — Exams; MIT OCW — Assignments

F.2.7 Synthesis

Topic	Recommended Resources
Retrosynthesis and multi-step synthesis	MIT OCW — Lecture Handouts; Organic Chemistry Tutor
Named reactions	Master Organic Chemistry; Organic Chemistry Tutor

F.3 Recommended Starting Points

If you are beginning the general chemistry review (Part II):

Start with Khan Academy — Structure and Bonding, then move to Khan Academy — Acids and Bases. Use OpenStax Ch. 6, Ch. 7, Ch. 8, Ch. 13, and Ch. 14 for reading.

If you are building foundational organic chemistry knowledge (Part III):

Start with Khan Academy — Resonance and Acid-Base Chemistry. Then read LibreTexts Ch. 1 and Ch. 2. The Master Organic Chemistry — Intro to Resonance article is especially useful for building intuition about resonance.

If you are working through reaction mechanisms (Part IV):

The Master Organic Chemistry — SN1/SN2/E1/E2 Wrapup is one of the clearest summaries available. Pair it with LibreTexts Ch. 11 for reading and the Organic Chemistry Tutor for worked examples.

If you are preparing for spectroscopy (Part VII):

Professor Dave Explains covers NMR and IR particularly well for students encountering these techniques for the first time. Pair with LibreTexts Ch. 12 (IR and MS) and Ch. 13 (NMR) for reading.

F.4 A Note on Using These Resources

No single resource covers everything perfectly.

Many students find it helpful to watch a video first to get an initial sense of a topic, then do some reading for depth, then return to the video after the reading has provided more context.

The resources listed here are all free and widely used. They are not the only good options — individual instructors, university libraries, and course materials may provide equally useful alternatives.

The goal is not to use all of these resources.

The goal is to find the combination that helps ideas become clear.

Glossary

Alphabetical reference of recurring terminology and conventions used throughout this guide. Terms are added the first time they're formally introduced in the text and checked for consistent usage (spelling, capitalization, phrasing) in later chapters.

Terms

Acetal — A carbon bonded to two alkoxy (–OR) groups, formed when a hemiacetal reacts with a second equivalent of alcohol; important in carbohydrate chemistry. *(Part V Ch. 12, Carbonyl Compounds and Nucleophilic Addition)*

Acid chloride — A carboxylic acid derivative with Cl in place of OH (–C(=O)Cl); the most reactive of the common carbonyl derivatives toward nucleophilic acyl substitution. *(Part V Ch. 13, Carboxylic Acids and Their Derivatives)*

Activating / deactivating group — A ring substituent that increases (activating) or decreases (deactivating) an aromatic ring's reactivity toward electrophiles by donating or withdrawing electron density via resonance or induction. *(Part VI Ch. 17, Substituent Effects and Aromatic Compounds)*

Acylium ion — A resonance-stabilized R–C≡O⁺ cation, the electrophile generated in Friedel-Crafts acylation. *(Appendix C, Reaction Summary Tables)*

Alcohol — A compound containing an O–H group bonded to a saturated carbon; capable of hydrogen bonding. *(Part III Ch. 1, Functional Groups)*

Aldehyde — A carbonyl compound with the C=O group at the end of a carbon chain, bonded to at least one hydrogen; reactive toward nucleophiles. *(Part III Ch. 1, Functional Groups)*

Aldol reaction — The addition of an enolate to a carbonyl compound, forming a new carbon-carbon bond and a β-hydroxy carbonyl product. *(Part V Ch. 14, Enols, Enolates, and Carbon-Carbon Bond Formation)*

Alkane — A hydrocarbon containing only single bonds; generally nonpolar and relatively unreactive. *(Part III Ch. 1, Functional Groups)*

Alkene — A hydrocarbon containing at least one carbon-carbon double bond. *(Part III Ch. 1, Functional Groups)*

Alkyl halide — A compound with a halogen (F, Cl, Br, I) bonded to an sp^3 carbon; the halogen is a good leaving group, making these the classic substrate for substitution and elimination. *(Appendix A, Functional Group Atlas; first used Part IV Ch. 7)*

