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Keep Calm and Learn O-Chem

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KEEP CALM AND LEARN O-CHEM

An illustrated survivor's manual by Hope Spargo
“It’s the end of the world as we know it.”

-R.E.M.
To Dr. Vyvyan

For showing me the stories behind the chemistry,
and patience in the face of ungainly learning curves.

To Mom

For library cards and paint sets,
and responding to “I can’t do it” with a calendar.
Introduction

This is it. The impossible task. The subject you’ve been told will simultaneously wreck your GPA, your home life, and your sanity. Cold. Merciless. Unforgiving. The subject between you and your future.

Organic chemistry.

Hold up.

This subject is not bent on destroying everything perfect and good in life. It is not malicious. It’s a science, and it does some pretty amazing things in the realms of medicine, agriculture, and materials development, to name a few. O-chem is responsible for both mild delights (like aspirin for headaches, fancy Tupperware, and not-boring colored fabrics) and modern miracles (like chemotherapy and biologically compatible prosthetics).

And it’s a totally learnable subject. It’s true; there’s a lot of content and some spatial gymnastics, but it’s not fundamentally inaccessible material.

There’s a misconception that the people who “get” organic chemistry are somehow different from the average person. Nobody emerges from the womb as an “o-chem person”; it takes work. Learning organic chemistry is like learning a new language. There are unique symbols, terms, and rules. Like language, it also has an underlying logic and structure. It would be dishonest to approach this subject with the expectation that there’s a quick way to achieve mastery; just like learning to speak a new language, learning o-chem takes deliberate practice and time.

But it can be done.

My hope is that this book will serve as an accessible means to lower the activation energy barrier between those approaching organic chemistry for the first time and personal competence with the subject. It features illustrations and metaphors I’ve found helpful in my own struggles with the material. Starting with “Why?” (Why study this, why is it named that, why does it work that way, etc.) sets the investigative stage for understanding o-chem. The feeling that everything is rote memorization is a red flag. Taking the initial time to master why something works establishes a logical foundation for the rest of one’s studies.

You’ve got this.

Cheers,
Hope Valentine Spargo
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Chapter 1
Know thy enemy.

What’s o-chem?

In a nutshell, organic chemistry (o-chem) is how much fun you can have with carbon.

And its friends.

And, if you’re into organometallic chemistry, its really fancy friends.

Where can carbon be found?

• In pretty much every living thing
  
  *Every biological macromolecule contains carbon.*
  
  DNA and RNA? ✓
  Carbohydrates? ✓
  Proteins? ✓
  Fats? ✓

• In every delicious (and not-so-delicious) thing
  
  Sugar ✓
  Alcohol ✓
  Aroma-compounds ✓

  *(Responsible for the flavors and smells of food.)*

• In medications
• In fertilizers and pesticides
• In polymers and plastics
<table>
<thead>
<tr>
<th><strong>What do people do with o-chem?</strong></th>
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<tbody>
<tr>
<td><strong>Medicine</strong></td>
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<tr>
<td>Most of our physiology can be understood through the lens of organic chemistry. It’s a useful way to look at the onset of disease, and how to develop treatments for it.</td>
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<td><strong>Research</strong></td>
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<tr>
<td>This seems like low-hanging fruit, but within organic chemistry research there’s natural product discovery and synthesis, organometallic catalysis, novel reactions, drug development, nanostructure assembly, electrochemistry, polymer chemistry, and more.</td>
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<tr>
<td><strong>Materials Development</strong></td>
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<tr>
<td>Do you like water bottles, being able to glue things together, and buildings with structural integrity? Thank an organic chemist.</td>
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<tr>
<td><strong>Environmental Science</strong></td>
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<tr>
<td>Many environmental contaminants are organic molecules. Their identity and impact can be assessed with organic chemistry.</td>
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<td><strong>Fuel Production</strong></td>
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<tr>
<td><strong>Cooking</strong></td>
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<tr>
<td>Why does meat brown when cooked? How do eggs go from transparent and jiggly to opaque and solid? What is it about spices that make them smell wonderful? O-chem has answers.</td>
</tr>
<tr>
<td><strong>Brewing</strong></td>
</tr>
<tr>
<td>The flavors of the malt and hops. The varying complexity of the sugars. The reactions responsible for turning said sugars into alcohol and CO₂ bubbles.</td>
</tr>
</tbody>
</table>

*Thanks, o-chem.*
What Organic Chemistry is Not

- Out to get you
- Inherently evil
- Useless
- Impossible to understand
- “Just memorization”

Study Tips

A lot of this book focuses on the basics. When you do get to reactions,

- Figure out the mechanism
- Make sure you can explain why it works
- If it feels like too much memorization, stop.
  