Alkyne — A hydrocarbon containing at least one carbon-carbon triple bond. *(Part III Ch. 1, Functional Groups)*

Allylic — Describes a position adjacent to a carbon-carbon double bond; allylic carbocations and radicals are resonance-stabilized. *(Part III Ch. 2, Resonance)*

Alpha (α) proton / position — A hydrogen (or carbon) directly adjacent to a carbonyl group; alpha protons are unusually acidic because their removal produces a resonance-stabilized enolate. *(Part V Ch. 14, Enols, Enolates, and Carbon-Carbon Bond Formation)*

Amide — A compound containing a carbonyl bonded to a nitrogen (–C(=O)–N–); forms the peptide bond in proteins. *(Part III Ch. 1, Functional Groups)*

Amine — An organic base containing nitrogen. *(Part III Ch. 1, Functional Groups)*

Anhydride — A carboxylic acid derivative formed from two acyl groups joined by an oxygen (–C(=O)–O–C(=O)–); more reactive than esters or amides toward nucleophilic acyl substitution. *(Part V Ch. 13, Carboxylic Acids and Their Derivatives)*

Anti-periplanar — A geometry in which two groups (the leaving group and the departing hydrogen in E2) are positioned on opposite sides of the molecule in the same plane; required for E2 elimination. *(Part IV Ch. 8, Elimination Reactions)*

Arene — An aromatic ring system (e.g., benzene); resists addition and undergoes electrophilic aromatic substitution instead. *(Appendix A, Functional Group Atlas)*

Aromaticity — The unusual stability of certain cyclic, planar, fully conjugated systems (like benzene) arising from complete electron delocalization; requires satisfying Hückel's rule. *(Part VI Ch. 15, Benzene and Aromaticity)*

ARIO — A mnemonic for ranking acid strength by conjugate-base stability: Atom (electronegativity/size), Resonance, Induction, Orbital (hybridization). *(Part III Ch. 3, Acids and Bases)*

Axial — A substituent position on a cyclohexane chair that points perpendicular to the ring's average plane, alternating up and down around the ring. *(Part III Ch. 4, Stereochemistry)*

Brønsted-Lowry acid/base — An acid is a proton donor; a base is a proton acceptor. The definition organic chemistry uses almost exclusively. *(Part II, Acids and Bases)*

Cahn-Ingold-Prelog (CIP) rules — The priority system (by atomic number, then outward along the chain) used to rank substituents for both R/S stereocenter and E/Z double-bond nomenclature. *(Appendix E, IUPAC Nomenclature Reference)*

Carbanion — A carbon bearing a negative charge and a lone pair, typically with three bonds. *(Part IV Ch. 6, Introduction to Mechanisms)*

Carbocation — A carbon bearing a positive charge and only three bonds; stability increases with resonance delocalization and alkyl substitution. *(Part III Ch. 2, Resonance)*

Carboxylic acid — A compound containing both a carbonyl and a hydroxyl group on the same carbon (–COOH); relatively acidic. *(Part III Ch. 1, Functional Groups)*

Chair conformation — The lowest-energy three-dimensional shape of cyclohexane, in which every bond angle is near 109.5° and every neighboring pair of hydrogens is staggered. *(Part III Ch. 4, Stereochemistry)*

Chemical shift — The position (in ppm) at which a nucleus resonates in an NMR spectrum, reflecting its electronic environment (shielding/deshielding). *(Part VII Ch. 19, Nuclear Magnetic Resonance Spectroscopy)*

Chirality — The property of an object (or molecule) that is not superimposable on its mirror image. *(Part III Ch. 4, Stereochemistry)*

Claisen condensation — The reaction of an ester enolate with another ester, forming a new carbon-carbon bond and a β-keto ester product. *(Part V Ch. 14, Enols, Enolates, and Carbon-Carbon Bond Formation)*

Conformation — A three-dimensional shape a molecule adopts through bond rotation, without breaking any bonds; conformations interconvert freely and are distinct from configurations. *(Part III Ch. 4, Stereochemistry)*

Conjugate acid / conjugate base — The species formed when an acid loses a proton (conjugate base) or a base gains one (conjugate acid). *(Part II, Acids and Bases)*

Conjugation — An arrangement of alternating multiple and single bonds (or a lone pair/charge adjacent to a π bond) that allows electron delocalization. *(Part III Ch. 2, Resonance)*

Coupling constant (J) — The frequency spacing (in Hz) between split peaks in an NMR signal, reflecting the geometric relationship between coupled protons (e.g., larger for trans-alkene protons than cis). *(Appendix D, Spectroscopy Reference)*

Curved arrow — The notation organic chemists use to show electron movement (not atom movement) during a reaction. *(Part III Ch. 5, Electron Flow)*

Delocalization — The spreading of electron density over multiple atoms rather than concentrating it on one, which generally increases stability. *(Part III Ch. 2, Resonance)*

Diastereomer — A stereoisomer that is not a mirror image of another stereoisomer. *(Part III Ch. 4, Stereochemistry)*

Diaxial interaction (1,3-) — Steric strain between an axial substituent and the axial hydrogens two carbons away on the same face of a cyclohexane chair; grows with substituent size and disfavors the axial position. *(Part III Ch. 4, Stereochemistry)*

Electronegativity — An atom's tendency to attract shared electrons in a bond; increases across a period and up a group. *(Part II, Atomic Structure and Periodic Trends)*

Electrophile — An electron-poor atom or molecule that accepts an electron pair to form a new bond (e.g., carbocations, positively charged or polarized species). *(Part III Ch. 5, Electron Flow)*

Electrophilic aromatic substitution (EAS) — The reaction pattern by which aromatic rings react: an electrophile attacks the ring, aromaticity is temporarily lost, then restored by loss of a proton; includes halogenation, nitration, sulfonation, and Friedel-Crafts reactions. *(Part VI Ch. 16, Electrophilic Aromatic Substitution)*

E/Z nomenclature — The unambiguous system for naming double-bond geometry: Z (zusammen) means the two higher-priority groups are on the same side, E (entgegen) means opposite sides; priority assigned by CIP rules. *(Appendix E, IUPAC Nomenclature Reference)*

E1 / E2 — The two dominant elimination mechanisms: E2 is a one-step, concerted removal of a proton and a leaving group requiring anti-periplanar geometry, favored by strong bases; E1 is a two-step mechanism proceeding through a carbocation intermediate (shares substrate/solvent preferences with SN1), favored by weak bases and prone to rearrangement. *(Part IV Ch. 8, Elimination Reactions)*

Enantiomer — A mirror-image stereoisomer of a chiral molecule. *(Part III Ch. 4, Stereochemistry)*

Enol / Enolate — A tautomer of a carbonyl compound with a C=C–OH group (enol), or its deprotonated, resonance-stabilized conjugate base (enolate) formed by removing an alpha proton; enolates act as powerful nucleophiles. *(Part V Ch. 14, Enols, Enolates, and Carbon-Carbon Bond Formation)*

Equatorial — A substituent position on a cyclohexane chair that points roughly in the plane of the ring, outward; generally preferred over axial for larger substituents. *(Part III Ch. 4, Stereochemistry)*

Equilibrium constant (Ka) — A numerical measure of the position of equilibrium for a reversible reaction; for acids, related to pKa by pKa = −log(Ka). *(Part II, Equilibrium)*

Ester — A compound containing a carbonyl bonded to an alkoxy group (–C(=O)–O–); common in fats and lipids. *(Part III Ch. 1, Functional Groups)*

Ether — A compound containing an oxygen atom bonded between two carbon groups; less reactive than alcohols. *(Part III Ch. 1, Functional Groups)*

Formal charge — The charge an atom would have if bonding electrons were shared equally; calculated from valence electrons, lone pair electrons, and bonds. *(Part II, Lewis Structures)*