  Breathe.

  Identify the role of each reagent. Including solvent.
  Ask yourself what the reaction fundamentals are.
- If you don’t know, go back to the basics.
- Ask questions.
  
  Sooner rather than later.

Let’s do this.
Rule #1: Organic chemists are lazy.

...You mean to say that this caterpillar is symbolically the same as this zig-zag?

This is caffeine.

Beautiful.
Bodacious.
Bummer to draw.

This, also, is caffeine.

Simple.
Sleek.
So much faster.

These svelte little *skeletal structures* are the most efficient way to draw a molecule.

For Carbon:
- Every angle and the end of every line represents a carbon atom.
- Assume carbon has 4 bonds *(Unless charge is denoted).*
- If a bond isn’t explicitly drawn, assume hydrogen has you covered.

For everything else:
- Double-bonds look like this. 
- Triple-bonds look like this.
- Lable all other *heteroatoms* (non-carbon or carbon-bound hydrogen atoms)

Examples

What’s up with wedges & dashes?

**Wedge:** Indicates an atom is coming “out of the page” towards you. Like an aggressive comic book.

**Dash:** Indicates an atom is going “into the page” away from you. Like a receding echo.

Common Abbreviations

R = Any *alkyl* group
(Contains at least one carbon)

X = Any *halogen*
(F, Cl, Br, I, etc.)

...So lazy.
Woah.

WOAH.

What are quantum mechanics doing in an organic chemistry book?

Surely the subject is evil enough without introducing particle physics. It’s okay; this is general chemistry with a few more balloon-animals and a lot cooler reactions.

**WHY IT MATTERS**

*Knowing the secret lives of electrons makes it easier to predict ...*

- What bonds they’ll form
- What shape they’ll be
- How they may react

**SECTION TOPICS**

- Electrons: Codependent, yet repulsed by one another
- Orbital Shapes = Electron Homes
- O-chem Fraternity σ π: Bond types
- Electronegativity never goes away

**THROWBACK: General Chemistry and Physics**

Electrons, like planets and nosy parents, orbit around a focal point. These orbitals can have different shapes, like different rooms in a house. Both electrons and nosy parents are very particular about who they associate with and where they hang out. Here are their guiding rules:

1. **Pauli Exclusion Principle**
   *No more than two electrons can occupy a single orbital. Two electrons in the same orbital must have opposite spins.*

2. **Aufbau Principle**
   *Each successive electron must fill the lowest energy orbital available.*

3. **Hund’s Rule**
   *All orbitals at the same energy must contain a single electron before a second electron can be paired in the same orbital.*

Electrons have both wave and particle behavior. When electron waves add constructively, a covalent bond is formed.

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**Constructive Covalent**

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**Destructive Demise**
SHELLS
Okay, Aufbau. How are these orbital-energies organized? Into shells. Shells can be thought of as sets of increasingly elaborate homes for a molecule’s electrons. They’re organized by principal quantum number, \( n \). \( n \) can theoretically be any whole number from 1 to \( \infty \). In organic chemistry, we mostly care about the first 3.

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<tr>
<th>Shell</th>
<th>Orbitals Within Shell</th>
<th>Housing Equivalent</th>
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<tr>
<td>( n = 1 )</td>
<td>( s ) (1s)</td>
<td>Dorm Room</td>
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<tr>
<td>( n = 2 )</td>
<td>( s, p ) (2s, 2p(_x), 2p(_y), 2p(_z))</td>
<td>Regular House</td>
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<tr>
<td>( n = 3 )</td>
<td>( s, p, d ) (3s, 3p(<em>x), 3p(<em>y), 3p(<em>z), 3d(</em>{x^2-y^2}), 3d(</em>{xz}), 3d(</em>{yz}), 3d(_{xy}))</td>
<td>Victorian Mansion</td>
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ORBIALS
An orbital is the most probable location you can find an electron. In organic chemistry, we mostly deal with \( s \) and \( p \) orbitals. Fortunately, these have predictable shapes.

**S**
S orbitals are spherical, and can hold up to 2 electrons.

**P**
P orbitals are dumbell-shaped, and can hold up to 6 electrons. Subscripts indicate which 3D axis they’re on.

When Electrons Move In
Electrons occupy orbitals according to the rules on the preceding page.

“This is terrible. What does this have to do with o-chem?”

Well...
Bonding Patterns

These are the most common neutral hydrogen, carbon, nitrogen, oxygen, and halogen bonding patterns you’ll see in o-chem.