Fragmentation — The breaking apart of a molecular ion into smaller charged and neutral pieces inside a mass spectrometer, producing a pattern of peaks that helps reveal structure. *(Part VII Ch. 20, Mass Spectrometry and Structure Determination)*

Friedel-Crafts reaction — An electrophilic aromatic substitution that forms a new carbon-carbon bond to the ring (alkylation or acylation). *(Part VI Ch. 16, Electrophilic Aromatic Substitution)*

Functional group — A recurring arrangement of atoms that determines a molecule's characteristic physical and chemical behavior. *(Part III Ch. 1, Functional Groups)*

Halonium ion — A bridged, three-membered cyclic cation formed when X_2 adds to an alkene; forces the second halogen to attack from the opposite face, giving anti addition. *(Appendix C, Reaction Summary Tables)*

Hemiacetal — A carbon bonded to both an –OH and an –OR group, formed by addition of one equivalent of alcohol to a carbonyl; an intermediate on the way to an acetal. *(Part V Ch. 12, Carbonyl Compounds and Nucleophilic Addition)*

Heterocycle — A cyclic compound containing at least one ring atom other than carbon, most often nitrogen, oxygen, or sulfur. *(Part VI Ch. 17, Substituent Effects and Aromatic Compounds)*

Hückel's rule — A cyclic, planar, fully conjugated system is aromatic when it contains $4n+2$ π electrons, where n = 0, 1, 2, 3, and so on (giving 2, 6, 10, 14 π electrons). *(Part VI Ch. 15, Benzene and Aromaticity)*

Hybridization (sp^3, sp^2, sp) — The mixing of atomic orbitals that determines a carbon's geometry: sp^3 is tetrahedral, sp^2 is trigonal planar, sp is linear. *(Part II, Hybridization)*

Hyperconjugation — The stabilizing donation of electron density from an adjacent sigma bond (e.g., C–H) into an empty or partially empty orbital, such as a carbocation or an aromatic ring. *(Part VI Ch. 17, Substituent Effects and Aromatic Compounds)*

Inductive effect — The stabilizing or destabilizing pull on electron density through sigma bonds caused by a nearby electronegative atom or electron-withdrawing group. *(Part III Ch. 3, Acids and Bases)*

Infrared (IR) spectroscopy — A technique that identifies functional groups from characteristic bond-vibration absorptions, typically reported by wavenumber. *(Part VII Ch. 18, Infrared Spectroscopy and Functional Group Identification)*

Integration (NMR) — The relative area under an NMR signal, proportional to the number of equivalent nuclei producing it. *(Part VII Ch. 19, Nuclear Magnetic Resonance Spectroscopy)*

Intermediate — A temporary, often unstable species (e.g., a carbocation, carbanion, or radical) formed partway through a reaction mechanism before the final product. *(Part IV Ch. 6, Introduction to Mechanisms)*

Inversion (Walden inversion) — The flip in stereochemical configuration at a reaction center, characteristic of SN2 backside attack. *(Part IV Ch. 7, Substitution Reactions)*

IUPAC nomenclature — The systematic naming system built from a parent chain (longest continuous carbon chain), a suffix (signaling the principal functional group), and prefixes/locants (identifying substituents and their positions). *(Part III Ch. 1, Functional Groups)*

Keto-enol tautomerism — The equilibrium between a carbonyl compound (keto form) and its enol form, which differ in the position of a proton and a double bond; the keto form is usually favored. *(Part V Ch. 14, Enols, Enolates, and Carbon-Carbon Bond Formation)*

Ketone — A carbonyl compound with the C=O group bonded to two carbons within a chain (not terminal). *(Part III Ch. 1, Functional Groups)*

LDA (lithium diisopropylamide) — A strong, sterically hindered, non-nucleophilic base used to cleanly deprotonate a carbonyl's alpha-carbon to form an enolate without competing as a nucleophile. *(Appendix C, Reaction Summary Tables)*