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Patterns

- Hydrogen has 1 bond
- Carbon has 4 bonds
- Nitrogen has 3 bonds and 1 lone-pair
- Oxygen has 2 bonds and 2 lone-pairs
- Halogens have 1 bond and 3 lone-pairs

Why is this, and what does it have to do with the nonsense on the previous page?

These are the orbital diagrams of our favorite atoms. The atoms will form as many bonds as it takes to fill their highest occupied shell. You may have previously encountered this as the octet rule. Every lone-pair comes from a pre-filled orbital.

Electrons are like co-dependent parents dealing with empty-nest syndrome. They don’t want to be by themselves, and they don’t like empty rooms in the house.
“But you promised balloon-animals...”
Yes. Here they are. Welcome to the whimsical world of

Hybrid Orbitals

S and p orbitals are pretty cute on their own, but like an obnoxiously adorable power-couple, they can do even more together. **Hybridization** of s and p orbitals also creates some interesting shapes. **Knowing common hybrid-orbital shapes is essential for visualizing organic reactions.**

**sp**¹
Linear
**Bonds between sp**¹ hybridized atoms form straight lines.
**Example:** Acetylene

**sp**²
Planar
**Bonds between sp**² hybridized atoms form flat planes.
**Example:** Ethylene

**sp**³
Tetrahedral
**sp**³ hybrid orbitals form the 4 corners of a pyramid.
**Example:** Methane

**Bonds Types and Fraternities:** σ π

**Sigma (σ) bonds** are formed when sp orbitals constructively overlap with other sp or s orbitals.

**Pi (π) bonds** are formed when p orbitals constructively overlap with other p orbitals.

- One covalent bond between atoms will always be a sigma bond.
- Additional double or triple bonds are pi bonds.
- Sigma bonds can freely rotate.
- Pi bonds are fixed in place to maintain their p orbital overlaps.
Electronegativity never goes away.

Remember this?

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**Electronegativity** can be thought of as how badly an atom wants electrons. The higher its electronegativity (the numbers on the table), the more it pulls electrons towards itself.

**Why do we care?**

Electronegativity has a huge impact on reactivity. Amongst other things, it determines:

1. **Polarity**
   
   If net electronegativity differences don’t cancel out, the molecule has a *dipole*. The larger the dipole moment, the greater the polarity. This in turn impacts...
   
   - Solubility
     
     *(making some solvents more appropriate than others)*
   
   - How one molecule can approach another
     
     *(determines which reactions can proceed)*

2. **Bond Strength**
   
   How tightly electrons are sandwiched between nuclei impacts...
   
   - How much energy is required to break a bond
   
   - How good a leaving group is
   
   - How acidic a proton can be
Chapter 3

Don’t name it; you’ll get attached

(3E)-4-ethyl-5-(1,1-dimethylethyl)non-3-en-7-yneoyl chloride

Ew. What is that? **Nomenclature**, the naming of things, is one of the wonkiest things about organic chemistry.

**IUPAC**

Chemicals often have informal and IUPAC names. The latter is established by the *International Union of Pure and Applied Chemistry*. Consistent nomenclature keeps scientists around the world on the same page.

It’s gross. But it’s useful.

**Section Topics**

- Nosy bankers and numbering carbons
- Main chain
- Side chains
- Functional groups
  - Identity
  - Priority

**Rule #2: Everything is cooler with a secret code**

There’s a lot to IUPAC nomenclature. To minimize suffering, pretend you’re not someone with a social life, but actually a **nosy, impatient banker**.

**Carbon = Currency**

**Functional Groups = Assets**

**As a super nosy banker, you want to know**

1. How much $ is in the primary account.
2. If there are any additional accounts, and if so,
   - How much $ is in them
   - Where are they
   - How many
3. If there are any assets
   - How many
   - How valuable are they
   - Where are they
Part 1
The Primary Account

If carbon is our currency, then the longest consecutive chain of carbons belong to the primary account. More formally, this is called the parent hydrocarbon chain.

Mr. Banker-man has a list of names for different size accounts.

<table>
<thead>
<tr>
<th>Name</th>
<th>Number of Carbons</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>1</td>
<td>CH₄</td>
</tr>
<tr>
<td>Ethane</td>
<td>2</td>
<td>H₃C-CH₃</td>
</tr>
<tr>
<td>Propane</td>
<td>3</td>
<td>H₃C-CH₂-CH₃</td>
</tr>
<tr>
<td>Butane</td>
<td>4</td>
<td>H₃C-CH₂-CH₂-CH₃</td>
</tr>
<tr>
<td>Pentane</td>
<td>5</td>
<td>H₃C-(CH₂)₃-CH₃</td>
</tr>
<tr>
<td>Hexane</td>
<td>6</td>
<td>H₃C-(CH₂)₄-CH₃</td>
</tr>
<tr>
<td>Heptane</td>
<td>7</td>
<td>H₃C-(CH₂)₅-CH₃</td>
</tr>
<tr>
<td>Octane</td>
<td>8</td>
<td>H₃C-(CH₂)₆-CH₃</td>
</tr>
<tr>
<td>Nonane</td>
<td>9</td>
<td>H₃C-(CH₂)₇-CH₃</td>
</tr>
<tr>
<td>Decane</td>
<td>10</td>
<td>H₃C-(CH₂)₈-CH₃</td>
</tr>
</tbody>
</table>

Important prefixes: Where Mr. Banker-man got lazy.

But what about double and triple bonds?

The “ane” at the end of the name only works for single-bonds. Double and triple bonds also have their own suffix.

<table>
<thead>
<tr>
<th>Name</th>
<th>Bond Type</th>
<th>Suffix Mnemonics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkane</td>
<td>Single</td>
<td>1 “a”: 1 bond</td>
</tr>
<tr>
<td></td>
<td>Double</td>
<td>2 “e”s: 2 bonds</td>
</tr>
<tr>
<td></td>
<td>Triple</td>
<td>3 points on “y”: 3 bonds</td>
</tr>
</tbody>
</table>

Ethane   Butene   Propyne

What about when there's multiple double and triple bonds?

Get stoked for prefixes and carbon-numbering...
Multiple bonds, multiple problems

Mr. Banker-man was doing well. He knew how many carbons were in the accounts. He knew what to do when there was a wonky bond. Then he encountered:

\[ \text{buta-1,3-diene} \]

He recognized the \textit{buta} prefix: 4 carbons. He recognized the \textit{ene} suffix: double bonds. But where did the "di" come from? And why were there numbers? He hated math!

Prefixes show how many of a certain feature there are.

Had there been 3 double bonds, Mr. Banker man would have called the molecule a \textit{triene}. He decided not to use the \textit{mono} prefix; it seemed redundant...

<table>
<thead>
<tr>
<th>Prefix</th>
<th>Number of Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mono</td>
<td>1</td>
</tr>
<tr>
<td>Di</td>
<td>2</td>
</tr>
<tr>
<td>Tri</td>
<td>3</td>
</tr>
<tr>
<td>Tetra</td>
<td>4</td>
</tr>
<tr>
<td>Penta</td>
<td>5</td>
</tr>
</tbody>
</table>

*From \textit{penta} on, the prefixes are the same as those for numbering the parent hydrocarbon chain.*

Locant: The location of a functional group.
Isomers: Molecules with the same formula, but different atomic arrangements.
Priority: The substituent (things attached to the carbon you’re focusing on) with the highest priority has the highest atomic number. If there are two atoms with the same identity bound to the carbon, go on to the next bond (and so on) until a difference is found. If the substituents are identical, they have the same priority.

Multiple bond types: Complex customers

All Mr. Banker-man wanted to do was assign accounts based on carbon number, maybe with a handful of double-bonds thrown in. He decided to put the number issue out of his mind. All was well, until an unsettling account made its way to his desk:

\[ (2E,6Z)\text{-dec-2,6-dien-4-yne} \]

He could no longer ignore the numbers. 

Alas.
Numbering the chain

Fortunately, once the main chain has been identified, there's only two numbering options:

Left to right
or
Right to left

*The chain should be numbered to have the smallest possible locant sum.*

Mr. Banker-man tried numbering the molecule both ways.

![Numbering examples](image)

Then he added them.

\[
\begin{align*}
2 + 6 + 4 &= 12 \\
4 + 8 + 6 &= 18
\end{align*}
\]

He decided to go with the name he got numbering left to right. He thought it was important to *keep the carbon number prefix* (dec-) *up front*, so he would remember how large the molecule was.

He noted where his double and triple bonds were, and modified the suffixes to account for their presence.

*Mr. Banker-man had a habit of procrastinating important, complex things.* So he put the alkyne last, instead of the alkene.

What to make of the \(E\) and \(Z\), though?

**Describing cis/trans isomers is EZ...**

Mr. Banker-man unfortunately likes puns. But sometimes they help him remember how to name alkene isomers, which are described with \(E\) and \(Z\) notation.