Le Châtelier's principle — A system at equilibrium shifts in a predictable direction in response to a change in reactant/product concentration, temperature, or pressure. *(Part II, Equilibrium)*

Leaving group — An atom or group of atoms that departs from a molecule during a reaction, taking a bonding pair of electrons with it; better leaving groups stabilize that negative charge more effectively. *(Part IV Ch. 6, Introduction to Mechanisms)*

Lewis structure — A diagram showing an atom's or molecule's valence electrons as bonds and lone pairs. *(Part II, Lewis Structures)*

Locant — A number or descriptor (e.g., R/S) identifying the position of a substituent or stereocenter on a parent chain. *(Part III Ch. 1, Functional Groups)*

Markovnikov's rule — In addition of HX (or similar) to an unsymmetrical alkene, the electrophile adds to give the more stable (more substituted) carbocation intermediate, predicting the major product. *(Part IV Ch. 9, Addition Reactions)*

Mass spectrometry — A technique that ionizes and fragments a molecule to reveal its molecular weight, isotopic pattern, and characteristic fragment losses. *(Part VII Ch. 20, Mass Spectrometry and Structure Determination)*

Meta director — A ring substituent (typically electron-withdrawing with a positive or partial-positive atom adjacent to the ring) that directs electrophilic aromatic substitution to the meta position, avoiding destabilizing charge buildup at ortho/para. *(Part VI Ch. 17, Substituent Effects and Aromatic Compounds)*

Molecular ion (M^+) — The peak in a mass spectrum corresponding to the intact, ionized starting molecule, before fragmentation; its mass gives the molecular weight. *(Part VII Ch. 20, Mass Spectrometry and Structure Determination)*

n+1 rule — In ^{1}H NMR, a proton with n neighboring protons that are equivalent to each other (but non-equivalent to the observed proton) is split into n+1 peaks; neighbors split into more than one non-equivalent set produce a more complex multiplet instead. *(Appendix D, Spectroscopy Reference; first introduced Part VII Ch. 19)*

Nuclear magnetic resonance (NMR) spectroscopy — A technique that reveals molecular structure from the chemical shift, integration, and splitting pattern of individual atomic environments (commonly ^{1}H and ^{13}C). *(Part VII Ch. 19, Nuclear Magnetic Resonance Spectroscopy)*

Nucleophile — An electron-rich atom or molecule that donates an electron pair to form a new bond (e.g., hydroxide, water, ammonia). *(Part III Ch. 5, Electron Flow; first mentioned Part II, Molecular Geometry)*

Nucleophilic acyl substitution — The mechanism by which carboxylic acid derivatives react: nucleophilic attack at the carbonyl carbon, formation of a tetrahedral intermediate, then departure of a leaving group restores the carbonyl. Relative reactivity follows leaving-group ability: acid chlorides > anhydrides > esters > amides. *(Part V Ch. 13, Carboxylic Acids and Their Derivatives)*

Ortho/para director — A ring substituent that directs electrophilic aromatic substitution to the ortho and para positions, typically by donating electron density (by resonance or, for halogens, despite net-withdrawing induction) into those positions. *(Part VI Ch. 17, Substituent Effects and Aromatic Compounds)*

pKa — The negative log of the acid dissociation constant (Ka); lower pKa indicates a stronger acid. *(Part II, Acids and Bases)*

pKaH — The pKa of a base's conjugate acid, used to report basicity indirectly; a higher pKaH means a stronger base. *(Appendix B, pKa Tables)*

Pi (π) bond — A bond formed from side-on overlap of unhybridized p orbitals; found in double and triple bonds and more reactive than sigma bonds. *(Part II, Chemical Bonding)*

Polar protic / polar aprotic solvent — Protic solvents (e.g., water, alcohols) have an O–H or N–H bond and favor SN1 by stabilizing cations and leaving groups through hydrogen bonding; aprotic solvents (e.g., acetone, DMSO) lack that bond and favor SN2 by leaving the nucleophile more reactive. *(Part IV Ch. 7, Substitution Reactions)*