There are usually 4 bonds on the fringes of an alkene to pay attention to. If the atoms bonded to the \(sp^2\) hybridized carbons differ, we say they have different priorities. We’ll talk more about priorities on the next page, but for now it’s enough to say that atoms with higher atomic numbers have higher priority.

<table>
<thead>
<tr>
<th>German</th>
<th>English</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E)</td>
<td>Entgeegen</td>
</tr>
<tr>
<td>(Z)</td>
<td>Zusammen</td>
</tr>
</tbody>
</table>

*Read in German accent.*

\(E\): Enemies are on opposite sides.

\(Z\): Zey are on zame zide.
### Part 2

**Additional Accounts**

<table>
<thead>
<tr>
<th>Name</th>
<th>Number of Carbons</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl</td>
<td>1</td>
<td>-CH₃</td>
</tr>
<tr>
<td>Ethyl</td>
<td>2</td>
<td>-CH₂-CH₃</td>
</tr>
<tr>
<td>Propyl</td>
<td>3</td>
<td>-CH₂-CH₂-CH₃</td>
</tr>
<tr>
<td>Butyl</td>
<td>4</td>
<td>-CH₂-CH₂-CH₂-CH₃</td>
</tr>
<tr>
<td>Pentyl</td>
<td>5</td>
<td>-(CH₂)₄-CH₃</td>
</tr>
</tbody>
</table>
"Hi, my name is Mr. Banker-Man, and I have a chemistry problem."

"Hi Mr. Banker-Man"

Part of functional group behavior is learning everyone's name.

This section introduces the main functional groups: atomic arrangements that determine the properties of a given molecule. It's a lot, but remember that we're all here for you.
Alcohol
R-OH
*Drunk people are easily surprised.

Thiol
R-SH
"How she blows!"

Ketone
\[ \text{R} - \text{C} = \text{O} \]

Phenyl
Phenyl-Ferris Wheel

Epoxide
\[ \text{C} - \text{C} \]

Aldehyde
R = H
Same as ketone, w/ H.

Amide
R\text{NH}_{2}

Ether
R-O-R'
Easter egg hunt

Carboxylic Acid
R = \text{COH}
Could make a box w/ two.

Imide
\[ \text{R} - \text{N} = \text{C} \cdot \]

Nitrile
R-CN:
Cyanide group

1imine
R-N=H

Hydroperoxides
R-O-O-M
Hydroperoxide
(HSA)

Haloalkane
R-X

Amine
R-NH_{2}

2 double-bonds

Imine: 2 "i"s,
2 bonds to N.

Halo of lone pairs.

*Rough Draft of Functional Groups and Mnemonics
WHY IT MATTERS
Even if two compounds have the same molecular formula, they can have different properties based on how they're arranged. One could be a medication; the other could be toxic.

SECTION TOPICS
- Definitions
  Isomers
  Chirality
- Stereochem Jones and the Chiral Center of Doom

Definitions
Brace yourself...

Stereochemistry
The study of how molecules are arranged in 3-D.

Stereocenter
A point in a molecule where swapping the position of any two groups would create a new stereoisomer. (E.g. an sp3 hybridized carbon with 4 different substituents, or an sp2 hybridized carbon with 3 different substituents).

Isomers
Compounds that have identical molecular formulas.

Constitutional Isomers
Compounds that have identical molecular formulas, but different connectivity.

Stereoisomers
Compounds that have identical molecular formulas and connectivity, but different orientations.

Geometric Isomers
Compounds that have identical molecular formulas and connectivity, but different orientations around a double bond (E vs. Z).

Optical Isomers
Compounds that have identical molecular formulas and connectivity, but different orientations around a stereocenter.

Diastereomers
Compounds that have identical molecular formulas and connectivity, but different orientations around a stereocenter. If a compound has two or more stereocenters, at least one stereocenter is not a mirror image of the other.

Enantiomers
Compounds that have identical molecular formulas and connectivity, but different orientations around a stereocenter, such that a non-superimposable mirror image is formed.

Chirality
Asymmetry
The definitions on the previous page can be summarized in the following borrowed graphic:

Many of them hinge on this idea of **chirality**, and require some way of classifying how molecules are connected. The **Cahn-Ingold-Prelog priority rules** have this on lock, but they're pretty dry.

Let's talk about treasure hunting instead.
Stereochem Jones is a world-class adventurer. She uses a *tetrahedral codex* to find the best treasures.

Treasure = Atomic Number
↑ Atomic Number, ↑ Value

H < C < O < Br

Hunting for treasure is a perilous job. Given that a booby-trap could go off at any minute, Stereochem Jones has learned to prioritize pursuit of the most valuable treasures first. Realistically, she can only get to 3 of 4 possible treasures before a rogue boulder tries to take her out. This means she has two possible paths:

**Clockwise**

R

*Latin rectus:* "Right"

**Counter-Clockwise**

S

*Latin sinister:* "Left"
Jones's Treasure Hunting Strategy

1. Assign Priority

Behold: A tetrahedral codex.

2. Plan Route

Stereochem Jones doesn’t bother with the hydrogen; there’s only time for 3 treasures. To simplify the codex she...

1. Assign Priority

Behold: A tetrahedral codex.

<table>
<thead>
<tr>
<th>Atom</th>
<th>H</th>
<th>C</th>
<th>O</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic #</td>
<td>1</td>
<td>6</td>
<td>8</td>
<td>17</td>
</tr>
<tr>
<td>Priority</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

2. Plan Route

Stereochem Jones doesn’t bother with the hydrogen; there’s only time for 3 treasures. To simplify the codex she...

And finally...
3. Adventure On
There are 5 kinds of reactions in organic chemistry. That’s it. You (probably) have that many fingers on one hand.

**Why it Matters**

*Mental efficiency.*
- Memorizing ∞ reaction mechanisms
- Losing social life
- Crying self to sleep

**Section Topics**

- The Big Five
- Nucleophiles and Electrophiles
- Relationships and Reactions: Both Unnecessarily Complicated
- SN1, SN2, E1, E2
- Reagent examples

If someone’s telling you horror stories about having to memorize hundreds of reactions, please consider any of the following responses:
- Ignore them
- Politely disagree with them
- Slap them

While there are many reagents available to get from molecule A to molecule B, they usually follow one of these five basic patterns. If you recognize the pattern, you probably know the mechanism.

### The Big Five

1. **Substitution**  
   *One atom/functional group is replaced with another.*
   
   \[ A-B + C \quad \rightarrow \quad B-C + A \]

2. **Elimination**  
   *Two atoms/functional groups take off, often leaving an alkene behind.*
   
   \[ A-B-C-D \quad \rightarrow \quad B-C + A + D \]

3. **Addition**  
   *Two atoms/functional groups are added, often across an alkene.*
   
   \[ A-B + C-D \quad \rightarrow \quad C-A-B-D \]

4. **Rearrangement**  
   *Two atoms/functional groups swap places or orientations.*
   
   \[ A-B-C-D \quad \rightarrow \quad D-B-C-A \]

5. **Redox**  
   *One molecule donates its electrons to another.*
   
   \[ A^- + B \quad \rightarrow \quad A^+ + B^- \]
Nucleophiles and Electrophiles

These are the yin/yang of organic chemistry. Almost every reaction can be described in terms of nucleophilic and electrophilic interactions.

<table>
<thead>
<tr>
<th>Nucleophile</th>
<th>Electrophile</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;Lover of nuclei&quot;</td>
<td>&quot;Lover of electrons&quot;</td>
</tr>
</tbody>
</table>

Nucleophiles are...
- e⁻ rich
- Stoked to donate their electrons
- Lewis bases (benevolent base)

Electrophiles are...
- e⁻ poor
- Stoked to receive electrons
- Lewis acids (accepting acid)

Positively charged sites can be found
- Near electronegative atoms
- Attached to good leaving groups
- On atoms with incomplete valence shells

Electrophiles are the space-stations of organic chemistry

Nucleophiles are the rocket-ships of organic chemistry.

Trends in Nucleophilicity

To predict reactions later, we need to understand what makes a strong nucleophile (that is to say, a species that will readily donate its electrons). In general...

1. **Nucleophilicity increases as atomic charge becomes more negative**
   
   Example: \( \text{OH}^→ \text{H}_2\text{O} > \text{H}_3\text{O}^+ \)
   
   ↑Nucleophile Strength, ↑ Negative Charge

2. **Nucleophilicity increases with basicity**

   Example: \( \text{CH}_3^- > \text{NH}_2^- > \text{OH}^- > \text{F}^- \)

   ↑Nucleophile Strength, ↑ Basicity

3. **Nucleophilicity increases with polarizability**

   Example: \( \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^- \)

   ↑Nucleophile Strength, ↑ Polarizable
Substitution
One atom/functional group replaces another.

This is Bob and Sal.
They’ve been together for a while. They aren’t super happy.
(Sal initially confused Bob’s boring-ness with “stability”.

This is Tom.
Tom is pretty lonely.
He’s also much more fun than Bob.