Protecting group — A group temporarily added to block one reactive site on a molecule so a reaction can be carried out selectively elsewhere, then removed afterward. *(Part VIII Ch. 22, Named Reactions and Protecting Groups)*

Racemization — The formation of a racemic (1:1 enantiomer) mixture, typical of SN1 reactions where a planar carbocation intermediate is attacked from either face; real SN1 reactions often give partial rather than complete racemization, since ion pairing can bias attack toward one face. *(Part IV Ch. 7, Substitution Reactions)*

Radical — A species with an unpaired electron, formed when a bond breaks homolytically. *(Part IV Ch. 6, Introduction to Mechanisms)*

Regiochemistry — The question of which position on a molecule a reaction occurs at, distinct from stereochemistry (which spatial arrangement results) and connectivity (which atoms are bonded). *(Part IV Ch. 9, Addition Reactions)*

Resonance — The use of multiple valid Lewis structures ("resonance structures" or "contributors") that differ only in electron placement to represent a single molecule's true electron distribution (the "resonance hybrid"); delocalization generally increases stability. *(Part III Ch. 2, Resonance; first mentioned Part II, Medium Priority)*

Retrosynthesis — A planning strategy that works backward from a target molecule, breaking it into simpler precursors by asking "how might this be constructed?" rather than "what would this produce?" *(Part VIII Ch. 21, Retrosynthesis and Multi-Step Synthesis)*

Ring flip — The interconversion of one cyclohexane chair into another via bond rotation, which swaps every axial position for equatorial (and vice versa) without breaking bonds or changing configuration. *(Part III Ch. 4, Stereochemistry)*

Shielding / deshielding — The degree to which nearby electron density shields (upfield shift) or exposes (downfield/deshielded shift) a nucleus from an applied magnetic field, determining its chemical shift. *(Part VII Ch. 19, Nuclear Magnetic Resonance Spectroscopy)*

Sigma (σ) bond — A bond formed from head-on orbital overlap; forms the single-bond backbone of every organic molecule. *(Part II, Chemical Bonding)*

SN1 / SN2 — The two dominant substitution mechanisms: SN2 is a one-step, concerted backside attack favored by strong nucleophiles and unhindered substrates (inversion of configuration); SN1 is a two-step mechanism proceeding through a carbocation intermediate, favored by stable cations and polar protic solvents (racemization). *(Part IV Ch. 7, Substitution Reactions)*

Splitting pattern — The division of an NMR signal into multiple peaks caused by coupling with neighboring, non-equivalent hydrogens. *(Part VII Ch. 19, Nuclear Magnetic Resonance Spectroscopy)*

Stereocenter — An atom (usually carbon) whose four different substituents give it two non-superimposable spatial arrangements, described by R/S configuration. *(Part III Ch. 4, Stereochemistry)*

Steric effects (steric strain) — Repulsive interactions between atoms or groups in close spatial proximity that raise energy and disfavor certain conformations, geometries, or reaction pathways. *(Part IV Overview, Mechanistic Thinking)*

Tetrahedral intermediate — The sp^3 carbon species formed when a nucleophile adds to a carbonyl carbon, before a leaving group departs (in substitution) or a proton transfer restores neutrality (in addition). *(Part V Ch. 13, Carboxylic Acids and Their Derivatives)*

Valence electrons — The electrons in an atom's outermost shell, responsible for bonding. *(Part II, Atomic Structure and Periodic Trends)*

VSEPR theory — Valence Shell Electron Pair Repulsion; predicts molecular geometry from the number of bonding and lone electron pairs around a central atom. *(Part II, Molecular Geometry)*

Wavenumber — The unit (cm^{-1}) used to report absorption position in an IR spectrum; proportional to vibrational frequency. *(Part VII Ch. 18, Infrared Spectroscopy and Functional Group Identification)*

Zaitsev product — The more substituted (generally more stable) alkene formed as the major product of an elimination reaction, favored except when a bulky base is used. *(Appendix C, Reaction Summary Tables)*

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