One day Tom accidentally bumps into Bob and Sal.
Sal is so pleasantly surprised, she takes Tom’s hand and just keeps walking.
Bob goes home and watches Netflix all by his stable self.
And everyone is happier for it.
Substitution reactions require
- A good leaving group (LG), like Bob.
- A nucleophile, like Tom.

What makes a good LG?
*Good leaving groups are strong, independent compounds that don’t need no other atoms.*
They’re happy and stable by themselves.

More specifically...
- They’re weak bases
- Their negative charge tends to be stabilized by electronegative atoms (like halogens, oxygen, and nitrogen).

Gen Chem Flashback
The conjugate of a strong acid is a weak base.
So...
- $\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$
- $\text{HBr} \rightarrow \text{H}^+ + \text{Br}^-$
- $\text{HI} \rightarrow \text{H}^+ + \text{I}^-$
- $\text{H}_2\text{SO}_4 \rightarrow \text{H}^+ + \text{SO}_4^-$
- $\text{H}_3\text{O}^+ \rightarrow \text{H}^+ + \text{H}_2\text{O}$
Etc.

*Note: F is an exception. Due to its electronegativity, fluorine forms very strong bonds, and doesn’t want to go anywhere.*

There’s several classes of substitution (nucleophilic, electrophilic, radical, organometallic, etc.). Fortunately, [nucleophilic substitution](https://en.wikipedia.org/wiki/Nucleophilic_substitution) describes most organic substitution reactions.

*S\text{N}_1* and *S\text{N}_2* Reactions

**S\text{N}_1**
- Substitution
- Nucleophilic
- Unimolecular

**S\text{N}_2**
- Substitution
- Nucleophilic
- Bimolecular
In $S_N1$, the LG takes off before the nucleophile even gets on scene. This usually leaves a carbo- cation intermediate, and messes with the hy- bridization of the orbitals.

Because the nucleophile can move its electrons into either side of the vacant $p$ orbital, $S_N1$ reac- tions form a racemic mixture of products.

The LG is like an 18 year old that melo- dramatically moves out of their stable parent’s home in the middle of the night. (Really, they’re adult enough to make it independently, and the parents had empty-nest remodeling plans anyways.)

However, they weren’t expecting to remod- el so soon. When the contractor shows up with the new addition (the nucleophile), it’s a coin- flip which wing of the house it gets attached to.

In $S_N2$, the LG takes off just as the nucleophile attacks the substrate.

When the nucleophile attacks, an $sp^2$-ish intermediate is formed. Ultimately, $S_N2$ reactions cause an inversion of stereochemistry. Kind of like a molecular umbrella disaster.

The nucleophile is like your infuriatingly extroverted ex showing up at a party; you see them coming and peace out the back door just as they arrive.
How to predict \( S_N^1 \) vs. \( S_N^2 \)

While there are some cases where it'll definitively be \( S_N^1 \) and others where it'll definitively be \( S_N^2 \), I will tell you now:

*Sometimes both mechanisms happen during the same reaction.*

Here are some trends you can expect to observe.

<table>
<thead>
<tr>
<th>Carbon Center</th>
<th>( S_N^1 )</th>
<th>( S_N^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 3^\circ &gt; 2^\circ &gt;&gt;&gt; 1^\circ )** Why:** Greater substitution = Greater stability for carbocation intermediate that forms when the LG takes off. Substituents donate electron density to the electron-poor carbon.</td>
<td>( 1^\circ &gt; 2^\circ &gt;&gt;&gt; 3^\circ )** Why:** Less substitution = Less steric hindrance, which makes it easier for the nucleophile to approach. Remember: Your ex can't get to the party if there are trees in front of the door.</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Nucleophile</th>
<th>Weak</th>
<th>Strong</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{Nucleophilicity is like extroversion.} An introvert (weak nucleophile) would prefer to walk into a stable house (the substituted carbocation), while an extrovert (strong nucleophile) has the energy to crash a party (the less substituted carbon) if the door is open.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Polar Protic</th>
<th>Polar Aprotic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Examples: Water, methanol</td>
<td>Examples: Acetone, acetonitrile</td>
<td></td>
</tr>
<tr>
<td>Why: Polar protic solvents are easily ionized, which helps them stabilize carbocation intermediates. The solvent may participate in the reaction.</td>
<td>Why: Polar aprotic solvents help dissolve the nucleophile, but won't participate in the substitution reaction.</td>
<td></td>
</tr>
</tbody>
</table>
Sal and Tom like each other very much. Unfortunately, they’re both millennials stuck living at their parents’ homes.

Tom’s mother is tired of doing her entitled son’s laundry. So she kicks him out of the house.

Tom is devastated; he has his master’s degree, yet no job to make ends meet. He abashedly informs Sal of his uncertain housing situation.

Sal is unperturbed; her unpaid internship just turned into a temporary position with benefits, and she was planning to move out soon anyways.

They decide to move into a studio apartment together. Both parents were relieved to get their children out of the house, yet fundamentally uncomfortable with the pre-marital arrangement.

Elimination
Two substituents leave, forming an additional bond between the remaining atoms.
Example

A-B-C-D → A + B=C + D

Elimination reactions require
- At least one good leaving group (LG), like Tom’s mom.
- A proton, like Sal’s dad.
- Basic conditions.

E1 and E2 Reactions

E1
- Elimination
- Unimolecular

E2
- Elimination
- Bimolecular

Just like in the S\textsubscript{N} 1 reaction, a carbocation intermediate is formed. Then a base comes along and nabs a proton from an adjacent carbon. The lonely electrons left behind form a pi bond between the two carbons.

Like the S\textsubscript{N} 2 reaction, everything happens at once. When the base takes the proton, the leftover electrons make their way over to the adjacent carbon. There’s too much electrostatic repulsion for the LG to handle, so it leaves as the pi bond is formed.

Here, the angsty 18 year old still abandons his stable home, but this time a robber (rather than a contractor) shows up and steals the dog house that was outside the teen’s window. To cover up the exposed patch, the parents scuff it into a pathway.

Say you’re at a party you don’t rally want to be at. But your friend is there, so it’s not so bad. Then their significant other (a base) swoops in to pick them up. You’re not about to make uncomfortable small-talk for the next hour, so you take off too.

Your friend brought nachos (electrons) to the party. No one is upset they got left behind. They will be judiciously distributed.
How to predict E1 vs. E2

Alas, just as with substitution, *Sometimes both mechanisms happen during the same reaction*. The strength of the base in solution is one of the few mechanistic predictors.

<table>
<thead>
<tr>
<th></th>
<th>E1</th>
<th>E2</th>
</tr>
</thead>
</table>
| **LG Carbon Center** | *3° > 2° >>> 1°*  
*Why:* Greater substitution = Greater stability for carbocation intermediate that forms when the LG takes off. *Substituents donate electron density to the electron-poor carbon.*  |Irrelevant  
*Why:* The electrons from the disrupted C-H bond drive the reaction forward; the LG carbon center is never electron deficient. |
| **Base Strength**    | **Not critical to the reaction**  
*Why:* The carbocation intermediate is unstable. It’s energetically favorable for the electrons from the C-H bond to stabilize the positive charge, thus it requires very little energy to remove the C-H proton.  | **A strong base is necessary for the reaction to proceed**  
*Why:* The electrons from the disrupted C-H bond are the driving force behind the reaction. Without the carbocation, there’s little electronic reason for the electrons to pop over and fulfill their pi-bond destiny. |
| **Base Size**        | • If the acidic carbon *(the C-H that gets its proton stolen)* is highly substituted *(“bulky”), only a small base can abstract a proton  
*Example:* hydroxide  | • If the acidic carbon isn’t super substituted *(1° and some 2° carbons)*, a bulky base can be tolerated.  
*Example:* tert-butoxide |
Things were going well enough for Sal and Tom, but one can only stare lovingly into another’s eyes for so long.

One bland Friday, Sal and Tom heard rapid knocking. Before they could reach the door...

Ed and Zed burst into the apartment.

Addition
Two atoms/functional groups add across a double (or triple) bond.
Example

B = C + A - D → A - B - C - D
The first playlist came to a close. An abrupt, uncomfortably silent, close. Zed went over to adjust the music.

In his absence, Sal started to awkward silent-dance. Ed, sensing the instability of the situation, did a 360°, and took Sal’s hand.

Zed’s new playlist came on. Unperturbed that his place had been taken, he took Tom’s hand. Raucous dancing ensued for the rest of the night.
Example

A-B-C-D → D-B-C-A
The following morning, everyone was exhausted. Tom loved making breakfast, and knew everyone could use some.

Upon opening the refrigerator, he discovered that he was out of eggs.

Tom made wonderful, tiny omelets for everyone. Zed was happy to get the egg off his hand.

Holding a chicken with one arm is rough.
Example

\[ A(e^-) + B \rightarrow A^+ + B(e^-) \]
Author’s Note

What is presented here is the first draft. There are reactions and illustrations to be added. There is formatting to be done. There are low-quality images to replace. There are entire sections that need to be re-worked. I am aware.

"I myself am very far from satisfied with this but, well, getting better must come through doing it and through trying."

-Vincent van Gogh